SYNTHETIC APPROACHES TO METHYL-SUBSTITUTED 4,5-BENZOTROPONES

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MICHIGAN STATE UNIVERSITY
KEITH OWEN BODRERO
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This is to certify that the

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SYNTHETIC APPROACHES TO METHYL-SUBSTITUTED
4,5-BENZOTROPONES

presented by

Keith Owen Bodrero

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry

Harold Hart

Major professor

Date March 16, 1976

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A B S T R A C T

SYNTHETIC APPROACHES TO METHYL-SUBSTITUTED 4,5-BENZOTROPONES

By

Keith Owen Bodrero

Three different general synthetic approaches were studied for the synthesis of 2,3,6,7-tetramethyl-4,5-benzotropone, 1. The first approach involved the elaboration of a preformed benzotropone. The starting compound for this method, 2,7-dimethyl-4,5-benzotropone 5, underwent conjugate addition of dimethylcopper lithium reagent to yield 2,3-dihydro-2,3-dimethyl-4,5-benzotropone, 20. The palladium on charcoal catalyzed dehydrogenation of 20 was investigated. The product mixture included 1,2,3-trimethylnaphthalene 23, 1,2,4-trimethylnaphthalene 24, 1,3-dimethyl-1-ethyl-β-naphthone 22, and 2,3,7-trimethyl-4,5-benzotropone 21. Bromination of 20 gave 2,3-dihydro-3-bromo-2,3,7-trimethyl-4,5-benzotropone 26, which rearranged thermally to 1,3-dimethyl-1-(1-bromoethyl)-β-naphthone 27. Base-catalyzed dehydrobromination of 26 did not give 21. Reaction of 26 with silver acetate produced 1,3-dimethyl-1-(1-acetoxyethyl)-β-naphthone 33. Compound 33 underwent thermal elimination on FFAP to give 1,3-dimethyl-2-acetoxynaphthalene, 34. Both 33 and 27 underwent vacuum pyrolysis to 1,3-dimethyl-2-naphthol, 32. Pyrolysis of 26 gave 21 in 28% yield along with 23 produced by thermal decarbonylation of 21. Pyrolysis of

27 gave 1,3-dimethyl-1-vinyl-β-naphthone, 31. Compound 20 underwent conjugate addition of dimethylcopper lithium reagent to give 2,3,6,7-tetrahydro-2,3,6,7-tetramethyl-4,5-benzotropone, 35. However the dehydrogenation of 35 yielded only 1,3,4-trimethyl-1-ethyl-β-naphthone, 36. Bromination of 35 gave very complex product mixtures with only low yields of dibrominated products.

The second approach was the ring expansion of an appropriate precursor. The starting material, 1,2,3,4-tetramethylnaphthalene, 38, was treated with dibromocarbene to form 5,6-benzo-1,2,4,7-tetramethyl-3,3,8,8-tetrabromotricyclo[5.1.0.$0^{2,4}$]octane, 39, 4,6,7-trimethyl-5-bromo-2,3-benzoheptafulvene, 40, and the benzospirononatriene 41 presumably formed by dibromocarbene addition to 40. If the phase transfer method of dibromocarbene generation was used products 40, 41, and homobenzoheptafulvene, 4,6,7-trimethyl-5-bromo-6,7-dihydro-6,7-(dibromocyclopropyl)-2,3-benzoheptafulvene, 53, were formed. Compound 40 reacted with dimethylcopper lithium reagent to give 4,5,6,7-tetramethyl-2,3-benzoheptafulvene, 59. Experiments and information regarding the structural assignments of 40 and 59 were discussed. The oxidation of 40 to 1 was attempted without success. The isomerization of 39 to a benzoheptafulvene using silver salts was also attempted without success.

Also falling under the second approach was a 1,4-homoelimination procedure. This utilized as substrate the diol formed by adding methyllithium to dimethylcyclopropanaphthoquinone 64. It was carried out with diphosphorous tetraiodide and did not lead to a tetramethyl-benzoheptatriene as expected, but to a monoalcohol wherein the cyclopropyl ring was still intact.

The third and successful approach involved bridge elimination of the adduct formed by carbene addition to a Diels-Alder reaction product. Benzyne plus tetramethylfuran gave 1,2,3,4-tetramethylnaphthalene-1,4-endoxide, 76. Addition of dichlorocarbene to 76 and rearrangement gave 1,7-dichloro-2,3,6,7-tetramethyl-3,6-oxo-4,5-benzocyclohepta-1,4-diene, 85. Dehydrochlorination and hydrogenation gave 7-chloro-2,3,6,7-tetramethyl-3,6-oxo-4,5-benzocyclohepta-1,4-diene, 89. When treated with boron trifluoride in acetic acid, 89 gave 6-chloro-4,5,7-trimethyl-2,3-benzoheptafulvene, 94, which gave 1 in aqueous acid. By-products formed in this approach are also discussed along with certain reactions of the intermediates.

The fourth part of this research involved an nmr spectral study of the tropylium ions formed from 21 and 1 and the tropylium ions and ion quenching products formed from the tertiary alcohols obtained by adding methyllithium to 5, 21, and 1. Further, the pyrolysis of 21 and 1 to methylnaphthalenes was carried out and the photolytic decarbonylation of 1 was accomplished. The formation of epoxides by the reaction of meta-chloroperbenzoic acid with 5 was also discussed.

SYNTHETIC APPROACHES TO METHYL-SUBSTITUTED 4,5-BENZOTROPONES

By

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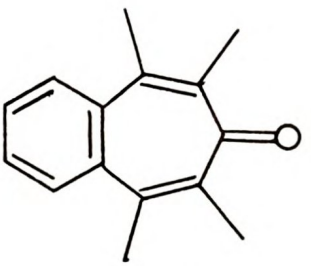
SYNTHETIC APPROACHES TO METHYL-SUBSTITUTED 4,5-BENZOTROPONES

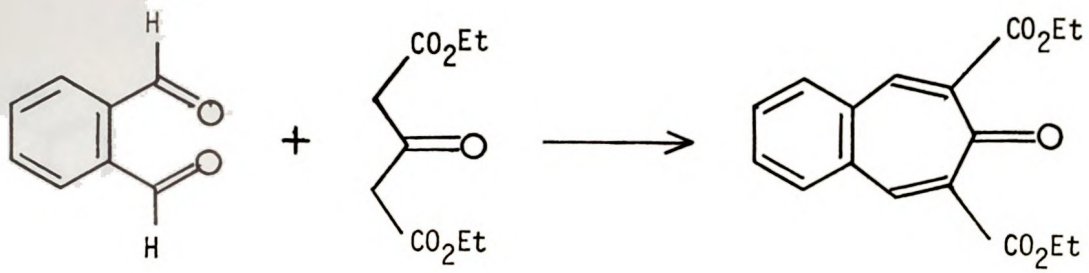
INTRODUCTION

Benzotropones have been the object of much study.[1] Theoretical calculations and predictions have been made concerning their characteristics, particularly their aromaticity, and much work has gone into the synthesis of suitable compounds to test those predictions. Since certain naturally occurring molecules also contain troponoid structures, further interest has been generated in this class of compounds. Various synthetic routes to benzotropones and their derivatives have been developed, and many of their possible reactions have been investigated. Since the primary object of this investigation was the synthesis of 2,3,6,7-tetramethyl-4,5-benzotropone, 1, we will review here briefly the synthesis and reactions of 4,5-benzotropones.



1

The first 4,5-benzotropone was synthesized by Thiele and Schneider[2] in 1909. They condensed o-phthalaldehyde with the diethyl ester of acetonedicarboxylic acid in the presence of base.

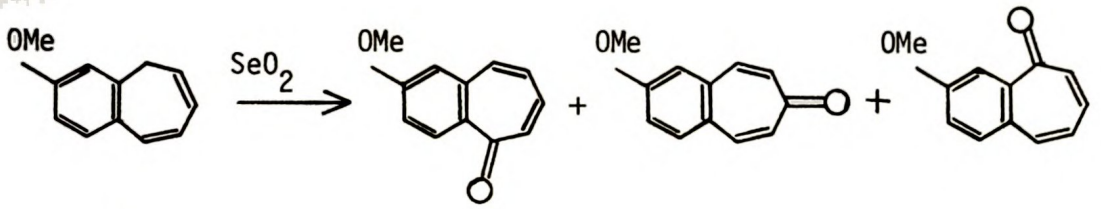


2

By using the same double Claisen type of reaction, other 4,5-benzotropones were obtained by Thiele,[3] including the 2,7-dimethyl, 2,7-diphenyl, 2-methyl, 2-ethyl, and 2-propyl derivatives. The parent unsubstituted ring system was obtained by step-wise decarboxylation of 2,7-dicarboxylic acid-4,5-benzotropone obtained by hydrolysis of the diester 2.

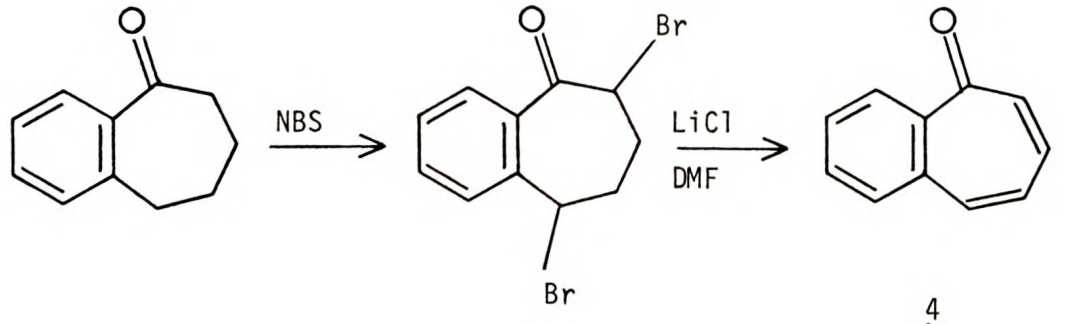
The syntheses of benzotropones[1] reported in the literature fall into several categories. The first was that used by Thiele, the Claisen type condensation. Once the benzotropone ring system had been constructed, it was further elaborated to achieve the desired products. Davey and Gottfried[4] used this method to synthesize several derivatives substituted in the 2 and 7 positions. They also developed transformations to some tri-substituted compounds.

A variation of this method involves oxidation of benzocycloheptatrienes.[5] For example, the reaction of benzocycloheptatriene 3 with SeO_2 yielded a complex mixture containing three isomeric benzotropones.



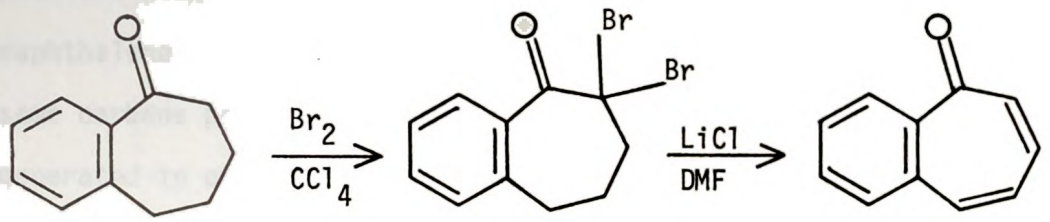
3

Dehydrogenation of tetrahydro derivatives has provided another route to benzotropones.[6] Also bromination-dehydrobromination sequences have been used to convert benzocycloheptanones to benzotropones. For example, Collington and Jones[7] synthesized 2,3-benzotropone 4 from 2,3-benzocycloheptanone by brominating with N-bromosuccinimide (NBS) and dehydrobrominating with lithium chloride (LiCl) in dimethyl formamide (DMF).



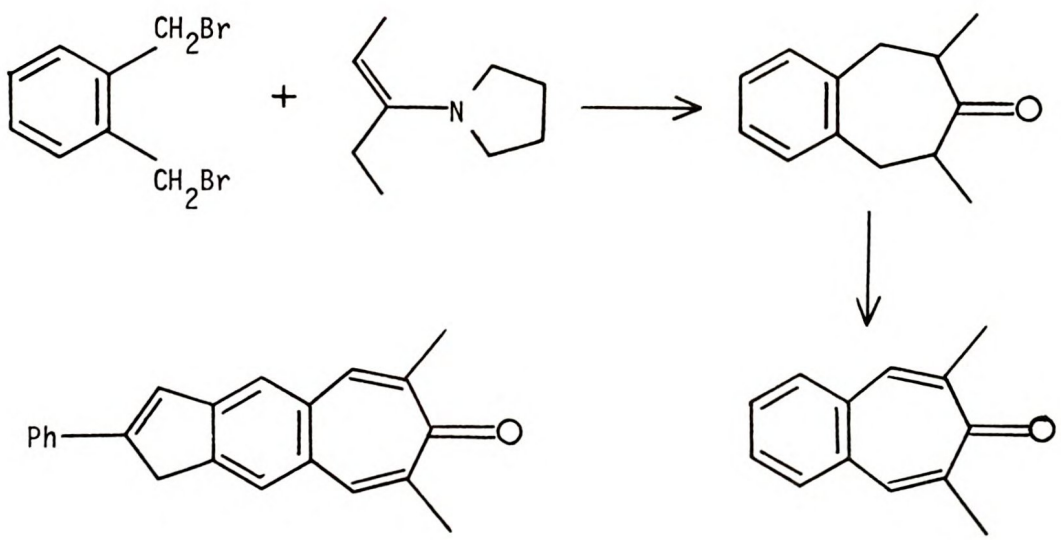
4

More conveniently it was found that bromination with bromine in carbon tetrachloride lead to the 7,7-dibromo compound, which was also dehydrobrominated to 4 in high yield.



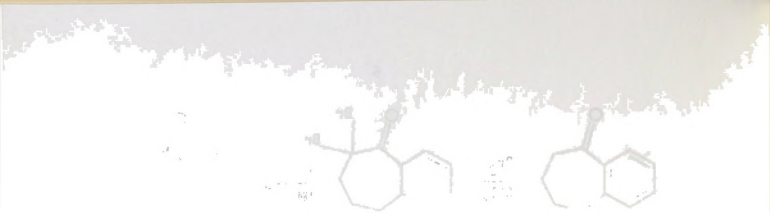
4

A combination of methods to form 4,5-benzocycloheptenones was used by Bordwell;[8] the condensation of α,ά-dibromo-o-xylene with the pyrrolidine enamine of 3-pentanone gave a benzocycloheptanone which was brominated and dehydrobrominated to yield 2,7-dimethyl-4,5-benzotropone, 5. This method was extended to the indenotropone 6.

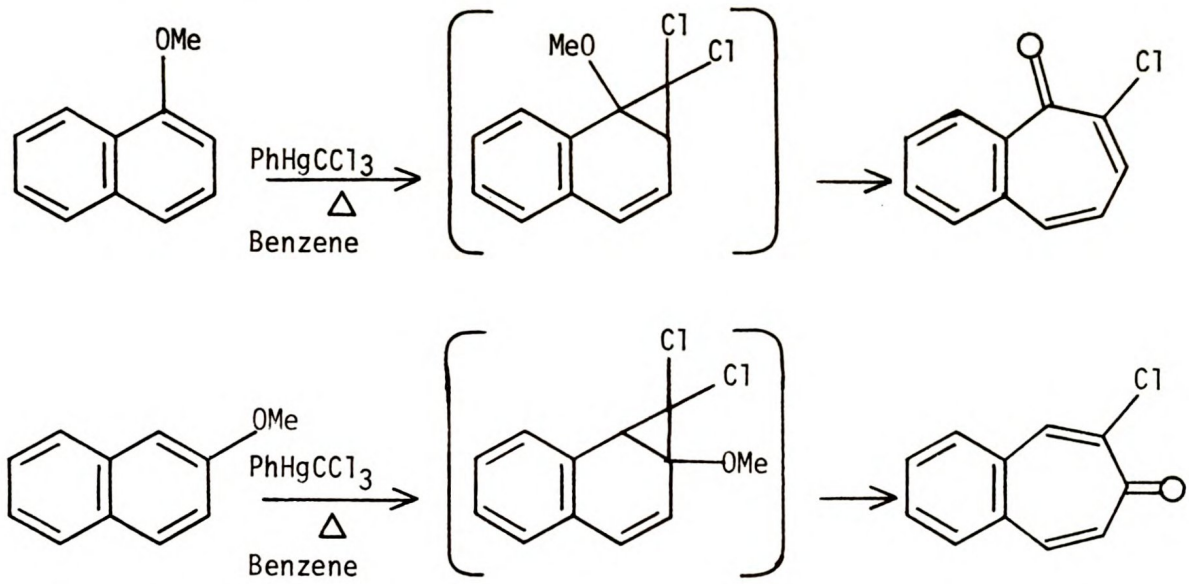


6 5

An alternative synthetic method that has been used involves ring expansion of appropriate precursors. Saraf[9] reported a synthesis of both 2,3- and 4,5-benzotropones which begins with isomeric methoxynaphthalenes. 1-Methoxynaphthalene formed 7-chloro-2,3-benzotropone upon

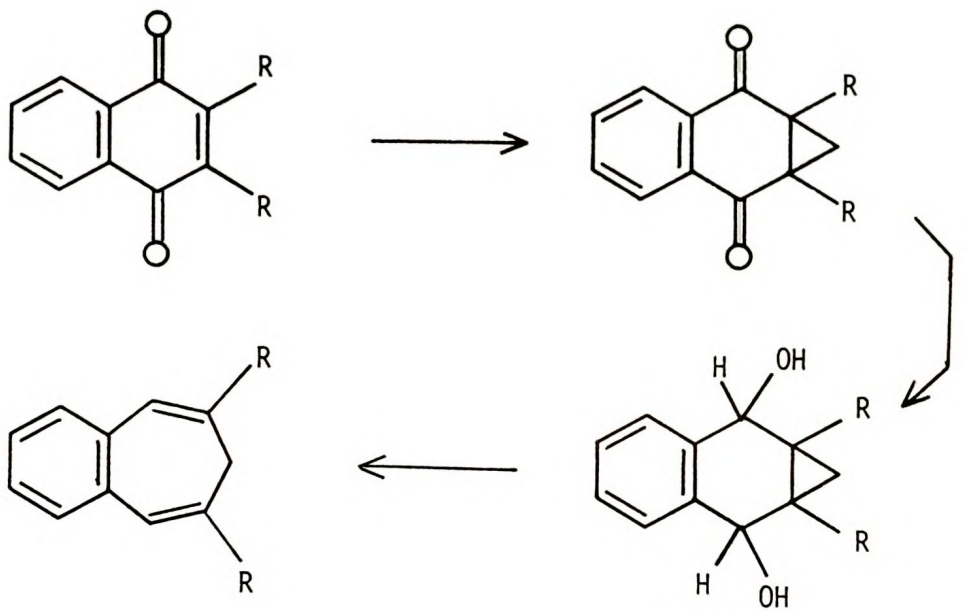


reaction with phenyl-(trichloromethyl)-mercury, whereas 2-methoxy-naphthalene formed the 2-chloro-4,5-benzotropone when reacted with the same carbene precursor. Similar reactions using dihalocarbenes generated in other ways have also been reported.[10]



A variation of the ring expansion technique was suggested by work published in 1974 by Hanafusa.[11] A 1,4-homoelimination on the diol derived from the diazomethane adduct to naphthoquinone gave the benzocycloheptatriene, 7. Such a procedure, followed by oxidation, could be used to achieve a benzotropone synthesis. A related approach[12] gave naphthoquinone 8 by elaboration of compound 9.

The ring expansion of benzenoid compounds, besides being used for tropone synthesis, has also lead to benzoheptafulvenes. Hart and Oku[13] reacted dibromocarbene with octamethylnaphthalene and reported two products, the unrearranged bis-adduct 10, and the rearranged mono-adduct, benzoheptafulvene 11. Such a synthesis could be used to form



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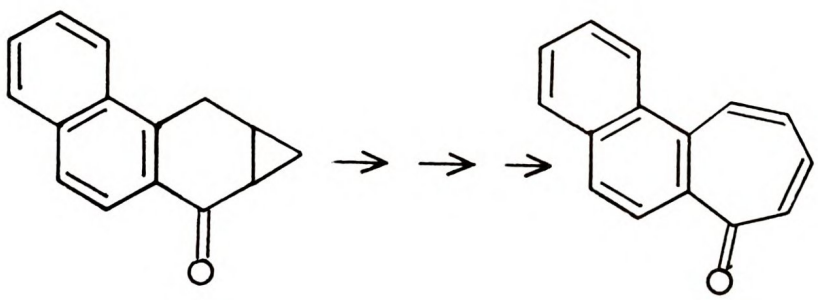

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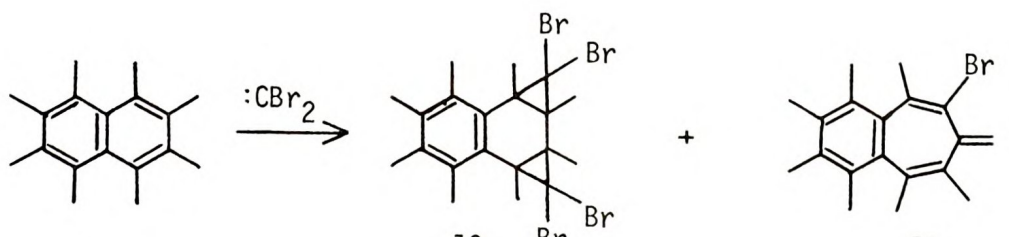
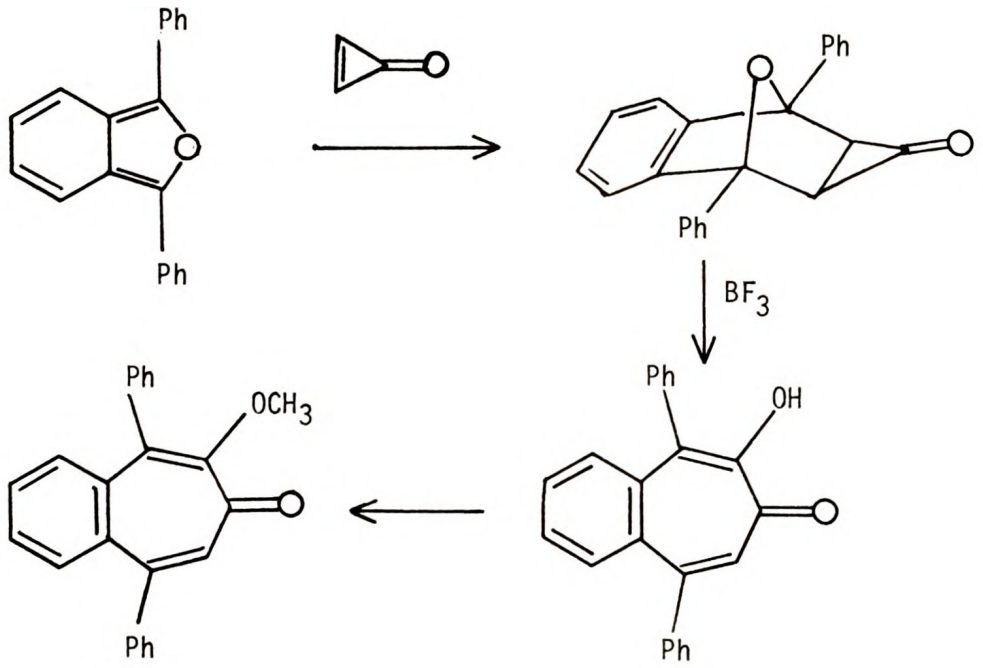


10 11

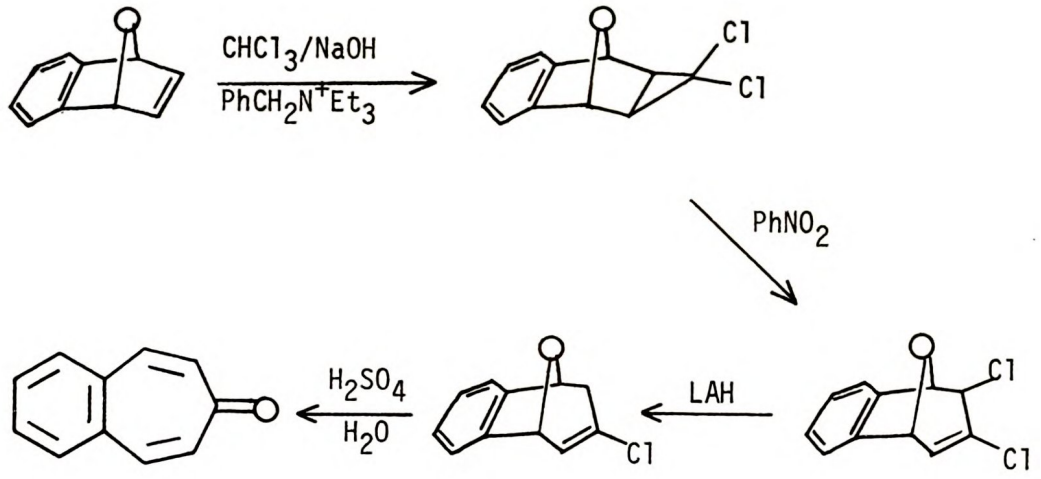
a tropone. This approach to benzotropone synthesis is discussed further in the results section of this thesis.

Yet another, and quite different synthetic approach to benzotropones involves elimination from a bicyclic precursor. This approach was used by Breslow[14] and co-workers. They formed trisubstituted benzotropones by the reactions outlined below, while investigating the addition of cyclopropenone to reactive dienes.



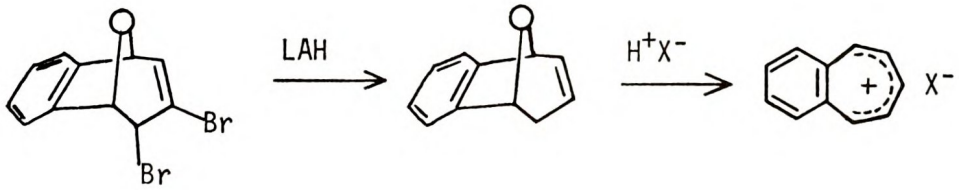
The most efficient synthesis of 4,5-benzotropone itself was reported by Battiste.[15] It involved cleavage of an oxygen-bridged cycloheptadiene. A good yield of the parent 4,5-benzotropone, 12, was obtained using the reactions outlined in Scheme 1. Application of this synthetic method to the synthesis of tropone itself, however, was unsuccessful.

Scheme 1



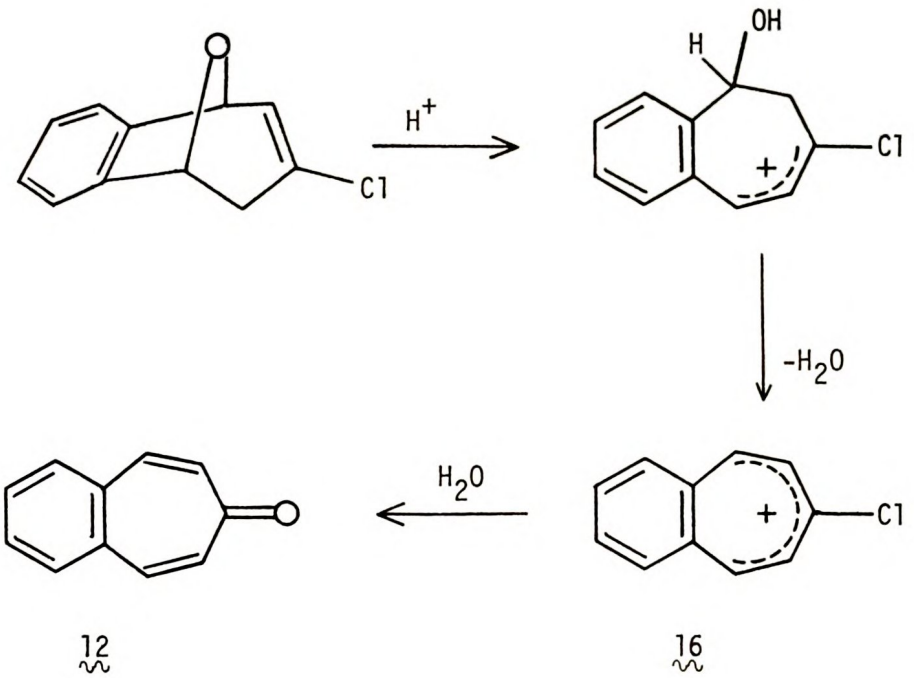
12

Wittig[16] prepared the benzotropylium ion 13 from 14, obtained by reduction of 15, which was formed by a carbene addition similar to that shown in Scheme 1. Benzotropone prepared according to the route developed by Battiste presumably involved the intermediate



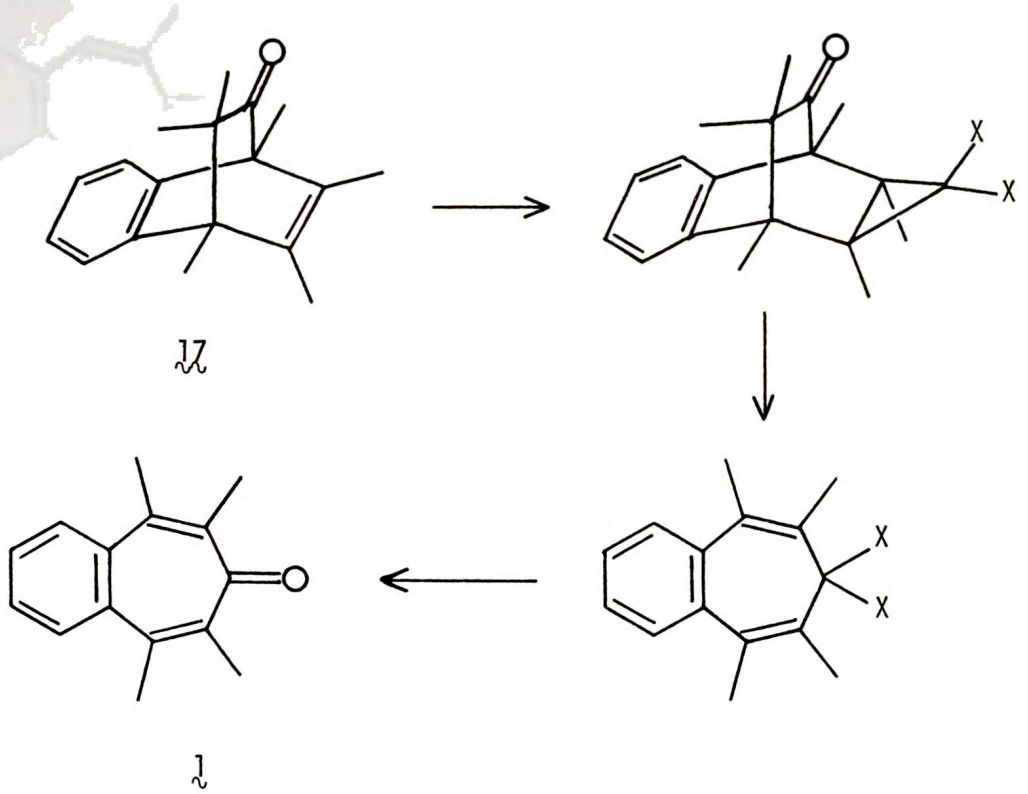
15 14 13

chlorobenzotropylium ion 16, which was then quenched by water to form the 4,5-benzotropone.



12 16

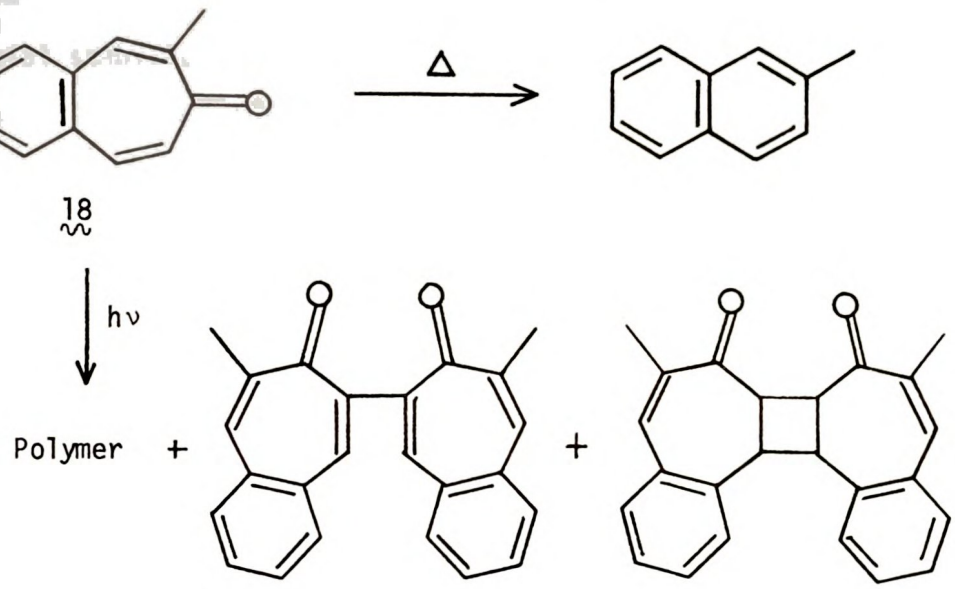
Other bridge elimination routes can be envisioned, such as the reaction of a carbene with a bicyclo[2.2.2]benzodienone, 17, subsequent bridge elimination, and elaboration to a benzotropone. An attempt using this approach will be discussed in the results section of this thesis.



17

1

The reactions of benzotropones have been reviewed.[1] Of particular interest are ring contraction reactions of benzotropones to naphthalene derivatives. Pyrolysis of 4,5-benzotropones resulted in carbon monoxide extrusion to form the ring contracted naphthalene.[17] However, 4,5-benzotropones were found to be relatively stable; for example, 2-methyl-4,5-benzotropone, 18, was 95% recovered after pyrolysis at 700°. Photolysis of 4,5-benzotropones, instead of yielding benzenoid compounds or valence isomers as occurs with tropones and 2,3-benzotropones, led only to dimeric products.[18] Photolysis of 18 gave the dimer in 9-10% yield, a dehydrogenated dimer in 2-3% yield, and polymer.[19] Similarly 2-phenoxy-4,5-benzotropone yielded dimeric products.[20]



18

4,5-Benzotropones undergo nucleophilic addition not only at the carbonyl carbon but also at the $\Delta^{2,3}$ double bond. Several carbon nucleophiles gave Michael addition products when reacted with 2.[21]

Hydrogenation of benzotropones gives the corresponding benzocycloheptanones.[10c,22] The diepoxide of 2,7-diphenyl-4,5-benzotropone has been synthesized using alkaline hydrogen peroxide solution.[23] Several benzohomotropones have recently been synthesized.[1,24]

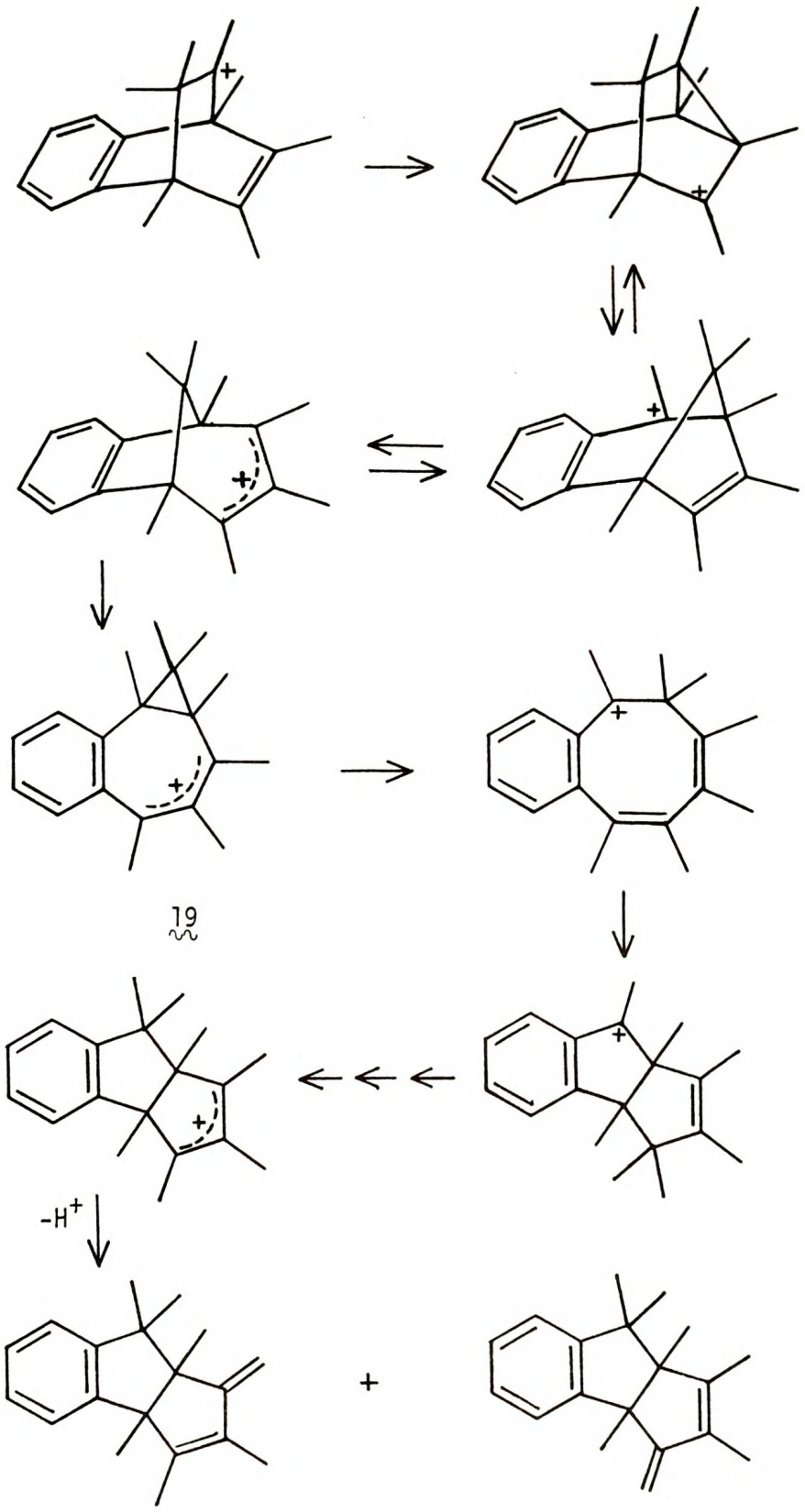
Tropylium ions have been generated from benzotropones. Protonation of benzotropone yields the hydroxybenzotropylium ion. Reduction of a benzotropone to the alcohol and subsequent acid solvolysis yields benzotropylium ions,[1] as would the reaction with a Grignard reagent, followed by acid solvolysis. Benzotropylium ions are the benzo analogs of the 6π electron tropylium ions derived from tropone.

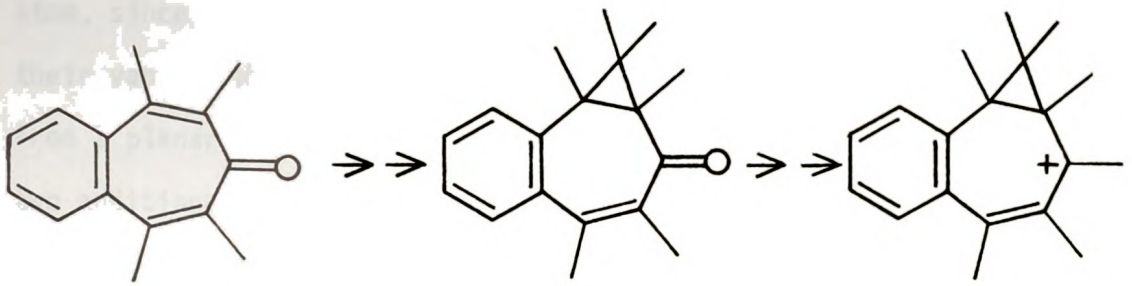
Huckel was the first to suggest that such carbonium ions would enjoy special stability because of the aromatic 6π electron character of their bonding. This prediction has been born out by synthesis and study of these ions. Recently, homotropylium ions and benzohomotropylium ions have been synthesized and studied.[24]

The benzoheptafulvenes have also been generated. Some have been made directly from benzotropones by reaction with diphenyl ketene,[25] with phosphonium ylide,[26] or by reaction of the ketone with a Grignard reagent and subsequent dehydration of the alcohol.[27] Others have been formed by dibromocarbene reaction with methylnaphthalenes and subsequent rearrangement.[13,28] Others have been synthesized by a specific, directed synthesis.[29,30] The benzoheptafulvenes thus formed generally polymerize readily.

In connection with a study on carbonium ion rearrangements carried out by Hart and Love,[31] the homobenzotropylium ion 19 was hypothesized to be a reaction intermediate (Scheme 2). It was the initial purpose of the present research to synthesize ion 19 by an alternate and more direct route, to test its feasibility as an intermediate in Scheme 2. A logical precursor of 19 would be 2,3,6,7-tetramethyl-4,5-benzotropone, (1), which could then be elaborated, via a homotropone, to 19.

Scheme 2

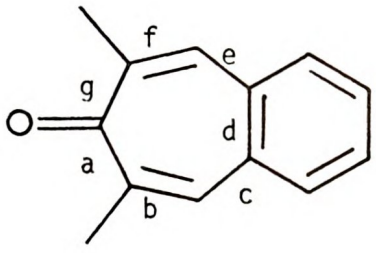


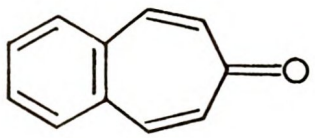


1 19

Synthesis of 1 would provide the first example of a 4,5-benzotropone with all four seven-membered-ring positions substituted.

Of interest with regard to the synthesis of 1 is the X-ray crystal structure of 2,7-dimethyl-4,5-benzotropone, 5, published by Sasada[32] in 1973. It was found that 5 exists in a shallow boat form where α, the dihedral angle between the bottom and bow of the boat, is 11.5^{o} and β, the dihedral angle between the bottom and stern, is 4.7^{o}. These values compared to $\alpha = 3.6^{o}$ and $\beta = 3.7^{o}$ in 4,5-benzotropone itself, (12). The tropone ring showed definite bond alternation. The average length of bonds c and e was 1.445 Å, the double bonds b and f averaged 1.335 Å (close to the values in 12). Bonds a and g adjacent to the carbonyl group are elongated (1.484 Å) compared to 12, (1.446 Å). It was also found that the methyl hydrogen atoms were locked by the oxygen





5 12

atom, since the oxygen-hydrogen distance found was close to the sum of their van der Waals radii. Methyl substitution causes greater deformity from a planar structure and greater bond strain. The substitution of two additional methyls to form 1 might be expected to add even greater strain to the molecule.

With regard to the development of specific substitution patterns in 4,5-benzotropones, the foregoing discussion can be summarized into the following general methods of synthesis:

A. Manipulation of a preformed benzotropone ring system and regeneration of that ring system to achieve appropriate substitution.

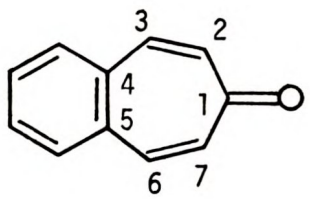
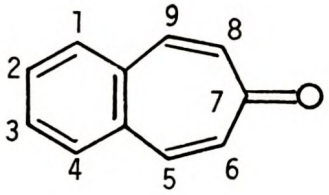
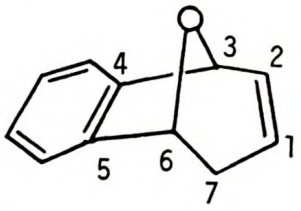
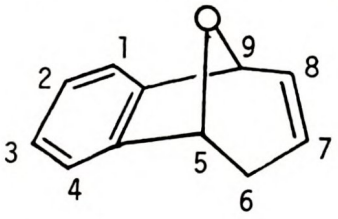
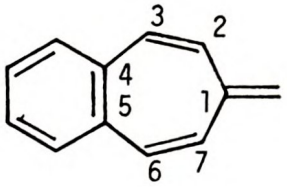
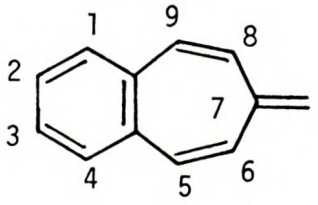
B. Formation of an appropriate precursor which, through ring expansion and manipulation, yields the desired product.

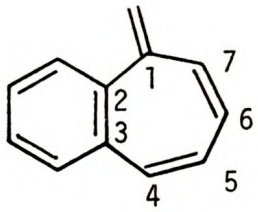
C. Formation, through the Diels-Alder reaction, of an appropriate precursor which by carbene addition and bridge elimination yields the desired substitution pattern.

This thesis deals with the synthesis of compound 1. Parts A, B, and C deal respectively with methods A, B, and C above. Part D will deal with the benzoheptafulvenes and benzotropylium ions derived from the benzotropones synthesized, and with selected reactions of the benzotropones.

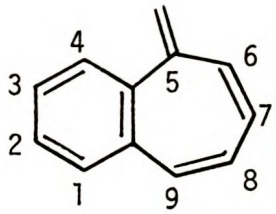
A note on nomenclature

The system of nomenclature used throughout this thesis will be that of common usage. A comparison of common names and chemical abstracts names is given here to aid the reader.

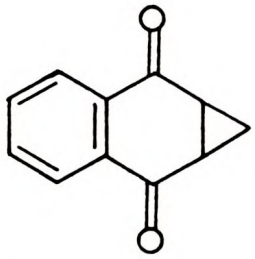
Common	Chemical Abstracts
	
12 4,5-Benzotropone	12 7H-Benzocyclohepten-7-one
	
3,6-Epoxy-4,5-benzocyclohepta-1,4-diene	5,9-Epoxy-6H-benzocycloheptene
	
4,5-Benzoheptafulvene	7H-benzocycloheptene-7-methylene



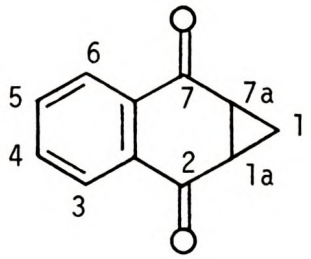
2,3-Benzoheptafulvene



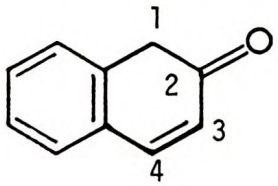
5H-Benzocycloheptene-5-methylene



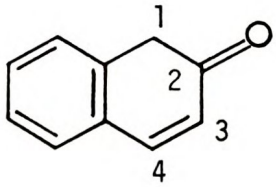
Cyclopropanaphthoquinone



1a,7a-Dihydro-1H-cyclopropa[b]naphthalene-2,7-dione



β-Naphthone



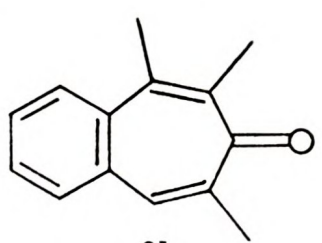
2(1H)-Naphthalenone

Other ring systems found in this thesis will be named with the most convenient descriptive name.

Particularly with regard to the benzotropone series several nomenclature usages have been in effect over the years. When searching Chemical Abstracts for benzotropones, benzotropone derivatives, or benzotropylium ions, the following names should be searched:

to 1936	Benzocycloheptadienone Benzocycloheptene Benzosuberanone
1937-1946	Cycloheptabenzenone
1947-1956	Benzotropone Cycloheptabenzenone Benzotropylium
1957-1965	Benzotropone Benzotropylium Benzocycloheptenone
1966-on	Benzocycloheptenone Benzocycloheptenylium

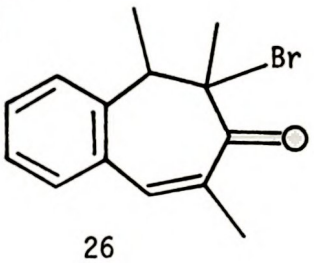
With regard to the benzoheptafulvene series, the common nomenclature and the current Chemical Abstracts usage should suffice although working backward from current literature and reviews was found to be most satisfactory in terms of completeness of survey. Some examples will be given here with common name, Chemical Abstracts name, and structure to guide the reader in further translation of common names into chemical abstracts usage. The common name is listed first and the chemical abstracts name second.



21

2,3,7-Trimethyl-4,5-benzotropone

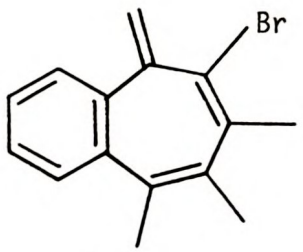
7H-5,6,8-Trimethylbenzocyclohepten-7-one



26

2,3-Dihydro-2-bromo-2,3,7-trimethyl-4,5-benzotropone

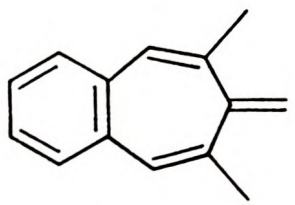
7H-5,6-Dihydro-6-bromo-5,6,8-trimethyl-benzocycloheptene-7-one



43

7-Bromo-4,5,6-trimethyl-2,3-benzoheptafulvene

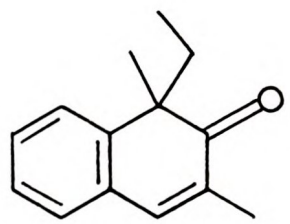
6-Bromo-7,8,9-trimethyl-5H-benzocycloheptene-5-methylene



101

2,7-Dimethyl-4,5-benzoheptafulvene

6,8-Dimethyl-7H-benzocycloheptene-7-methylene



22

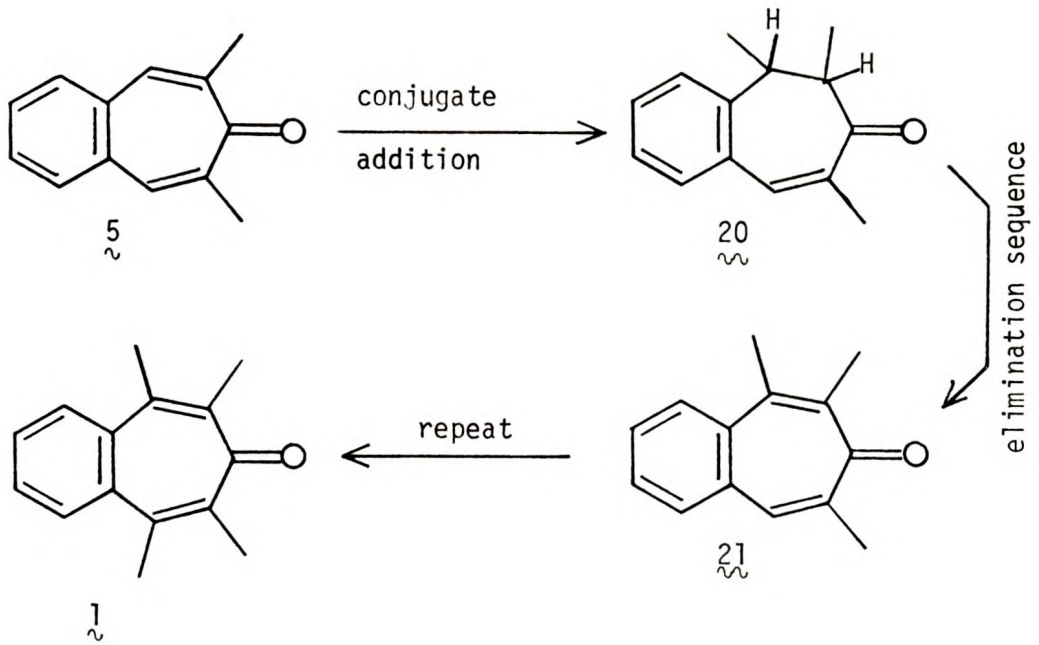
1-Ethyl-1,3-dimethyl-β-naphthone

1-Ethyl-1,3-dimethyl-2(1H)-naphthalenone

RESULTS AND DISCUSSION

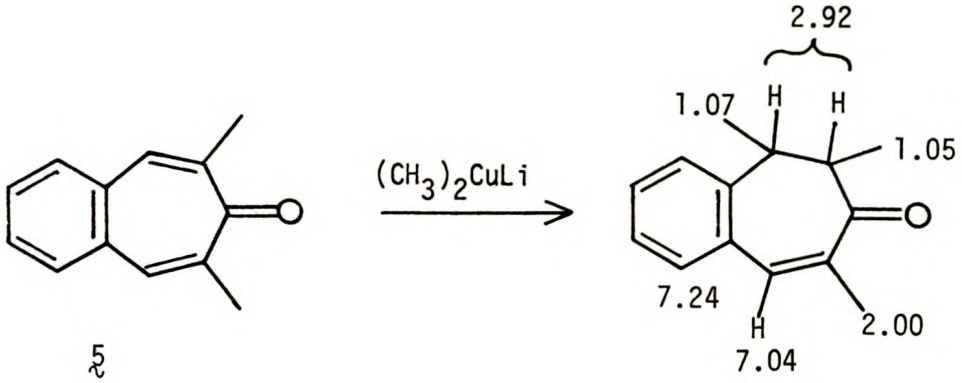
A. THE ELABORATION BY SUBSTITUTION OF A PREFORMED BENZOTROPONE

2,7-Dimethyl-4,5-benzotropone, 5, was synthesized as the starting material for this approach. The procedure used was essentially that of Thiele.[3] The straightforward scheme envisioned for the synthesis of 1 was



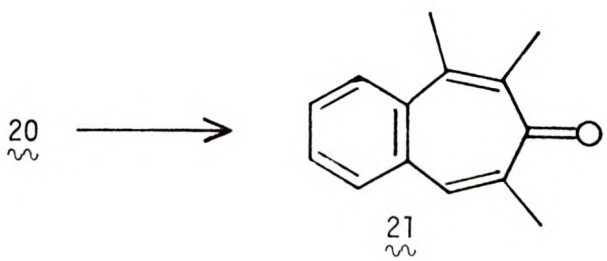
Conjugate addition to 5 by the procedure of House,[33] of dimethylcopper lithium reagent gave a nearly quantitative yield of 2,3,7-trimethyl-2,3-dihydro-4,5-benzotropone, 20, which was 90% one of the two possible stereoisomers. With the removal of one double bond, the carbonyl absorption in the infrared (ir) spectrum changed from 1600 cm^{-1} in the starting material to 1660 cm^{-1}. The nuclear magnetic resonance (nmr) proton chemical shifts were assigned as shown. The splitting

pattern was consistent with this structure. The ultraviolet (uv) spectrum showed (cyclohexane) λ max at 226, 232 and 293 nm.



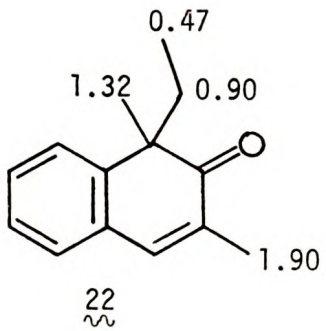
5 20

The transformation of 20 to 21 might be carried out in several ways. Dehydrogenation[6] of 20 was attempted using chloranil, but without success. A complex mixture of products resulted which contained little if any 21. The reaction of 20 with palladium on charcoal in an inert atmosphere led to many products along with recovered starting compound 20. The reaction was carried out at 215° using trichlorobenzene as solvent with a continual flow of nitrogen through the flask. The reaction was followed by gas chromatography and showed an initial build-up of a product followed by the formation of several other products.



21

After cooling and filtering the reaction mixture to remove the palladium on charcoal catalyst, the solvent was removed by distillation and the residue was separated on an SE-30, 20%, 5' x ¼" column at 150°. The five principal peaks were collected. That of shortest retention time was due to 1-ethyl-1,3-dimethyl-β-naphthone, 22. This product had an nmr spectrum with a triplet at δ 0.47, J = 8 Hz, a singlet at δ 1.32, a doublet at δ 1.90, J = 1 Hz, and a multiplet at δ 0.90, J = 8 Hz.



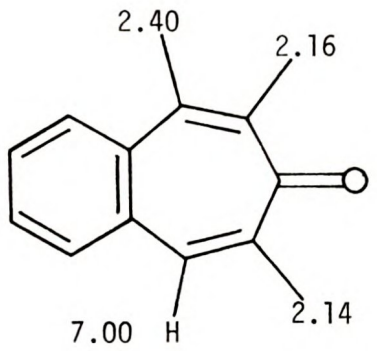
22

The infrared spectrum showed a carbonyl absorption at 1660 cm^{-1} indicating a conjugated carbonyl group. The mass spectrum indicated that the product was an isomer of 20, with a parent peak at m/e 200 and a base peak at m/e 172. The ultraviolet spectrum was similar to that of 20, indicating an α,β unsaturated ketone.

Peak 2 corresponded to a mixture of 1,2,3-trimethylnaphthalene 23, 1,2,4-trimethylnaphthalene 24, and the minor isomer of 20. The trimethylnaphthalenes were separated and individually purified by further gas chromatography. They were identified by determining their spectral characteristics and comparing them with literature values.[34]

Peak 3 corresponded to the major isomer of 20. Peak 4 was small and that product was not fully characterized. Peak 5 was due to the

desired 2,3,7-trimethyl-4,5-benzotropone, 21. The ir band for the carbonyl was at 1610 cm^{-1}, the ultraviolet spectrum showed λ max at 238 nm (ε = 50,400), 267 (22,700) and a shoulder at 325 nm (ε = 2830). The mass spectrum had a weak parent peak at m/e 198 (4%) and two intense peaks at m/e 170 (99%) and 155 (100%). The nmr spectrum was assigned as shown on the structure. The methyl groups at δ 2.14 and 2.16 overlapped and in the 60 MHz spectrum appeared as a broad peak with a shoulder. A 100-MHz spectrum and double resonance study confirmed this assignment by showing the δ 2.16 peak to be a quartet and the δ 2.14 peak to be a doublet. Irradiation of the peak at δ 7.00 decoupled the δ 2.14 peak without affecting the peak at δ 2.16.

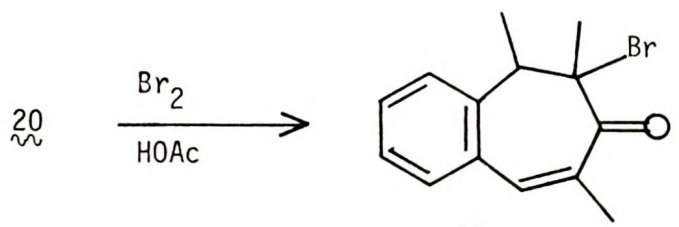


21

An exploratory reaction using sulfur to dehydrogenate 20 led to a lower yield of 21, along with both trimethylnaphthalenes, unreacted starting material and a new product 25 which was characterized as a dimethylnaphthol. It was formed in larger amounts than any of the other products. A positive identification was not made. (Compare 1,3-dimethyl-2-naphthol 32, Experimental J.) The ir spectrum of 25 showed hydroxyl absorption at 3670 cm^{-1}. The mass spectrum had a parent peak at m/e 172 which was also the base peak. The ultraviolet spectrum

(cyclohexane) showed some fine structure with the principal λ max being at 231 nm (ε = 61,500), 280 (4500), 315 (1640) and 328 (2050). The product was crystalline (colorless), mp 82-84°, when collected from an SE-30 column. The broad melting point obtained indicated that the small amount collected was not completely pure.

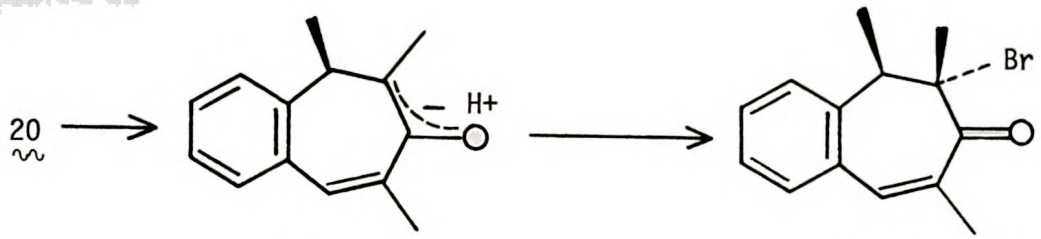
Although the dehydrogenation reaction was useful, it did not provide a practical method for obtaining 21, so a bromination-dehydrobromination procedure was sought. Bromination with base led to complex mixtures from which only tiny amounts of the desired product 26 and its structural isomer 27 could be isolated. However, the reaction of 20 with bromine in acetic acid led to 26, 2,3-dihydro-2-bromo-2,3,7-trimethyl-4,5-benzotropone. Compound 26 was purified by recrystallization from methanol to form colorless prisms, mp 81-82°. Chromatography of 26 sometimes caused it to rearrange to 27.



26

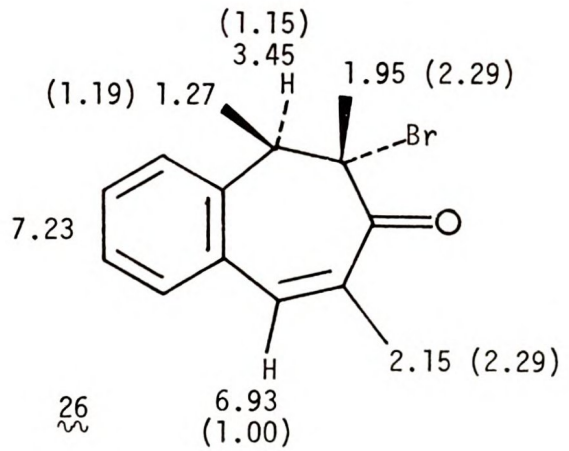
Only one stereoisomer of 26 was formed. Its stereochemistry was assumed to be cis with respect to the methyl groups at positions 2 and 3, since approach of bromide ion to the enolate intermediate 28 would be more likely to occur from the side opposite the 3-methyl group. The ir carbonyl absorption of 26 was at 1652 cm^{-1}; the ultraviolet spectrum (cyclohexane) showed λ max at 233 nm (ε = 12,700), 306 (9700) and a

shoulder at 326 nm (5900). The mass spectrum indicated that one bromine



28 26

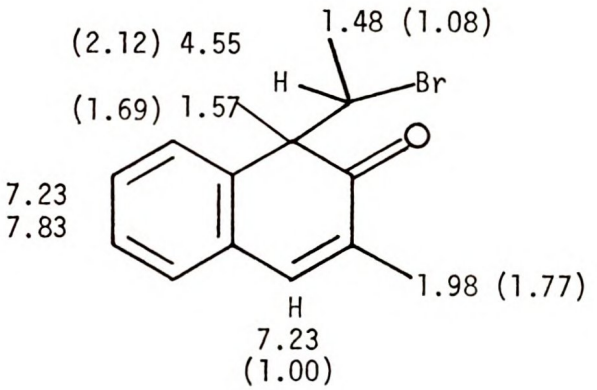
atom was present, since the p and (p + 2) peaks had equal intensities (12% of base) at 278 and 280 amu. The base peak was at m/e 199 and corresponded to the loss of a bromine atom. The nmr spectrum was assigned as shown, with europium shift numbers in parenthesis.



26

When 26 and LiCl in DMF were refluxed, in an attempt to affect dehydrobromination, a new compound was formed that was isomeric with 26. The isomeric bromide 27 was formed as a consequence of the thermal rearrangement of 26, as subsequent reactions of 26 in DMF or dimethyl sulfoxide (DMSO) without base showed. Compound 27 was also produced by gas chromatography of 26 on FFAP at 215° or by thin layer chromatography of 26 on silica gel. Compound 27 was a ring contraction

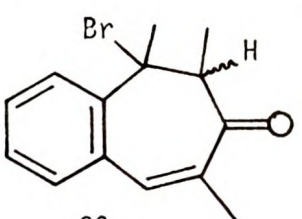
product, 1-(1-bromoethyl)-1,3-dimethyl-β-naphthone. It was an oil. The infrared spectrum of 27 showed a conjugated carbonyl absorption at 1652 cm^{-1}. The ultraviolet spectrum had λ max at 233 nm (ε = 16,500), 241 (17,000), 301 nm (sh, 8500), 311 (9600), and 324 (sh, 7200). The mass spectrum showed p and (p + 2) peaks with an intensity of 13% each, at 278 and 280 amu. The base peak again was at m/e 199. The principal difference between 26 and 27 came in their nmr spectra. The nmr spectrum of 27 was assigned as shown with normalized Eu shifts in



27

parentheses. In particular, the shift of the quartet (equal in area to one hydrogen) from δ 3.45 to δ 4.55 required this structural assignment.

Since 29 or 30 were also plausible structures for the rearrangement product of 26, further evidence was sought for its structure.



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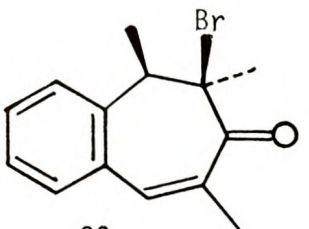
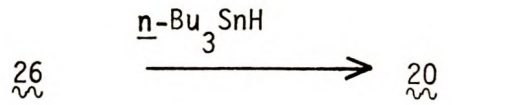
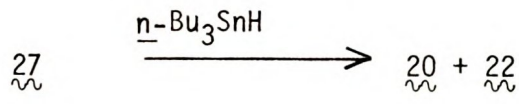


30

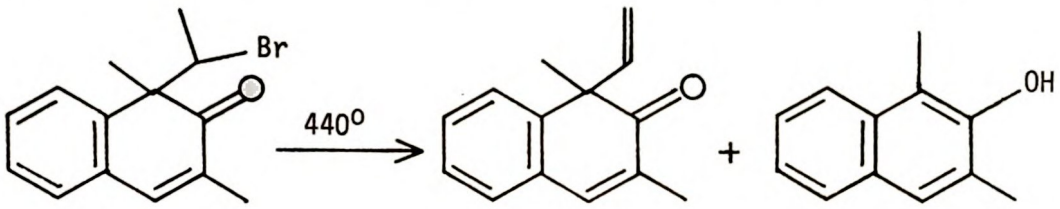
Both 26 and 27 were reduced with tri-n-butyl tin hydride. The reaction of 26 led to a complex mixture, but 20 was easily isolated by TLC and identified by spectral comparison. The reaction of 27 with n-Bu_3SnH also led to a mixture, from which two products could be isolated. Both 20 and 22 were identified by spectral comparison.





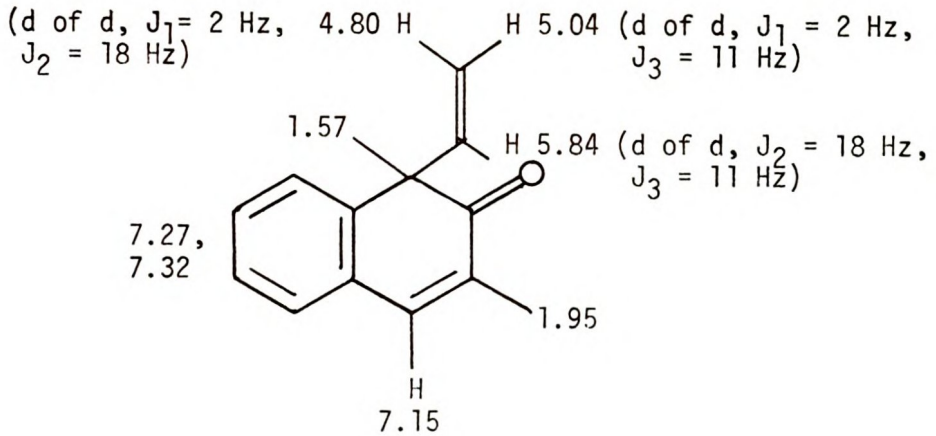
The pyrolysis of 27 was also carried out. Under vacuum at 440°, 27 pyrolyzed to two products, both of which were derivable from a β-naphthone. Higher temperatures caused the formation of unidentifiable materials, whereas, lower temperatures gave principally recovered starting material. The products obtained at 440° were formed in nearly equal amounts, but the total conversion was low. The product mixture was separated by gas chromatography using an SE-30 column. Three peaks were obtained and collected. The peak with the shortest retention time was due to 1-vinyl-1,3-dimethyl-β-naphthone, 31. The peak with an intermediate retention time was due to 1,3-dimethyl-2-naphthol, 32 and the last peak was due to recovered 27. The structure of 31 was assigned from its spectra. The infrared spectrum (CCl_4) showed a conjugated carbonyl absorption at 1660 cm^{-1}. The ultraviolet spectrum showed maxima at 232 nm (ε = 14,000), 238 (12,800), 297 (sh, 8300), 306 (9100),

and 319 (sh, 6400). The mass spectrum had a parent peak at m/e 198 and



27 31 32

a base peak at m/e 155. The nmr spectrum, which was complex, was assigned as shown.[35]

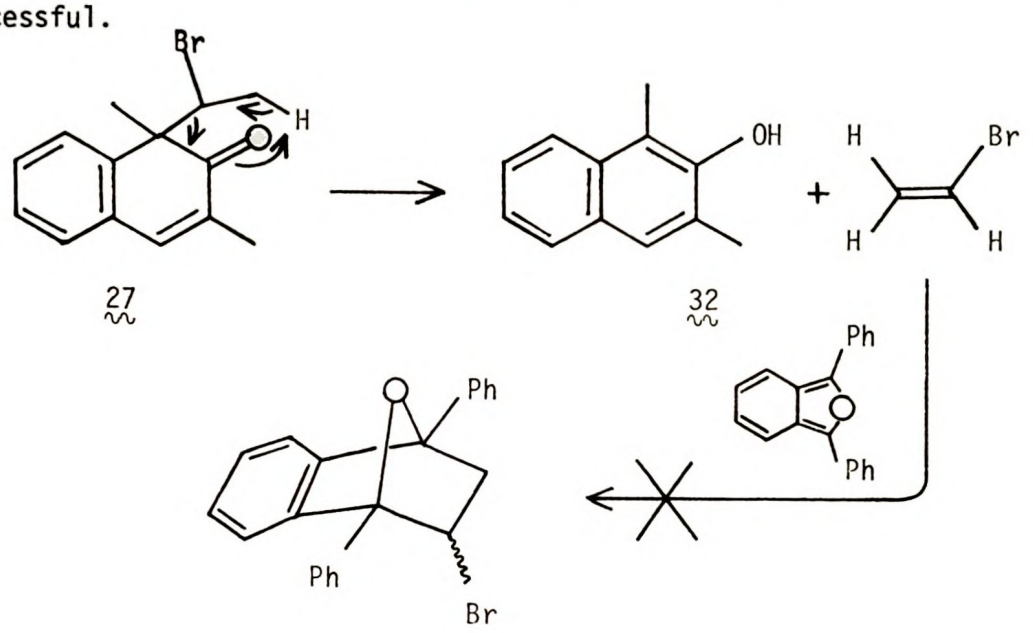


31

Compound 32 had a hydroxyl group as shown by a band at 3645 cm^{-1} in its ir spectrum. Its mass spectrum had a base and parent peak at m/e 172, and its nmr showed aromatic methyl groups at δ 2.37 and 2.45 and a broad peak at δ 4.58 due to the hydroxyl proton. The melting point of 32 was 89-90°, which compared well with the literature value[36] of 89-90°.

Whereas 31 is formed by the thermal dehydrobromination of 27, 32 can be formed by the thermal elimination of vinyl bromide. However,

attempts to trap the vinyl bromide with diphenylisobenzofuran were not successful.



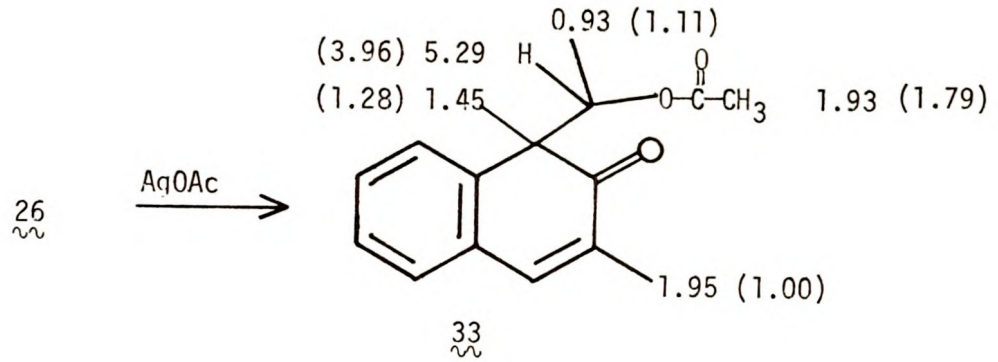
27 32

Compound 31 was also formed by chance as the product of a reaction of 26 with silver oxide (Ag_2O) in benzene which boiled dry overnight. Repetition of the reaction without allowing the solvent to go to dryness gave 27. This indicated that the reaction involved isomerization of 26 to 27, then thermal elimination to give 31.

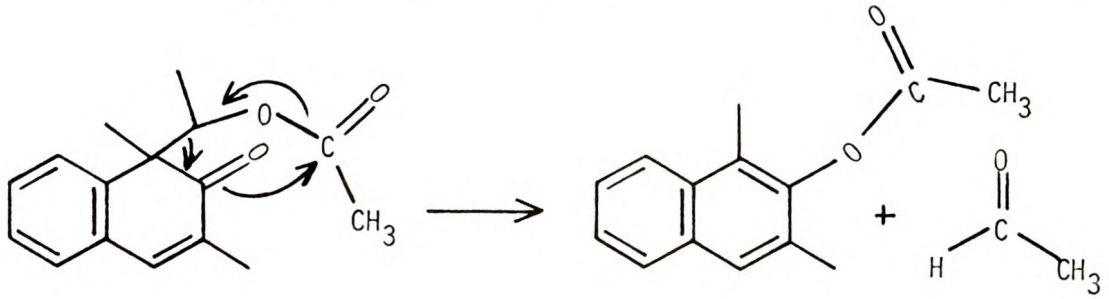
The evidence that 27 had the structure assigned was supported by its conversion to 31 and 32. The formation of 20 in the tin hydride reduction of 27 was the only inconclusive piece of evidence obtained. The pyrolysis of 26 was also carried out and the products obtained can only be derived from a dihydrotropone structure, which showed the basic structural difference between 26 and 27. The pyrolysis of 26 will be discussed in detail below.

Next the reaction of 26 with silver salts was attempted.[37] These led to rearrangement rather than to elimination. The reaction with

Ag_2O has already been discussed. Treatment of 26 with silver acetate led to a new compound, 33, which was an ester that did not contain bromine. The infrared spectrum of 33 showed two carbonyl absorptions,



at 1738 cm^{-1} and 1656 cm^{-1}. The uv spectrum was as expected for an unsaturated ketone. The mass spectrum showed an intense peak at m/e 214 and a base peak at m/e 172. Since the molecular weight of 33 was 258, the peak at m/e 214 corresponded to the loss of 44 amu. The attempted purification of 33 by gas chromatography on FFAP at 215° indicated that

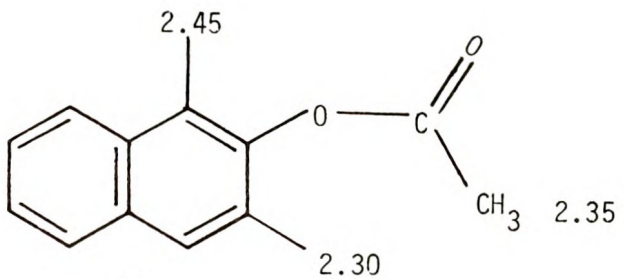


33 34

33 was thermally unstable and rearranged to the naphthalene derivative 34 by loss of acetaldehyde. This corresponded to a loss of 44 amu. The mass spectra of 33 and 34 were very nearly identical except that 33 showed an intense peak at m/e 43.

The nmr spectrum of 33 was assigned as shown on the structure. The vinyl methyl and the acyl methyl had very nearly the same chemical shifts. A 100 MHz nmr showed that there were indeed a methyl doublet and a methyl singlet with only slightly different chemical shifts. Furthermore, when the reaction of 26 was carried out in acetic acid-d_4 with silver acetate, the product lacked one methyl singlet in its nmr spectrum at δ 1.93. Further evidence that 33 had the β-naphthone ring structure was obtained when the reaction of 26 was repeated and stopped before the reaction was completed. The nmr spectrum showed that a mixture of 27 and 33 was present, with a ratio of 7:4. Further reaction of this mixture under the same conditions led to only 33. Thus it is clear that 26 rearranged to 27 which then reacted to give 33. The europium shift data on 33 indicated that the europium reagent coordinated predominantly with the ester carbonyl rather than the ring carbonyl.

The structure of 34 was indicated by a carbonyl absorption at 1750 cm^{-1} and a parent peak at m/e 214 with a base peak at m/e 172 (which would correspond to 1,3-dimethyl-2-naphthol, 32). In fact, the mass spectra of 34 and 32 were very nearly identical from 172 amu down. The nmr spectrum showed three methyl groups in the aromatic region, one



34

of which was very sharp and would be the acyl methyl group. The nmr spectrum was thus assigned as shown.

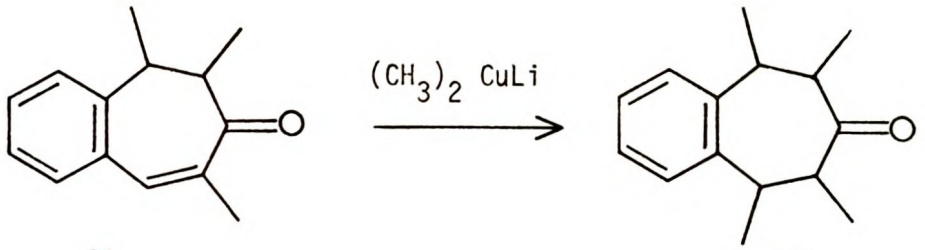
The vacuum pyrolysis of 33 was carried out to achieve a better synthesis of 34. However, the product obtained was 1,3-dimethyl-2-naphthol, 32. This result was consistent with the structure assigned to 33.

The dehydrohalogenation of 26 was attempted using several bases most common to this procedure,[7] LiCl and lithium carbonate (Li_2CO_3) in DMF, without success. Usually 26 was recovered unreacted or was isomerized to 27. Several other weak and strong bases were used without success. Usually a complex mixture of products resulted which lacked nmr absorptions in the appropriate region of δ 2.10-2.50. Only with the dimsyl anion ($CH_3SOCH_2^-$) did 21 appear to be formed in any significant amount. With potassium t-butoxide in DMSO, rather than elimination, reduction of 26 to 20 occurred.

Since there was some indication that 21 was formed in the gas chromatographic decomposition of 26, it was decided to try dehydrohalogenation of 26 by pyrolysis. This led to some success, with the best conditions found being a vacuum pyrolysis at 450°. The product was obtained in 28% yield and was identified by spectral comparison with a previously produced sample. The by-product of this reaction was 1,2,3-trimethylnaphthalene 23, (7% at 450°) which became the principal product at higher temperatures. This product was formed by the thermal decarbonylation of 21 (vide infra).

As a first step toward introducing the fourth methyl group required for the synthesis of 1, the reaction of 20 with dimethylcopper lithium

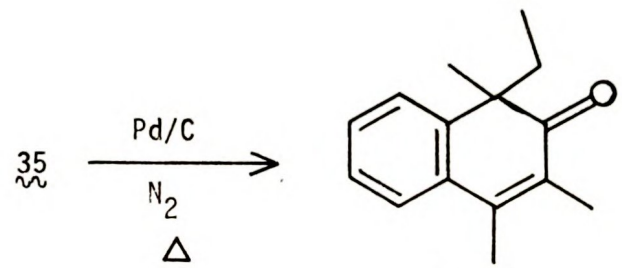
reagent was carried out.[33] The product, isolated in nearly quantitative yield, was 35 obtained as a mixture of three stereoisomers. One of the isomers was separated from the other two by gas chromatography. All three of the isomers had an element of symmetry, as was shown by the fact that each isomer displayed only two methyl doublet absorptions. The infrared absorption of the carbonyl group was 1690 cm^{-1}.



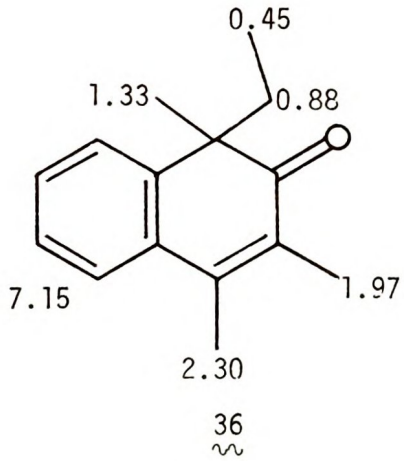
20 35

Compound 35 was brominated with bromine in acetic acid to give a complex mixture of products. A dibromide could be isolated from this mixture in low yield. The reaction of 35 with NBS also led to complex mixtures. The attempted dehydrobromination of these mixtures also led to complex product mixtures.

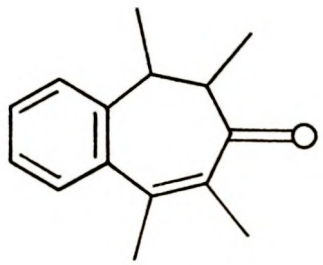
The dehydrogenation of 35 with chloranil was not successful. Attempted dehydrogenation using palladium on charcoal catalyst (as with 20) lead to no isolable benzotropones. The principal product, besides recovered starting material, was assigned structure 36. The reaction only occurred above 200° and then slowly. After four days the ratio of starting material to product was 4:6. The mixture obtained was separated by gas chromatography. The first peak obtained corresponded to 35; the second was due to 36. The nmr spectrum of 36 was assigned as



shown on the structure. The infrared spectrum showed a conjugated carbonyl absorption at 1652 cm^{-1}. The ultraviolet spectrum was consistent with the assigned structure.

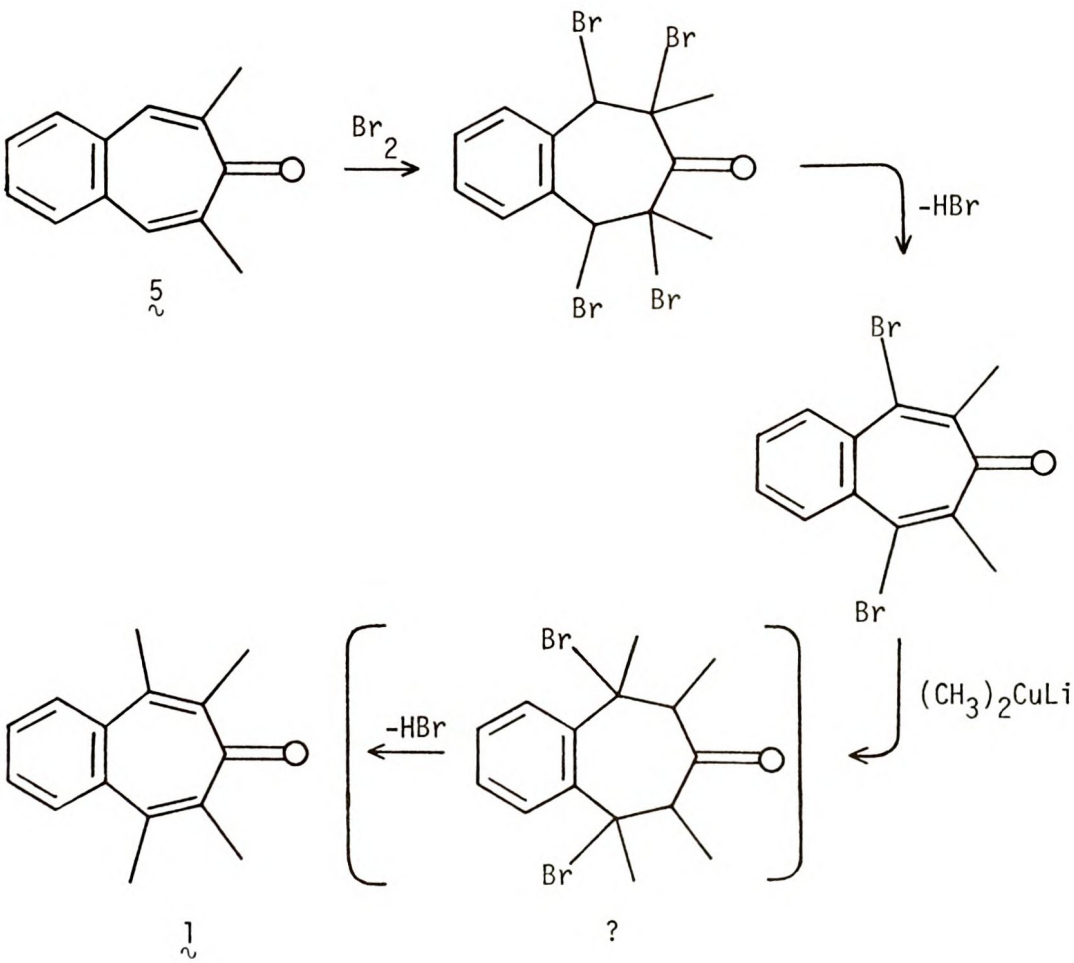


The mechanism for the formation of 36 must have involved a dehydrogenation step and a ring-contraction step. The sequence was probably ring contraction first, which was slow, followed by dehydrogenation, which was faster. This sequence is preferred to its converse since from the analogous reaction with 20 it was to be expected that 37 would be stable enough to the reaction conditions to be isolated; however, 37 was not formed from 20. Hence the ring contraction probably occurred before dehydrogenation.



37

An additional attempt to prepare 1 starting with compound 5 also did not give favorable results. The following reaction sequence was proposed:

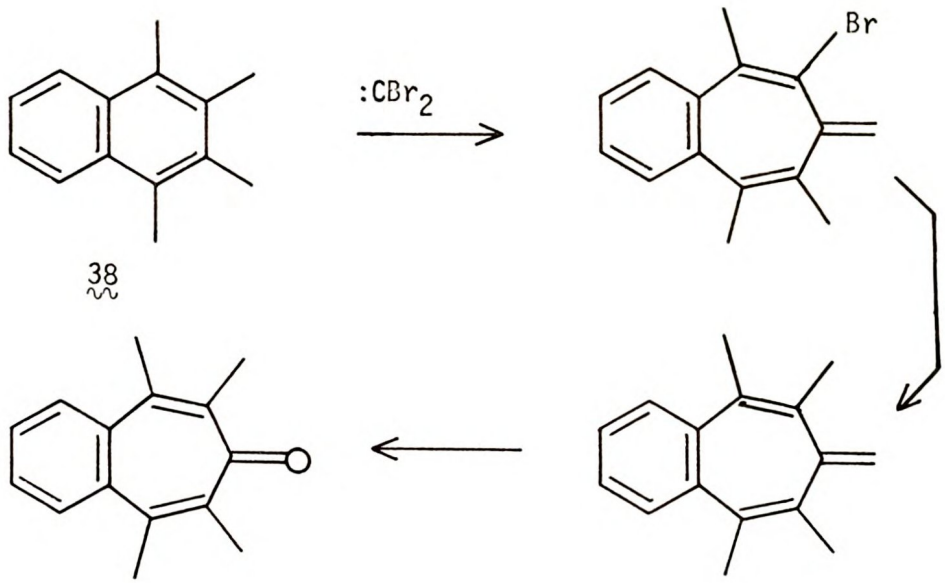


5 1 ?

However the reaction of $\underset{\sim}{5}$ with bromine led to a stable yellow compound which was very difficult to work with and could not be identified. Various reactions of this material led to nothing favorable; for example, reaction with base produced $\underset{\sim}{5}$.[4,8]

B. FORMATION OF BENZOTROPONES BY RING EXPANSION OF AN APPROPRIATE PRECURSOR

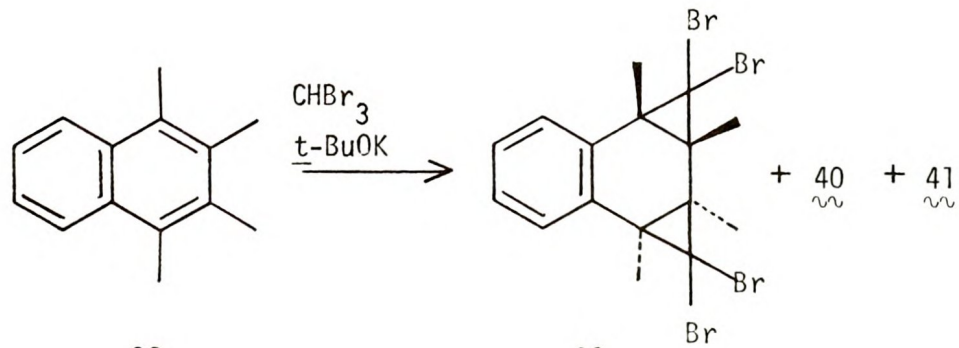
The following route to 1 was envisioned. Tetramethylnaphthalene, 38, was synthesized according to the procedure of Hausigk.[38] It was



38

1

treated with dibromocarbene generated in two ways. The first was the standard procedure using bromoform and potassium t-butoxide. This led to a mixture of recovered 38, two major products 39 and 40, plus a minor product 41.

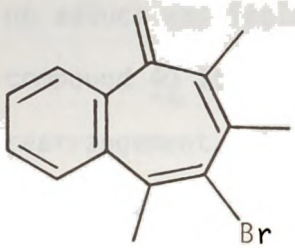


38 39

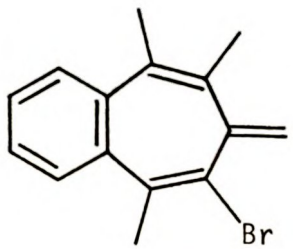
Product 39 was the unrearranged bis adduct 5,6-benzo-1,2,4,7-tetramethyl-3,3,8,8-tetrabromotricyclo[5.1.0.$0^{2,4}$]octane. The structural assignment of 39 was straightforward; it had only two methyl singlets in its nmr spectrum and a molecular weight of 524 (mass spectrum) with isotope peaks present for four bromine atoms. The structure was arbitrarily assigned the trans geometry since the cis structure would be extremely crowded.

Compound 40 displayed a strong terminal methylene absorption at 924 cm^{-1} in the infrared spectrum. The uv spectrum (cyclohexane) showed maxima at 241, 247, 253, 259, and 267 nm indicative of extensive conjugation. The nmr spectrum showed three methyl group absorptions; those at δ 1.92 and 2.02 were broad mutually coupled peaks whereas that at δ 2.43 was a sharp singlet. The methylene protons appeared at δ 5.05 and 5.11 as a pair of doublets (J = 2 Hz, 1H each). The mass spectrum of 40 indicated a parent peak at m/e 274 (29%), a (p + 2) peak at m/e 276 (28%), and a base peak at m/e 195 due to loss of bromine.

All of the data are consistent with a bromo-substituted benzoheptafulvene. Although the benzoheptafulvene was the desired product, the structural assignment of 40 was more difficult to make since there exist three possible isomers which fit both the mechanistic constraints of the reaction and the spectral data reasonably well. The energy barrier for interconversion between isomers through 1,5 hydrogen shifts was expected to be low. Structures 40, 42, and 43 are all possible mechanistically.



40



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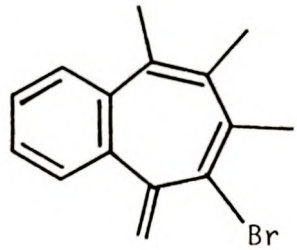


43

It would undoubtedly be possible to distinguish among the possibilities if all three compounds were available. Even though they are not, there are certain conclusions which can be drawn from the data available. Since all three structures could be expected to give similar ir and uv spectra, this information was least useful. Their nmr spectra are likely to be different, but difficult to predict. However, analysis of the expected coupling patterns allows some conclusions to be drawn. Structures 40 and 42 require two methyl groups to be coupled, with one not coupled. The extent of coupling, however, in 43 between the 6-methyl group and the 4- and 5- methyl groups is difficult to predict. The chemical shifts of the methyl groups have also provided clues. The electron-withdrawing effect of the bromine atom must be most pronounced on adjacent methyl groups. Structures 42 and 43 would have one methyl group shifted to lower field whereas with 40 the effect might be apparent with two methyl groups. In each case, the sharp methyl singlet is expected to be the lowest methyl signal in the spectrum. These arguments do not provide a clear answer to the assignment of this benzoheptafulvene.

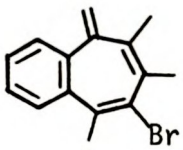
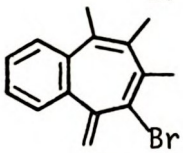
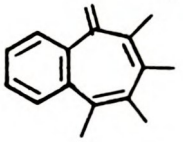
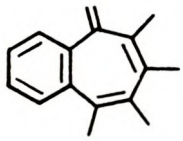
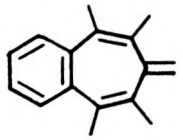
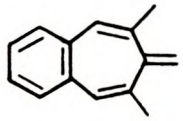
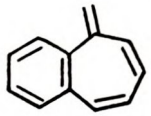
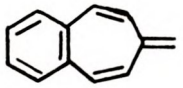
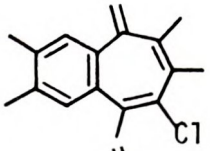
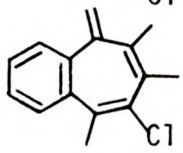
Clearly, a chemical means of determining the structure would be most satisfactory. Attempts to elucidate the structure through formation of a Diels-Alder adduct with maleic anhydride were not successful;

no adduct was isolable. In seeking further chemical information about compound 40 it was found that under certain conditions it underwent a rearrangement. Injection of 40 on FFAP at 190° gave two peaks. Peak one tailed into peak two. Reinjection of the material collected from peak two gave both peaks. Reinjection of the material collected from peak one gave only peak one. Therefore, the material of peak two was rearranging to that of peak one which was more thermally stable. The compound causing peak one was collected and its nmr spectrum showed that it was nearly identical with that of the originally injected compound. The nmr spectrum (CCl_4) of the compound from peak one had two broad methyl peaks at δ 1.89 and 2.03, a sharp methyl singlet at δ 2.37, one vinyl proton at δ 5.05, another at δ 5.10 and four aromatic protons at δ 7.17, 7.27, and 7.30. It appeared that this compound was one of the other possible isomers of 40. Further, the rearrangement of 40 in trifluoroacetic acid was carried out. After quenching, a mixture of both 40 and its thermally rearranged isomer was produced.

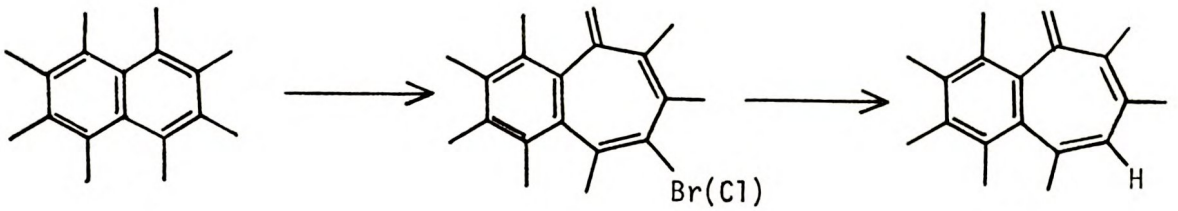
Table 1 shows the chemical shifts of ten benzoheptafulvenes. Of the compounds which were produced in this study, the structures of 94 (Section C), 101 (Section D), and 59 and 60 (see below) are certain. These compounds can be compared with similar compounds 44-47 from the literature,[30a,39] also shown in Table 1.

Comparing the 2,3-benzoheptafulvenes with the 4,5-benzoheptafulvenes, it is seen that the vinyl protons on the exocyclic double bond are in different environments in the two types of compounds. The chemical shift for 40 and its rearrangement product fit into the range for 2,3-benzoheptafulvenes rather than 4,5-benzoheptafulvenes.

Table 1. Nmr Spectral Comparison of Various Benzoheptafulvenes

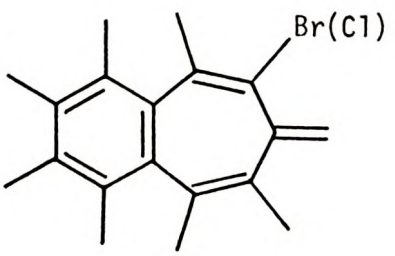
Structure		δ Sharp Me	δ Broad Me	δ Exocyclic Methylene
	40	2.43 (3H)	1.92 (3H) 2.02 (3H)	5.05 (1H) 5.11 (1H)
	43	2.37 (3H)	1.89 (3H) 2.03 (3H)	5.05 (1H) 5.10 (1H)
	94	2.17 (3H)	2.10 (3H) 2.23 (3H)	5.11, J = 0.5 Hz, (1H) 5.14, J = 0.5 Hz, (1H)
	59		1.75 (3H) 1.95 (6H) 2.17 (3H)	4.97 (2H) sharp
	60		2.10 (12H)	4.78 (2H) sharp
	101	2.00 (6H)		4.95 (2H) not sharp
	44 [30a]			5.02 (2H)
	45 [30a]			4.72 (2H)
	46 [39]	2.32 (3H)	1.83 (3H) 1.98 (3H)	5.04 (1H) 4.99 (1H)
	47 [39]	2.33 (3H)	1.86 (3H) 1.98 (3H)	5.04 (1H) 4.99 (1H)

A recent report has helped to definitively assign product 40. Oku[39] reported the formation of 48 from the sodium naphthalenide reduction of the benzoheptafulvene products of dichlorocarbene and dibromocarbene with octamethylnaphthalene. The benzoheptafulvene



49 48

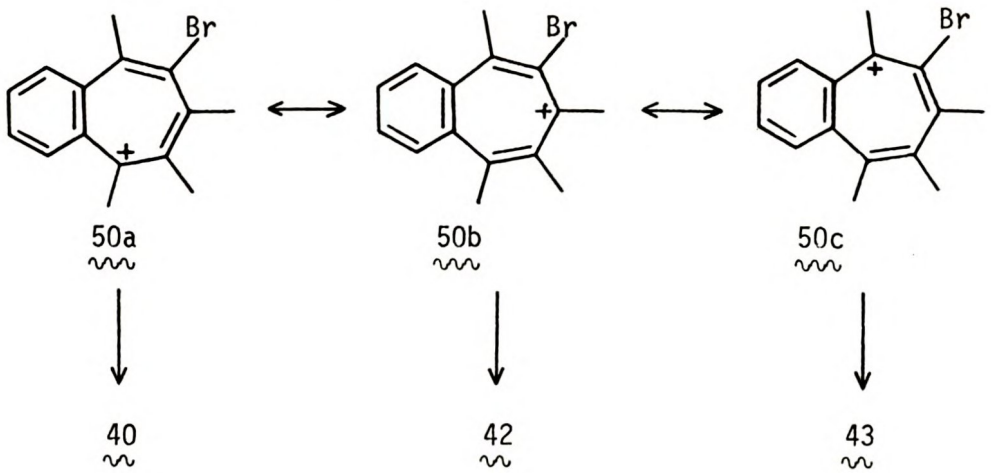
formed must then have been 49 rather than 11 as previously assigned.[13]



11

Oku[39] substantiated this assignment by studies of chemical shifts and coupling constants of a series of methyl substituted naphthalenes and by mechanistic considerations. One of Oku's arguments concerns the relative energies of the benzotropylium ion intermediate 50. Of the three contributing canonical forms 50a, 50b and 50c, form 50a is expected to be the lowest energy one, since the positive center is farthest from the electron-withdrawing bromine. Isomer 40 which derives from 50a would thus be expected by Oku to be the product obtained in the reaction. However the three contributing forms of ion 50 cannot be

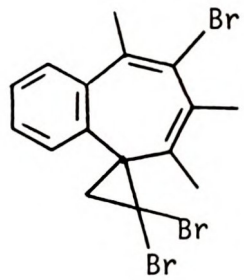
considered as separate ions, since they do not exist as such. There is only one intermediate ion, and the product that is formed will be determined by the relative energies of the transition states on the pathways from ion 50 to products. The product having the pathway with the lowest transition state energy will be the product formed, even if that requires loss of a proton from a methyl group remote from the positive charge in ion 50a.



Considering all the evidence, the best assignment for the benzoheptafulvene originally isolated is structure 40, 4,6,7-trimethyl-5-bromo-2,3-benzoheptafulvene. The structure of the rearranged isomer is best assigned as 43, 4,5,6-trimethyl-7-bromo-2,3-benzoheptafulvene.

Now we consider the structure of the minor product, 41. Oku[39] stated that benzospirononatriene products were only formed by carbene addition to dimethyl-substituted naphthalenes. In the present example, however, a significant amount of a benzospirononatriene 41 was formed. This product was considered to arise by the addition of dibromocarbene to the exocyclic double bond of 40. Since only 40 and not 42 or 43 was isolated, the benzospirononatriene isolated might be expected to have

structure 41. However the isolation of only one isomer of the bromo-substituted benzoheptafulvene does not mean that only one isomer was produced. The possibility exists that another of the isomers was produced but reacted faster with dibromocarbene than did 40 and hence was not isolated from the reaction as benzoheptafulvene but appeared only as adduct 41. The nmr spectrum of 41 has two mutually coupled methyl groups at δ 1.78 and 1.94 and a sharp methyl singlet at δ 2.54. Of the three possible isomers of benzospirononatriene, either structure 41 or 51 seem most consistent with this spectrum.



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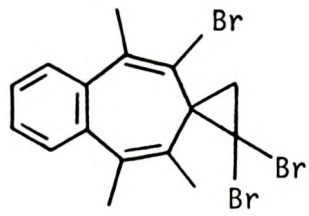

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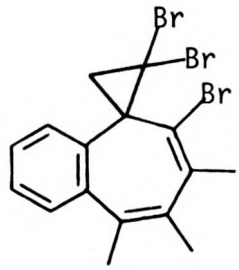
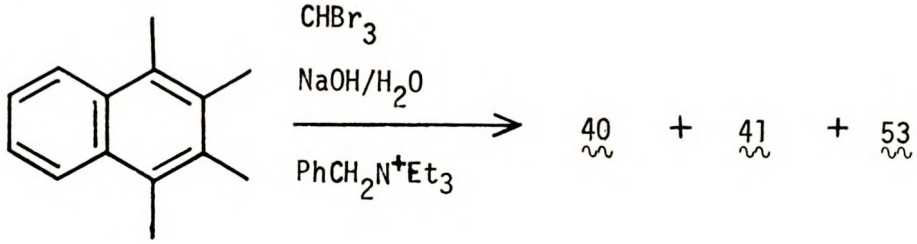


52

The second way that dibromocarbene was generated for reaction with 38 was by the method of Makosza.[40] With this method, the principal product formed was 40. No 39 was produced. Small amounts of 41 and 53 were also isolated. Compound 53 is also formed by the addition of dibromocarbene to 40. However, instead of attacking the more reactive exocyclic double bond, the carbene has added to one of the other seven-membered ring double bonds. The nmr spectrum of the benzohomoheptafulvene isolated showed only one vinyl methyl absorption and is consistent with isomeric structures 53, 54, or 55 but not with 56, 57,

or 58. The structure assigned is 53 which is derived from 40. Although



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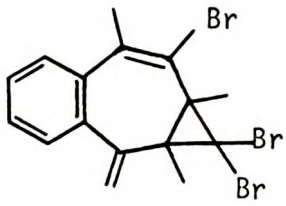
the yield of 53 was very low, it was easily isolated and identified because after column chromatography it was fairly pure and readily crystallized into cubic crystals. It had such a simple nmr spectrum that it attracted our curiosity.



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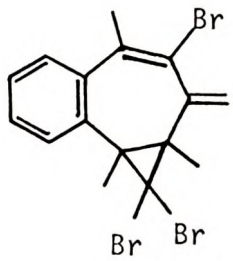

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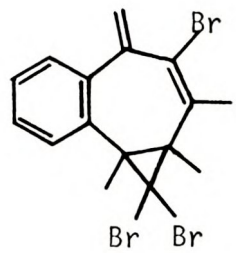

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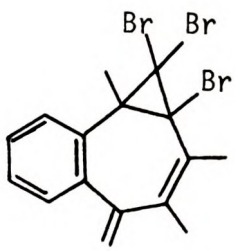

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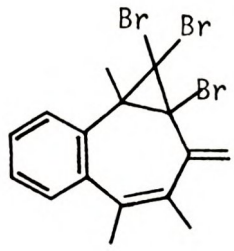

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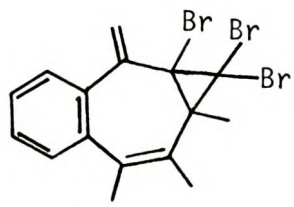
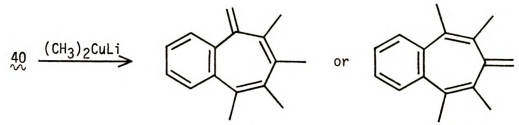


58

The reaction of 40 with dimethylcopper lithium reagent[41] led again to a problem of distinguishing between isomers that are readily interconverted by 1,5-hydride shifts. Tetramethylbenzoheptafulvene, the product formed, has two isomers 59 and 60. Again a chemical means of



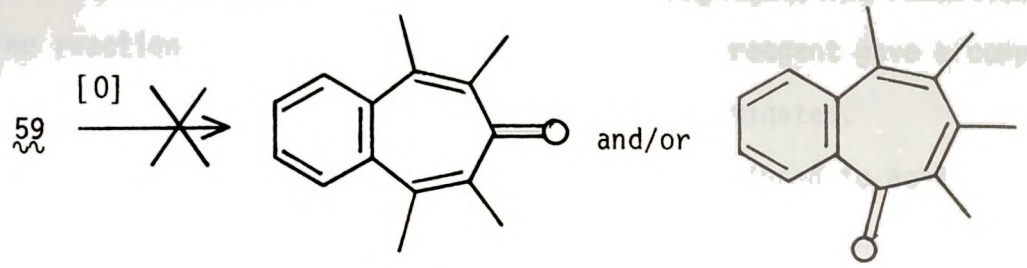
59 60

structure determination would be best; however, attempts to determine which structure was correct by Diels-Alder reaction met with no success. In the mass spectrum of the tetramethylbenzoheptafulvene isolated, the parent peak was at m/e 210 as expected, with a base peak of m/e 141. Its ir spectrum showed a terminal methylene absorption at 915 cm^{-1}. The nmr spectrum showed three broad methyl absorptions at δ 1.75 (3H), 1.95 (6H) and 2.17 (3H). The exocyclic methylene protons appeared at δ 4.97 as a sharp peak. The symmetry of structure 60 requires only two sets of methyl absorptions and identical vinyl protons. With structure 59 four non-equivalent methyl groups are expected, as well as non-equivalent methylene protons. Although neither structure fits expectation precisely, structure 59 is most satisfactory since it is feasible that two methyl groups in 59 could coincidently have the same chemical shift; the methylene protons might also be coincidentally equivalent. Structure 60 cannot display the nmr spectrum found for this compound because of its symmetry.

Injection of 59 on an FFAP gc column at 180° gave one principal peak. The product was collected and found to be a mixture of the material injected and another compound. The new compound had the same molecular weight and a similar infrared spectrum to the starting material. However its nmr spectrum was different; it had a single peak at δ 2.07 equal to 12 protons and a single peak at δ 4.77 equal to two protons. This compound was assigned structure 60. All the methyl groups were coincidentally equivalent.

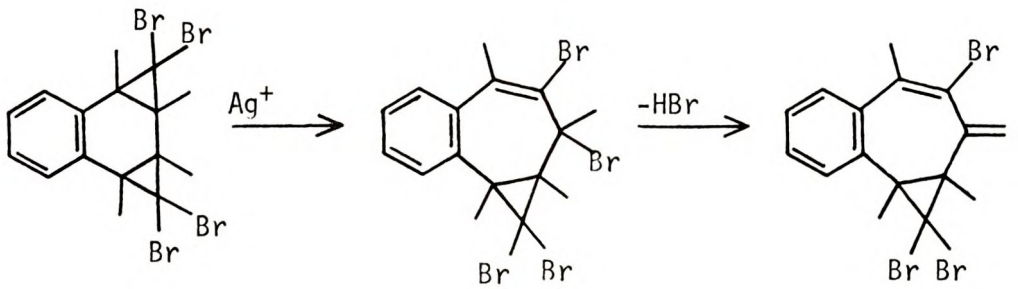
The reaction of 59 with trifluoroacetic acid also produced a mixture of these two compounds. Once formed, 60 appeared to be slightly less stable than 59, although both compounds slowly decomposed. Integration of the vinyl protons of the quenched mixture indicated that 59 : 60 were formed in a ratio of 2:1. The mixture was chromatographed on silica gel thick layer plates eluted with petroleum ether and a separation was obtained, although the compounds were not pure.

Compound 59 was treated with $KMnO_4$ and with HIO_4 in an attempt to oxidize the exocyclic double bond, to form the benzotropone. This reaction led to the isolation of a mixture of 59 and 60 and infrared analysis of the entire reaction mixture showed no carbonyl absorptions. Of course oxidation in an acidic medium could not be successful, since in acid the benzoheptafulvenes immediately form their corresponding benzotropylium ions.



1

Compound 53 would be an excellent precursor for the benzohomotropylium ion desired to test Scheme 2 (see page 14), but since it was produced in low yield this was not feasible. Compound 40 could be converted to 53 with dibromocarbene, but 41 would be the predominant product, since the exocyclic double bond is the most reactive double bond in 40. Only a very low yield of 53 could be expected. However, 39 was also a potential precursor of 53, through isomerization and loss of hydrogen bromide. An attempt was made to affect this conversion.



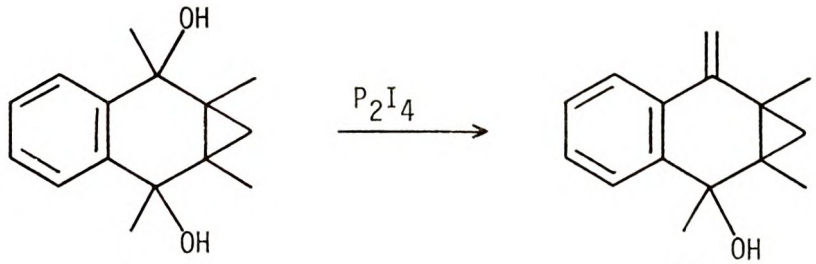
39 53

The reaction of 39 with silver salts, known to open dibromocyclopropane[37] rings, led to no reaction. Since that time a report of a ring opening reaction of the bis-dichlorocarbene adduct to octamethylnaphthalene has been published.[28] Oku obtained benzoheptafulvenes and

cyclooctatetraenes as products of a sodium naphthalenide reduction. The reaction of 39 with dimethylcopper lithium reagent gave a complex mixture of products which was not further investigated.

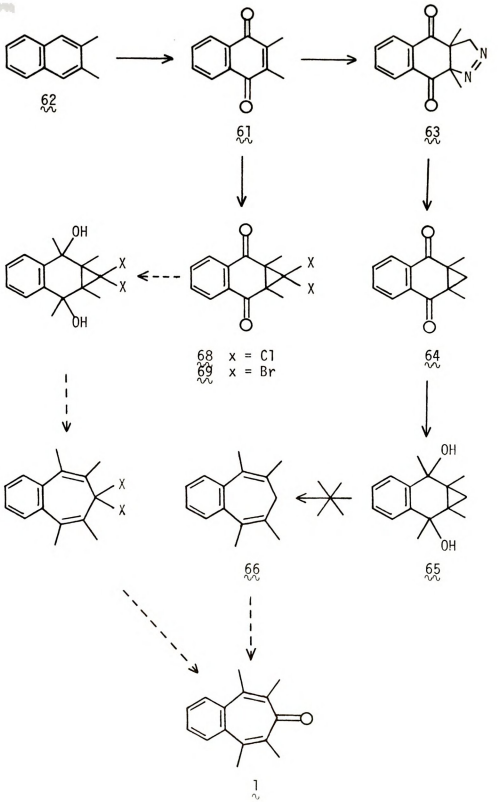
An alternative method of ring expansion designed to achieve benzotropone synthesis was envisioned as outlined in Scheme 3. This route was not followed through to completion, primarily because the method in section C was successful, but the results as far as they were carried will be presented here.

The starting material was 1,4-naphthoquinone, 61, synthesized by either chromic acid oxidation[42] or by hydrogen peroxide oxidation[43] of 2,3-dimethylnaphthalene, 62. Diazomethane was generated according to Moore and Reed[44] and allowed to react with 61 according to the procedure of Eistert,[45] to form the pyrazoline 63. This product was either pyrolyzed[45] or better photolyzed[46] to form 64. Compound 64 was then treated with two equivalents of methyllithium to form 65. The 1,4-homo-elimination procedure[11,47] using P_2I_4 [48] was then carried out. The product obtained was not the desired 66, but was assigned structure 67. The infrared spectrum of 67 showed a hydroxyl group with bands at 3640 and 3500 cm^{-1}. The nmr spectrum showed vinyl protons at δ 4.92 and 5.17, but no vinyl methyl absorptions. The cyclopropane ring remained intact as the doublets at δ 0.77 and 0.23 showed.



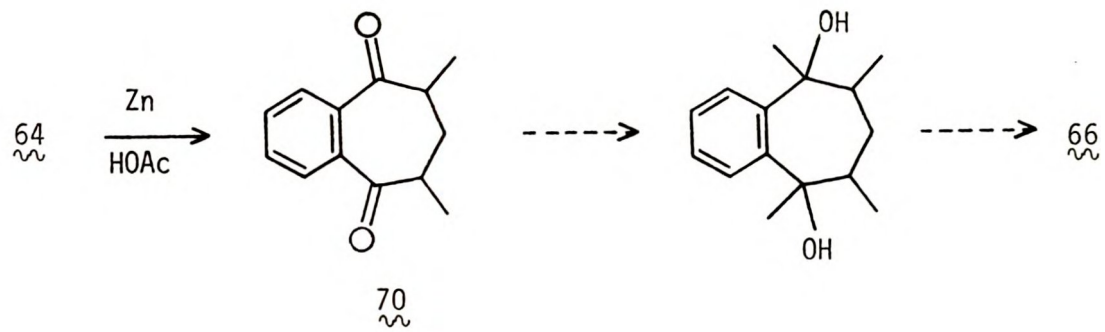
65 67

Scheme 3



Dichlorocarbene and dibromocarbene were also added to compound 61 to form compounds 68 and 69 (x = Cl or Br). These compounds were difficult to purify and were not obtained pure. This work was abandoned before further investigation of these products could be carried out.

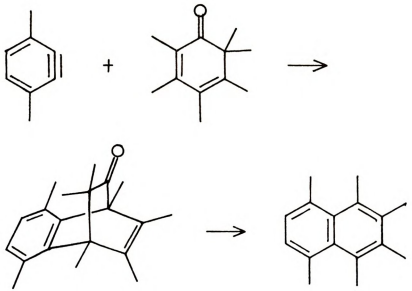
The reduction of 64 to 70 was also accomplished according to the procedure of Hanafusa[46] and Buchanan[49] but was not carried further because of abandonment of the approach.



70

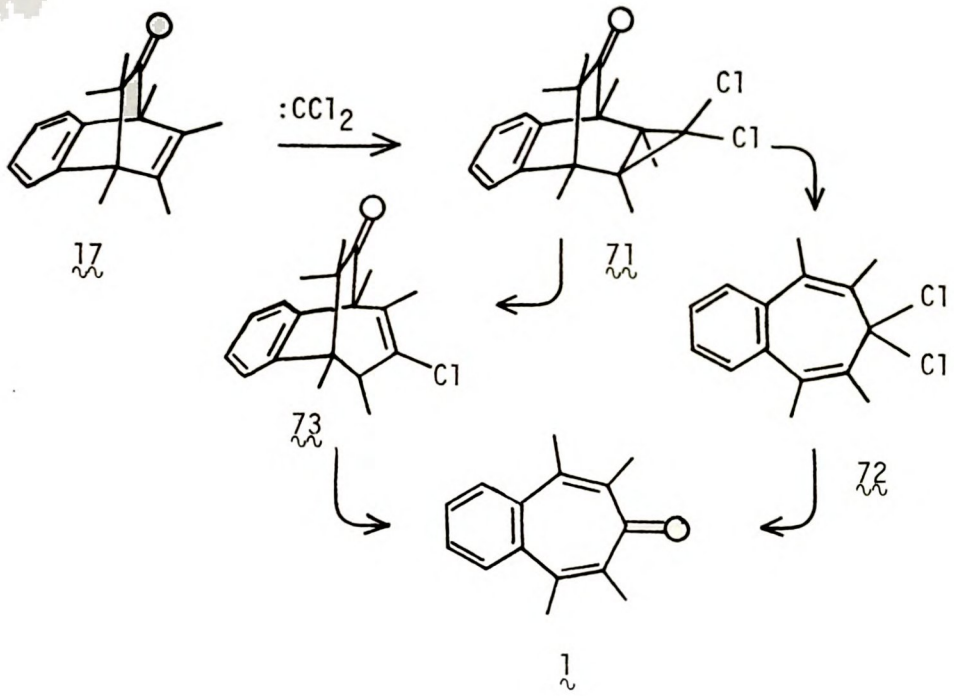
C. SYNTHESIS THROUGH BRIDGE ELIMINATION FROM BICYCLIC STRUCTURES

In 1967 Hart[50] reported the synthesis of hexamethylnaphthalene through the following reaction sequence:



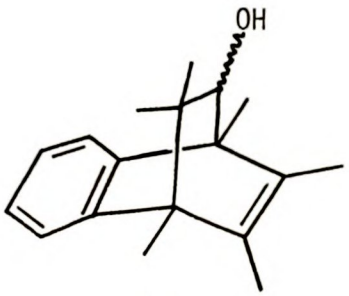
If such a method could be used to form substituted naphthalenes, it might well be adapted to the formation of benzotropones and benzoheptafulvenes.

For example, addition of dichlorocarbene to 17 might yield 71 which could undergo 1,4-homo-elimination of the bridge to give 72 which could be hydrolyzed to 1. Alternatively, 71 might be converted to 73 which through bridge elimination could lead to 1.



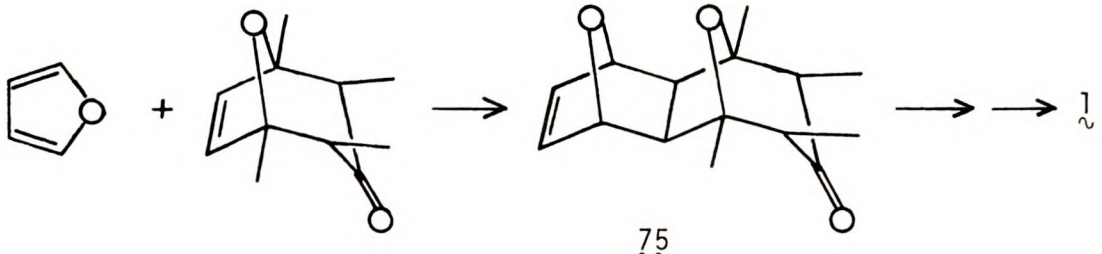
17 71 73 72 1

In following this approach, 17 was synthesized by established procedures.[51] It was then treated with dichlorocarbene generated both from chloroform and potassium t-butoxide as well as by the two phase method of Makosza.[40] However, no carbene adducts were obtained. Since the lack of reactivity might be due not only to steric hindrance, but also to inactivation of the double bond through homoconjugation with the carbonyl group, 17 was reduced to 74, obtained as a mixture of stereoisomers.[51] However, reaction of 74 with dichlorocarbene generated by both methods again gave no carbene adducts. Besides isolation of starting material, a small amount of 17 was produced in the reaction.



74

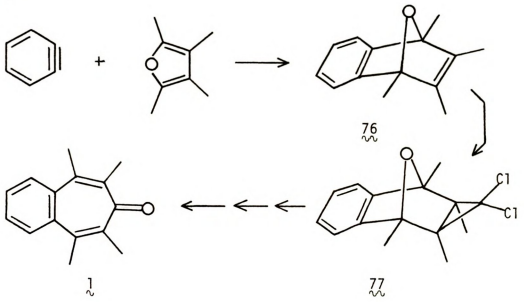
Another route envisioned could proceed through 75 (formed by a Diels-Alder reaction), followed by bridge elimination to give 1.



75

However, the attempt to form 75 did not succeed and was abandoned in favor of the following alternative.

The last route employing the bridge elimination strategy was a direct adaptation from a procedure of Battiste[15] (Scheme 1). As envisioned, compound 76 (formed by the reaction of benzyne with tetramethylfuran) and compound 77 (the dichlorocarbene adduct of 76) would be the key intermediates.

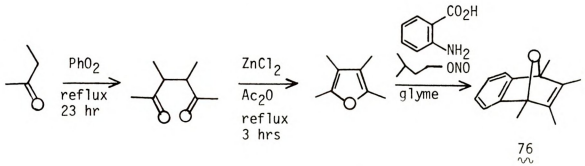


76

1

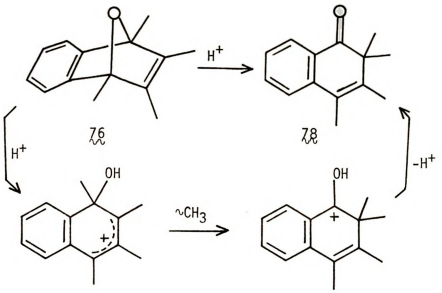
77

Tetramethylfuran was synthesized from 3,4-dimethyl-2,5-hexanedione, which in turn was synthesized from butanone by the procedures of Wolthius.[52] Rather than use the Wolthius method for synthesis of 76 it was desired to use anthranilic acid as the benzyne precursor.[53] Reaction did not succeed until glyme was used as the solvent.[54]



76

When 76 was gas chromatographed above 165°, a new compound was formed. This same compound was formed when 76 was treated with trifluoroacetic acid. The product, benzodienone 78 was identified by spectral comparison with the data previously published by Hart.[55]

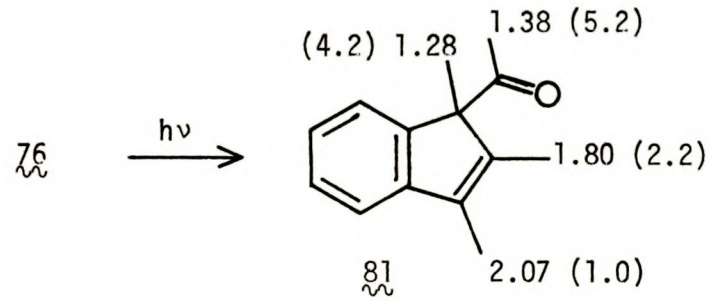


Formation of 78 presumably occurred by protonation and ring opening of 76 to give ion 79; methyl migration and proton loss yield 78. Murray[55] prepared 78 by direct oxidation of 1,2,3,4-tetramethylnaphthalene, presumably via a similar intermediate. In contrast, Wolthius[52] reported that the reaction of 76 with hydrogen chloride in methanol gave 1-(methoxymethyl)-2,3,4-trimethylnaphthalene.

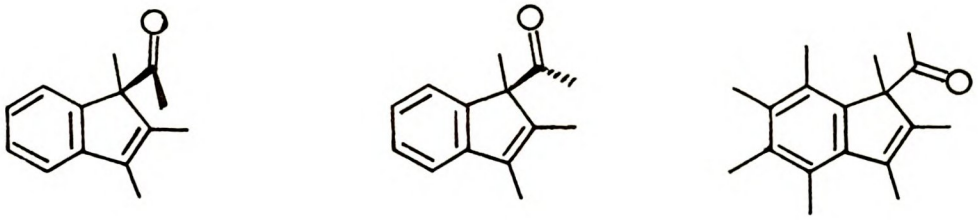
Compound 76 is a potential precursor to tetramethyl oxepin 80.[56] Therefore the photolysis of 76 was investigated. Sensitized photolysis

76 80

of 76 did not eliminate the oxygen bridge, but instead gave indene 81 by ring contraction. The ir spectrum of 81 had an absorption band at 1705 cm^{-1} indicative of an unconjugated carbonyl group. Its ultraviolet spectrum (cyclohexane) had λ max at 222 nm (ε = 13,000), 229 (sh, 12,000), 261 (7100) and 285 (sh, 2200). The parent peak by mass spectrometry was at m/e 200 with a base peak of m/e 157. The nmr spectrum was assigned as shown. The high chemical shift of the acetyl methyl group was unusual but it indicated that conformation 81a is preferred over conformation 81b. The same high chemical shift for an acetyl methyl group was found in the nmr spectrum of 82.[57] Spectral comparison of 81 with 82 substantiated the structural assignment of 81.

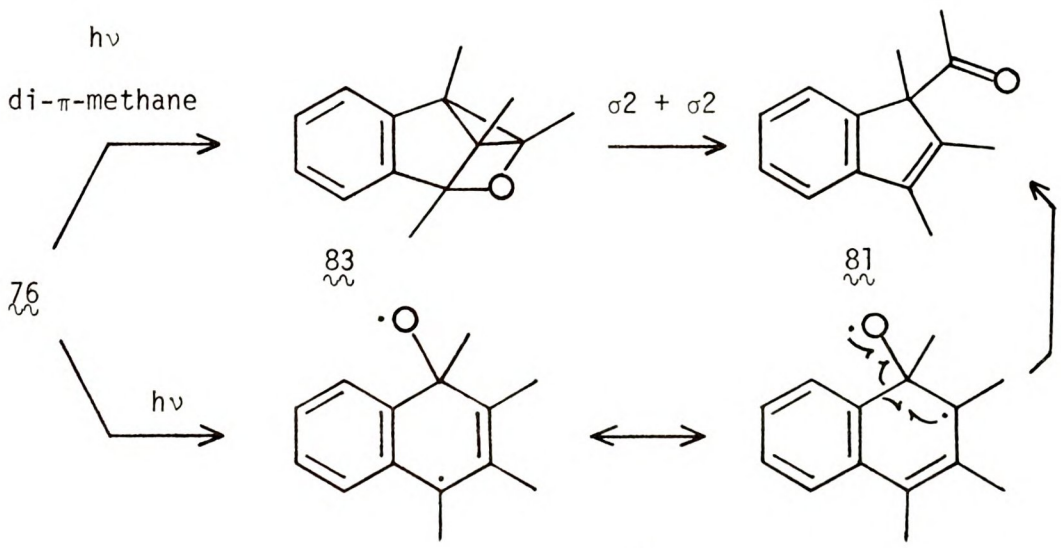


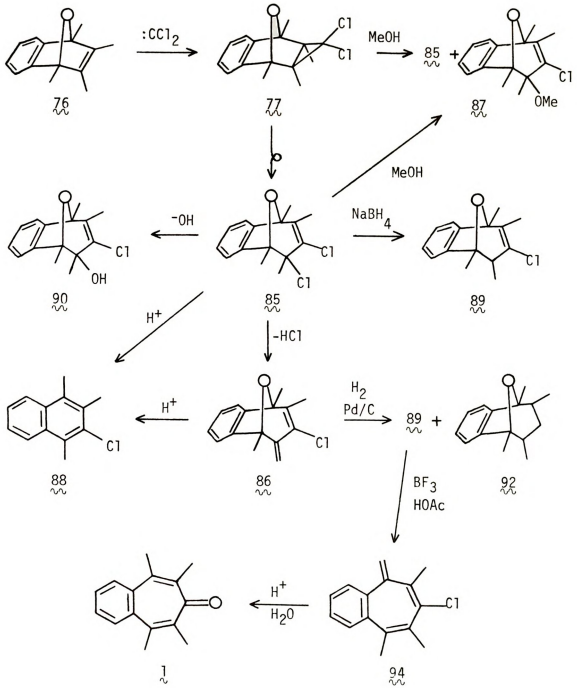
76 → 81



81a 81b 82

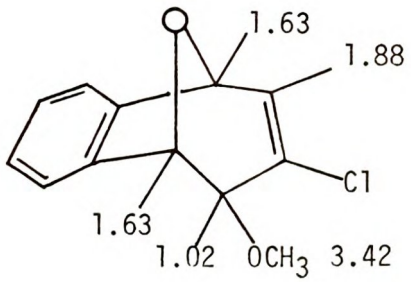
The formation of 81 from 76 was considered to occur mechanistically by a di-π-methane reaction to form 83, followed by a σ2 + σ2 thermal rearrangement. An alternate mechanism would begin by a homolytic cleavage of a carbon oxygen bond to form diradical 84. A second bond cleavage to form a carbonyl double bond and combination of the phenyl and allylic radicals would give 81.




:CCl2
MeOH
85 +
Cl
OMe
76
77
87
MeOH
-OH
NaBH4
Cl
OH
90
85
89
H+
-HCl
H+
H2
Pd/C
89 +
88
86
92
BF3
HOAc
H+
H2O
1
94

Reaction of 76 with dichlorocarbene generated by the method of Makosza[40] led to a mixture of products. The reaction product mixture consisted mainly of 85, but also usually contained minor amounts of 86. The initial addition product, 77, was isolated only once. It easily rearranged thermally to 85 by cyclopropane ring opening. The nmr spectrum of 77 had two methyl singlets at δ 0.92 and 1.80. Compound 77 was not fully spectrally characterized because of its instability with respect to 85.

Compound 77 crystallized upon addition of methanol, but methanol also caused rearrangement to 85 and solvolysis to 87. Compound 87 had a mass spectral parent peak at m/e 278 and a base peak at m/e 200. Its nmr spectrum had methyl singlets at δ 1.02 (3H), 1.63 (6H), 1.88 (3H), and 3.42 (3H). On the basis of these data, 87 was assigned as 1-chloro-2,3,6,7-tetramethyl-7-methoxy-3,6-epoxy-4,5-benzocyclohepta-1,4-diene.



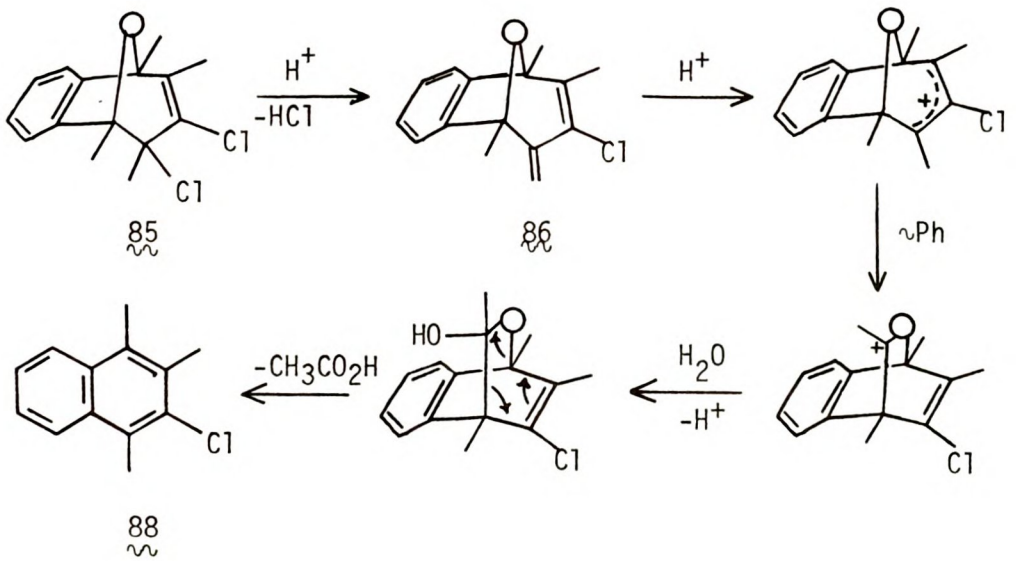
87

The nmr spectrum of 85 had methyl singlets at δ 1.53 (s, 3H), 1.65 (s, 3H) and 1.83 (s, 6H). Although all four methyl groups would be expected to be unique, two of them coincidentally have the same chemical shift. At 100 Hz the nmr spectrum showed that the δ 1.83 peak separated slightly to show two singlets of equal area. Diene 85 was

also difficult to obtain pure because it easily eliminated hydrogen chloride to give 86; thus the spectral data for 85 are not complete.

Gas chromatography of 85 gave pure 86 which was completely characterized. The nmr spectrum of 86 had methyl singlets at δ 1.68, 1.78 and 1.97, vinyl protons at 5.17 (s, 1H), 5.33 (s, 1H), and aromatic protons 7.12 (s, 4H). Mass spectrometry gave a parent peak at m/e 246 and a base peak at m/e 203. The other data were consistent with this structure and the assignment was straightforward.

The reaction of 85 with acid yielded a new product, 1,2,4-trimethyl-3-chloronaphthalene, 88. Compound 88 was identified by spectral analysis and comparison with the literature.[58] A mechanism for its formation follows:



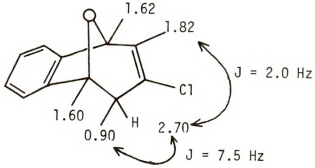
85 86 88

In accord with this mechanism, 86 was subjected to the same reaction conditions and it was found that again 88 was the product.

Since 89 was the compound desired, the reduction of 85 directly to 89 using a hydride reducing agent was investigated. Lithium aluminum

hydride does not efficiently reduce tertiary halides whereas sodium borohydride does. The procedures of Brown and Bell[59] and of Bell[60] were followed with the best results obtained using sodium borohydride in aqueous diglyme, stabilized with sodium hydroxide. Diene 89 was obtained under these conditions; however, the reaction was not clean and 86 and 90 were also formed. Tri-n-butyltin hydride was also explored as a direct reducing agent, but with only marginal success.

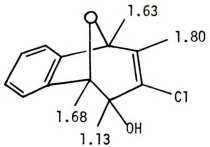
Compound 89 was crystalline, mp 78-79.5°. Its infrared spectrum showed absorption bands at 1645 cm^{-1} for the carbon-carbon double bond and at 1250 and 1175 cm^{-1} for the ether linkage. Mass spectrometry showed that one chlorine atom was present, with p and (p + 2) fragments at m/e 248 and 250. The base peak was at m/e 213, which corresponded to loss of a chlorine atom. The ultraviolet spectrum of 89 had a shoulder at 228 nm (ε = 5100), and λ max at 259 nm (600), 265 (780), and 273 (760). The nmr spectrum was assigned as shown in the diagram.



89

Compound 90 showed bands in its infrared spectrum at 3610 and 3500 cm^{-1} typical of an alcohol; the uv spectrum showed a shoulder at 234 nm (ε = 4610), and maxima at 259 (803), 266 (975) and 273 (923).

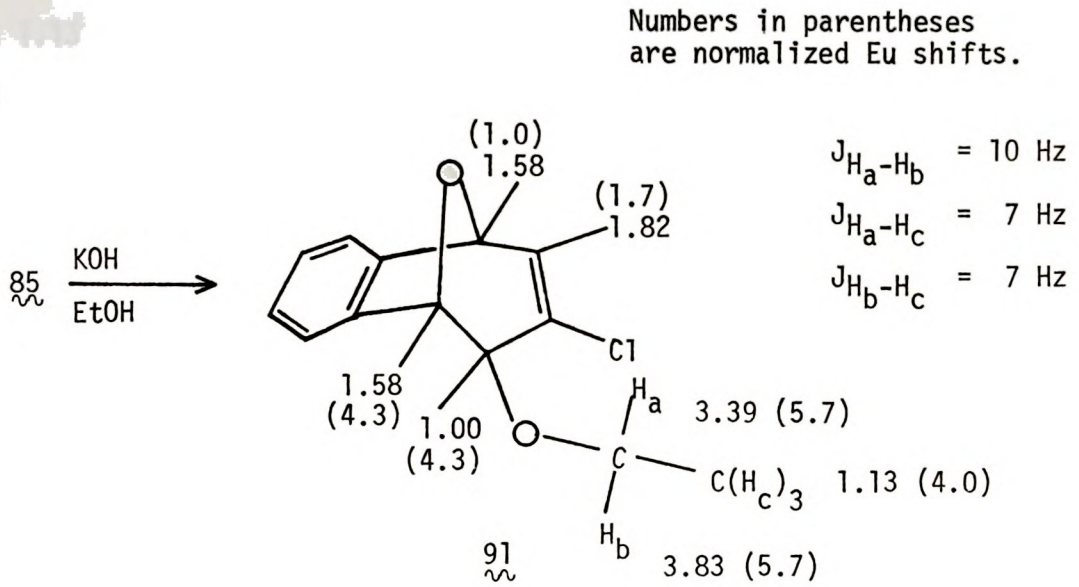
The nmr spectrum had four methyl singlets at δ 1.13, 1.63, 1.68 and 1.80 and a broad peak at δ 2.37 for the hydroxyl hydrogen. The mass spectrum showed a base peak at m/e 204. The molecular ion peak at m/e 264 was not recorded; the peak at highest m/e was 246 which corresponded to loss of water from 90.



90

Since 85 was readily dehydrochlorinated to form 86, an efficient means was sought to carry out this conversion. Pyrolysis using a hot tube at 450° gave an 80% yield of 86.

The reaction of 85 with potassium hydroxide in absolute ethanol gave a mixture of products. Besides 86, the ethoxy substitution compound 91 was formed as the major product, presumably through a nucleophilic displacement reaction. The mass spectrum of 91 indicated a molecular formula of $C_{17}H_{21}O_2Cl$ with a parent peak at m/e 292. Additional peaks were present equivalent to loss of methyl, ethyl, and ethoxy fragments. The nmr spectrum consisted of three singlets at δ 1.00 (3H), 1.58 (6H), and 1.82 (3H), the four aromatic protons at δ 6.97, 6.88 and 7.00, and 2 additional multiplets. (A Eu shift experiment showed that the peak at δ 1.58 was actually due to two coincidentally equivalent methyl singlets.) At δ 1.13 in the nmr



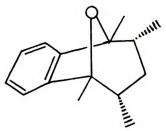
spectrum, was a multiplet that appeared to be a triplet of J = 7 Hz, (3H). Another complex multiplet was centered at δ 3.62 (2H). A 100 MHz nmr spectrum was obtained. This showed that the δ 3.62 multiplet was really made up of two multiplets centered at δ 3.39 and 3.83. Each multiplet consisted of two overlapping quartets. Splitting within each quartet was 7 Hz while splitting between the quartets in each set was 10 Hz. Careful measurement of the same values in the 60 MHz spectrum show them to be 7 and 10 Hz respectively, whereas the distance between sets had changed from 26 Hz in the 60 MHz spectrum to 44 Hz in the 100 MHz spectrum. Therefore the coupling constant between these two protons was 10 Hz, whereas the 7 Hz coupling constant must be associated with the peak at δ 1.13. Double irradiation decoupling experiments were also performed to substantiate this. Irradiation at δ 3.62 collapsed the δ 1.13 peaks toward a singlet, although collapse was not complete. Irradiation at either δ 3.39 or δ 3.83, the centers of each respective set of quartets, collapsed the δ 1.13 peaks to a doublet. The peaks

at δ 1.13 were thus in reality a doublet of doublets, each doublet having J = 7 Hz. A methyl group split by two nonequivalent protons having equivalent coupling constants fits this pattern. Irradiation in the δ 1.13 peaks affected the δ 3.62 multiplet variously depending upon exactly where the second frequency was applied. At best, two doublets J = 10 Hz were obtained at approximately δ 3.39 and δ 3.83. With the decoupling frequency located differently, either the left quartet of each set or the right quartet of each set would become a singlet while the remaining quartets became quartets of altered coupling constant (the high or low spin proton of each set was decoupled). Each set of quartets was thus a doublet of quartets caused by each proton splitting the other and each being split by the same methyl group.

Such a pattern became consistent with structure 91 as assigned when it was realized that protons a and b were diastereotopic and magnetically non-equivalent due to the assymetric center to which the ethoxy group was bonded. Such diastereotopic non-equivalence has previously been observed, even when the assymetric center was once removed from the protons in question by an oxygen atom.[61] Protons a and b have split each other into a doublet and each was in turn split by the methyl group into a quartet. The methyl group was split into a doublet of doublets which appeared as a triplet since both coupling constants were of the same value.

The best method found for converting 85 to 86 was simple column chromatography over basic alumina using cyclohexane. Elution with 10% ether in hexanes, rather than with cyclohexane, purified 85, but did not convert it to 86.

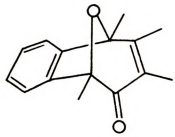
The hydrogenation of 86 proceeded best in cyclohexane with 10% palladium on charcoal as catalyst. The products were 89 (74%) and 92 (25%). Compound 92 was a crystalline material which showed a two methyl singlet and a two methyl doublet in its nmr spectrum. The product was symmetrical and its uv spectrum indicated no unsaturation except for the benzene ring: λ max 269 nm (ε = 200), 262 (1930), and 256 (1430). The molecular weight of 92, determined by mass spectrometry, was 206 amu, which precluded the presence of chlorine. If both double bonds were hydrogenated and the chlorine was reduced as well, 92 must be 1,2,4,5-tetramethyl-6,7-benzo-8-oxobicyclo[3.2.1]octane. The stereochemistry was not determined but was assigned with the hydrogens exo, since the exo face of 92 would be most accessible to the catalyst surface.



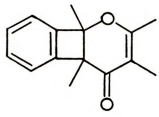
92

Photolysis of 77, 85, 86, and 89 gave no reactions or rearrangements. Battiste[15] used sulfuric acid to open the ring of an unsubstituted analog of 89; however, treatment of 89 with sulfuric acid was found to be ineffectual. Short reaction times allowed recovery of the starting material whereas longer reaction times or higher temperatures produced a complex mixture of decomposition products from which no pure materials were isolable. Reaction with fluorosulfonic acid at low temperatures

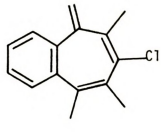
provided small amounts of two products 93 and 94. The information obtained on 93 indicated it to be consistent with an α,β-unsaturated ketone and structures 93a and 93b are suggested as possibilities. Attempts to produce 93 separately from 89 were unsuccessful. (See experimental section LL for data on 93.)



93a



93b



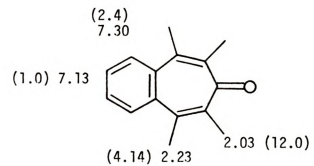
94

Compound 94 was preliminarily determined to be a benzoheptafulvene. However since very little was obtained by this reaction, its production by this method as a precursor to 1 was not feasible. An alternative procedure was sought. After several attempts[15, 16, 62] it was found that bubbling boron trifluoride gas through 89 in acetic acid solution gave a moderate yield of 94. The reaction was not entirely reproducible, and was best carried out on small quantities of 89.

Compound 94 was an oil which slowly darkened and decomposed on standing at room temperature. The infrared spectrum of 94 showed absorption bands at 1680 and 1640 cm^{-1} for the carbon-carbon double bonds and at 920 cm^{-1} for the terminal methylene group. The uv spectrum (cyclohexane) had a shoulder at 262 nm (ε = 5800) and another at 282 nm (4700). Mass spectrometry showed that one chlorine atom was present in the molecule, since it had p and (p + 2) peaks at 230 and 232 amu. The base peak at m/e 195 corresponded to loss of a chlorine atom from

94. The nmr spectrum of 94 consisted of two broad, mutually coupled methyl peaks at δ 2.10 and δ 2.23, a sharp methyl singlet at δ 2.17, vinyl protons at δ 5.13 (m, 2H), and aromatic protons at δ 7.17 and 7.33.

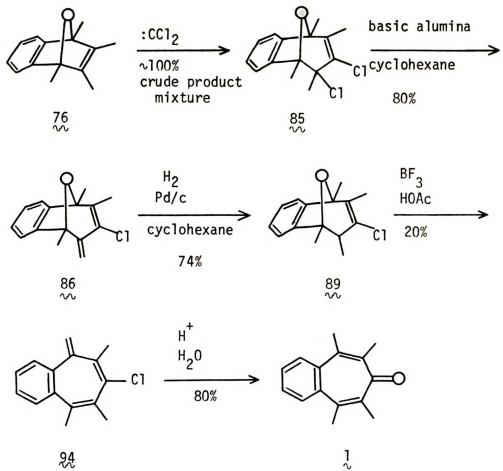
Reaction of 94 with acid in methanol-water yielded 2,3,6,7-tetramethylbenzotropone, 1. Compound 1 was crystalline, mp 104-105°. Its infrared spectrum indicated a doubly conjugated carbonyl group at 1622 cm^{-1}. Ultraviolet spectrometry showed maxima for a highly unsaturated ketone at 232 nm (ε = 30,000), 237 (30,000), 271 (8600), and 314 (2100). The molecular weight of 1 by mass spectrometry was 212 amu. The base peak was at m/e 184, which corresponded to the loss of carbon monoxide. The further loss of a methyl group gave another intense fragment at m/e 169. The nmr was assigned as shown with normalized Eu shifts in parentheses.



1

Purification of 1 was accomplished by gas chromatography (SE-30, 20%, 5' x ¼", 165°), recrystallization from MeOH or hexanes, or chromatography on florisil eluted with 10% ether in hexanes. Silica gel chromatography caused decomposition of 1.

In summary, the best route to 1 consisted of the following reaction sequence:



76 85 86 89 94 1

The overall yield of purified 1 obtained was 4%.

D. BENZOHEPTAFULVENES, BENZOTROPYLIUM IONS, AND REACTIONS OF BENZOTROPONES

The vacuum pyrolyses of 21 and 1 were carried out. Both underwent extrusion of carbon monoxide to yield methylnaphthalenes. Compound 21 gave 1,2,3-trimethylnaphthalene, 23 in 28% yield, whereas 1 yielded 1,2,3,4-tetramethylnaphthalene, 38, in 17% yield. The pyrolysis of 2-methyl-4,5-benzotropone 18, previously studied by Mukai,[17] gave 95% recovered benzotropone at 700°, while at 800° β-methylnaphthalene was obtained in 38% yield and 28% of the benzotropone was recovered. In the case of 21, the reaction was carried out at 700° and the product was purified by gas chromatography to yield 28% of 23; no 21 was recovered. With 1, pyrolysis at 600° and gc collection gave 12% of 38 and 7% of recovered 1. Increasing the number of methyl substituents therefore decreases the relative stability of 4,5-benzotropones.

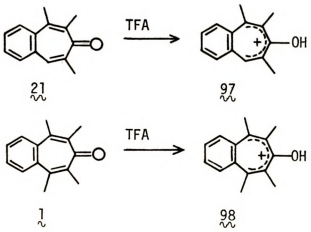
The direct photolysis of 1 was carried out; only a small amount of 38 was formed. The remainder of the product presumably was polymeric material. This is in contrast to the formation of dimers reported for the photolysis of 18.

The formation of epoxides from a 4,5-benzotropone has been reported only once. The reaction was carried out[23] with basic hydrogen peroxide to yield the α,β-diepoxide of 2,7-diphenyl-4,5-benzotropone in 67% yield. The reaction of meta-chloroperbenzoic acid with 2,7-dimethyl-4,5-benzotropone, 5, was investigated. It was found that both the monoepoxide 95 and diepoxide 96 were formed, but purified material was obtained in yields of only 7% and 8% respectively. Peracid epoxidation is not as effective as peroxide epoxidation, not only because of low

yields and many side products, but also because the reaction was very slow. To obtain the yields cited above, the reaction was allowed to proceed with an excess of meta-chloroperbenzoic acid for nine days. The same reaction carried out on 1 yielded only a small amount of product tentatively identified as monoepoxide by nmr and mass spectral analysis. Further investigations of these epoxides and their acid catalyzed rearrangements is an area open to additional study. The monoepoxide 95, when subjected to TFA, did react to give another compound that has not been identified.

Likewise there have been several efforts[24] to construct mono- and di-homotropones, especially with the goal of studying homotropylium ions. With 1 it was found that the addition of dibromocarbene did take place in low yield to give a compound tentatively identified as a monohomobenzotropone by nmr and mass spectral analysis. This also is an area in which further research is recommended.

The formation of benzotropylium ions and their study has been the subject of continued investigation. The ion formed from 5 has previously been described.[63] Compounds 21 and 1 were subjected to trifluoroacetic acid and were found to form stable ions in solution. Ion 97 formed from 21 gave nmr peaks at δ 2.67 (6H), 2.98 (3H), and 7.88, 8.23 and 8.33 (5H). When quenched in water, 97 regenerated 21. Compound 1 formed 98 in trifluoroacetic acid: nmr (TFA), 2.65 (6H), 2.88 (6H), 7.62-8.27 (4H). Ion 98 yielded 1 when quenched in water.



21 97

1 98

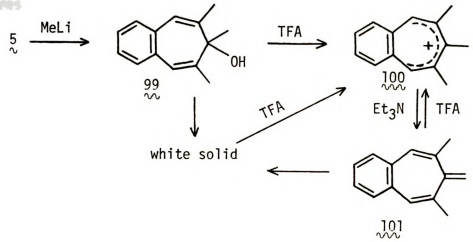
In order to generate the simple methyl substituted benzotropylium ions, compounds 5, 21, and 1 were treated with methyllithium. The resulting benzocycloheptatrienols were not very stable, although their stability increased with substitution. The nmr spectrum of compound 99 produced from 5, had a methyl singlet at δ 0.93, a doublet with J = 2 Hz equivalent to two methyl groups at δ 2.02, a two-hydrogen quartet at δ 6.22 with J = 2 Hz, and the aromatic protons had a chemical shift of δ 6.97. The hydroxyl proton of 99 appeared at δ 1.53. The infrared spectrum showed no carbonyl band, but a peak at 3470 cm^{-1} indicated an alcohol. On standing, alcohol 99 rapidly was converted to a white solid which gave a very indefinite nmr spectrum and could not be identified.[30] No epr signal was obtained from this material. Analysis indicated that it had a lower percentage of oxygen than did 99, but some oxygen was still present. The material could not be purified.

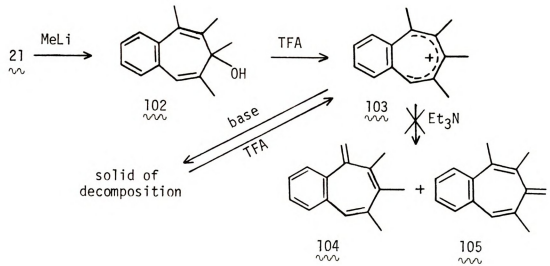
Reaction of 99 with trifluoroacetic acid yielded ion 100. This ion gave an nmr spectrum (TFA) of δ 2.97 (3H), 3.08 (6H), 8.28 (4H), 9.22 (2H). Ion 100 was stable in trifluoroacetic acid. It was quenched with triethylamine to form impure benzoheptafulvene, 101. Compound 101 was

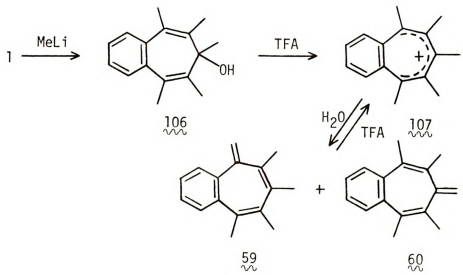
unstable and also rapidly decomposed to a white presumably polymeric solid.[30] It could be somewhat purified before decomposition by chromatography over alumina and was best handled under nitrogen. The nmr spectrum of 101 showed peaks at δ 2.03 (d, J = 2 Hz, 6H), 4.95 (2H), 6.23 (q, J = 2 Hz, 2H), and 6.87 (4H). Quenching 100 with water was found to lead to alcohols derived from both 2,3,- and 4,5-benzocycloheptatrienes, and quenching with sodium methoxide in methanol led to a similar mixture of methyl ethers. Likewise when protonated in trifluoroacetic acid, 101 also gave ion 100.

As mentioned, the decomposition of 99 led to a white solid. It was found that addition of trifluoroacetic acid converted this solid to ion 100. This white solid could be used to generate compound 101 through the intermediacy of ion 100. Otherwise, 101 could also be formed by the acid catalyzed dehydration of 99.

Compound 102, produced by the reaction of methyllithium with 21, gave an nmr spectrum having peaks at δ 0.86 (s, 3H), 2.00 (q, J = 1 Hz, 3H), 2.00 (d, J = 2 Hz, 3H), 2.08 (q, J = 1 Hz, 3H), 6.18 (q, J = 2 Hz, 1H), 6.92, 6.98 and 7.22 (4H). The hydroxyl proton was not located because of impurities; however, the infrared spectrum showed a band at 3650 cm^{-1} indicative of an alcohol. No carbonyl band was present in the infrared spectrum. Alcohol 102 was found to be more stable than 99 since it did not rapidly polymerize. Solvolysis of 102 in trifluoroacetic acid led to ion 103; nmr (TFA) δ 2.98 (9H), 3.32 (3H), 8.23 (3H), 8.70 (1H), 9.00 (1H). Quenching 103 with either water or triethylamine gave a very messy material with very broad nmr peaks at δ 0.6-2.4 and 6.8-7.4. Extraction of a carbon tetrachloride solution of this material with trifluoroacetic acid regenerated ion 103 with few impurities.


5
MeLi
OH
99
TFA
100
Et3N
TFA
TFA
white solid
101


21
MeLi
OH
102
TFA
103
Et3N
base
TFA
solid of
decomposition
104
105


1
MeLi
OH
106
TFA
H2O
TFA
107
59
60

Small peaks at δ 4.82 indicated that perhaps a small amount of the corresponding benzoheptafulvenes 104 and 105 were produced; however, these compounds were not produced in sufficient quantity for identification.

Compound 106 gave an infrared absorption at 3660 cm^{-1}; no carbonyl absorptions were present. The nmr spectrum of 106 had peaks at δ 0.62 (3H), 1.93 (6H), 2.07 (6H), 6.80-7.27 (m, 4H). The hydroxyl proton was not definitely located in the nmr spectrum because of impurities. Ion 107, formed by solvolysis of 106 in trifluoroacetic acid, showed peaks in its nmr spectrum at δ 2.83 (9H), 3.10 (6H), and 7.87-8.50 (m, 4H). This ion, when quenched with ice-water, led to a mixture of the benzoheptafulvenes 59 and 60 in the ratio of 6:4. Quenching 107 with triethylamine gave the same products in the ratio of 7:3. Benzoheptafulvenes 59 and 60 were previously obtained (Section B) as the products from the reaction of 40 with dimethylcopper lithium reagent. The trifluoroacetic acid solvolysis of a mixture of 59 and 60 led to one product, ion 107.

In conclusion, the research presented here gives an insight into the problems associated with the synthesis of 4,5-benzotropones and some of the potential for further study.

EXPERIMENTAL

A. GENERAL PROCEDURES

All nuclear magnetic resonance (nmr) spectra, unless otherwise noted, were measured in CCl_4 or $CDCl_3$ solution using TMS as an internal reference. The 60 MHz spectra were recorded on a Varian T-60 spectrometer; 100 MHz spectra were recorded on a Varian HA-100 spectrometer. Normalized europium shift numbers were obtained by adding small increments of Eu-Resolve II, tris-(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione)Eu(III), to a CCl_4 or $CDCl_3$ solution of the compound being investigated. After each such addition of shift reagent the nmr spectrum was recorded. The shift for each absorption was the difference between the frequency before and after the addition of shift reagent. Normalized europium shift numbers were the ratios obtained by dividing the shift for each signal in the spectrum by the shift of the least shifted signal.

Infrared (ir) spectra were recorded on a Unicam SP-200 spectrometer and were calibrated against a polystyrene film. Ultraviolet (uv) spectra were obtained with a Unicam SP-800 spectrometer. Mass spectra were recorded on a Hitachi-Perkin Elmer RMU-6 spectrometer operated at 70 eV by Lorraine Guile. A Thomas Hoover Melting Point Apparatus was used to obtain melting points, which are uncorrected. Varian Aerograph gas chromatographs were used for all gas chromatography. Analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan or Clark Microanalytical Laboratory, Urbana, Illinois.

B. PREPARATION OF 2,7-DIMETHYL-4,5-BENZOTROPONE (5)

The procedure of Thiele and Weitz[3] was adapted. o-Phthalaldehyde (55.2 g, 0.41 mole) and 35.2 g (0.41 mole) of 3-pentanone were placed in a flask and 600 ml of ethanol was added. The solution was stirred and 120 ml of a saturated solution of NaOH in ethanol was slowly poured into the flask, the contents of which were heated in an oil bath at 65° for 3 hours. During this time, the color of the reaction mixture went from light yellow to dark brown. After being cooled to room temperature, the flask contents were poured into a large beaker to which water was slowly added. The mixture was stirred until crystallization occurred. The solution was allowed to stand for one hour, then the crystals were filtered by suction. Further addition of water to the mother liquor allowed two additional crops of crystals to be obtained. In this way, 63.5 g (84%) of light yellow flaky crystals of 2,7-dimethyl-4,5-benzotropone, 5, were obtained. Repeated recrystallization (ethanol-water) gave a mp 83-84°.[3, 8, 63] Alternatively, purification could be accomplished by chromatography on florisil (hexanes-ether eluent). Ir (CCl_4) 3000 cm^{-1} (w), 1601 (s); nmr (CCl_4), δ 2.22 (d, J = 2 Hz, 6H, C-6 and C-8 methyls), 7.52 (6H, all other H's); mass spectrum, m/e (relative intensity), 184 (100), 156 (98), 141 (98), 128 (22), 115 (35), 102 (6), 91 (8), 89 (8), 76 (30), 63 (24), 51 (19); uv (cyclohexane) λ max 237 nm (ε = 44,000), 245 (sh, 39,000), 269 (37,000), 315 (3500), 333 (300), 348 (2000).

C. PREPARATION OF 2,3-DIHYDRO-2,3,7-TRIMETHYL-4,5-BENZOTROPONE (20)

A 100-ml three-necked flask was fitted with a condenser, drying tube, a mechanical stirrer, a septum and a N_2 inlet and outlet. The

flask was dried, flushed with N_2, and cooled in an ice bath. The septum was removed, anhydrous ether (500 ml) and 11.43 g of cuprous iodide were quickly added to the flask and the septum was replaced. Methyllithium in ether solution (72 ml, 1.65 M) was injected into the flask using a syringe.[33] The reaction mixture was stirred. The solution turned yellow, then white or gray. A solution containing 5.52 g of 5 in several ml of anhydrous ether was added slowly by syringe. The color of the mixture changed back to yellow. The reaction mixture was stirred for an additional 30 minutes and then the reaction was quenched by pouring the mixture with stirring into 400 ml of dilute aqueous NH_4Cl. The ether layer was separated and the aqueous layer was extracted twice with ether. The ether extracts were combined and washed twice with water, dried over anhydrous magnesium sulfate, filtered, and evaporated to give 20 as a yellow oil (6.00 g, 0.03 mole, 100%). Although two isomers of 20 could exist, the reaction product consisted predominantly of one isomer. Purification (G.C., FFAP, ¼" x 10', 215°) yielded pure material without separating the isomers, although unpurified material can be used in the subsequent reaction.

Ir (CCl_4) 3000 cm^{-1} (m), 1660 (s), 1625 (m), 1476 (m), 1390 (m), 1218 (m), 1047 (m); nmr (CCl_4), δ 1.05 (d, J = 7 Hz, 3H), 1.07 (d, J = 7 Hz, 3H), 2.00 (d, J = 2 Hz, 3H), 2.92 (q, J = 7 Hz, broad, 2H), 7.04 (q, J = 2 Hz, 1H), 7.23 (sharp, 4H); mass spectrum, m/e (relative intensity), 200 (41), 185 (12), 172 (25), 157 (100), 144 (26), 143 (31), 142 (36), 129 (26), 128 (32), 115 (24); uv (cyclohexane), λ max 266 nm (ε = 12,400), 232 (12,800), 293 (13,000), 314 (sh, 6400).

Anal. Calcd for $C_{14}C_{16}O$: C, 83.96; H, 8.05

Found: C, 83.93; H, 8.21

The minor isomer of 20 was isolated from the dehydrogenation reaction below and was purified by gas chromatography (SE-30, 20%, 5' x ¼" column at 165°) to a crystalline material. The minor isomer of 20 gave an nmr spectrum (CCl_4) with absorptions at δ 0.90 (d, J = 7 Hz, 3H), 1.17 (d, J = 7 Hz, 3H), 1.97 (d, J = 2 Hz, 3H), 2.80 (m, J = 7 Hz, 2H), 6.83 (q, J = 2 Hz, 1H), 7.07 (4H).

The minor isomer was assigned the structure of the more symmetrical but also more crowded cis-isomer, the major isomer as trans-20.

D. THE DEHYDROGENATION OF 2,3-DIHYDRO-2,3,7-TRIMETHYL-4,5-BENZOTROPONE (20) WITH PALLADIUM ON CHARCOAL

In a flask were placed 20 (300 mg), trichlorobenzene (4 g) and 200 mg of 10% palladium on charcoal. A slow nitrogen stream was passed through the flask. The flask contents were heated to 215° in a silicone oil bath. The reaction was followed by gas chromatography (SE-30, 20%, 5' x ¼" column at 165°) of aliquots of reaction mixture withdrawn, filtered with benzene, evaporated to an oil, and injected on the above column. After 110 hours, the reaction mixture was cooled and filtered to remove the catalyst. The solvent was removed by vacuum distillation at 50° and 2 mm. The residue was purified by gas chromatography (above column). Five peaks were collected. Peaks 1, 2, and 3 overlapped and together accounted for 55% of the total peak area; peak 5 accounted for 30% of the total peak area. Peak one was due to 1-ethyl-1,3-dimethyl-β-naphthone, 22; ir (CCl_4), 2980 cm^{-1} (m), 2940 (m), 1657 (s), 1467 (w), 1389 (w); nmr (CCl_4), δ 0.47 (t, J = 8 Hz, 3H), 0.90 (q, J = 8 Hz, 2H), 1.32 (s, 3H), 1.90 (d, J = 1 Hz, 3H), 7.05 (5H); mass spectrum, m/e (relative intensity), 201 (1), 200 (12), 199 (5), 198 (24), 185 (14), 183 (47), 172 (100), 157 (29), 155 (40), 153 (19), 145 (18), 143 (46),

141 (29), 129 (34), 128 (65), 115 (42), 44 (55); uv (cyclohexane), λ max 228 nm (sh, ε = 13,400), 233 (16,300), 241 (15,500), 295 (sh, 8300), 300 (8400), 319 (sh, 5600).

Peak two was due to a mixture of the minor isomer of 20, 1,2,3-trimethylnaphthalene 23 and 1,2,4-trimethylnaphthalene, 24.

Peak three was due to the major isomer of 20, plus some unidentified impurity.

The material responsible for peak four was not collected in sufficient amounts to identify.

Peak five was due to 2,3,7-trimethyl-4,5-benzotropone, 21, 20%, mp 75-76° (colorless needles recrystallized from MeOH). Ir (KBr), 2930 (w), 1610 (s), 1460 (w), 1324 (w), 1167 (w), 1041 (w), 925 (w), 790 (w), 768 (m), 752 (m); nmr (CCl_4), δ 2.14 (d, J = 2 Hz, 3H), 2.16 (q, J = 1 Hz, 3H), 2.40 (q, J = 1 Hz, 3H), 7.02 (q, J = 2 Hz, 1H), 7.22 and 7.47 (4H). The peaks at δ 2.14 and δ 2.16 appeared as a slightly broadened singlet at δ 2.16 having a sharp shoulder at δ 2.13. A 100 MHz spectrum obtained showed these peaks as a quartet wherein the two right hand members were enlarged in size. Irradiation of the δ 7.02 quartet uncoupled the doublet at δ 2.14 but did not affect the splitting of the quartet at δ 2.16. The mass spectrum showed peaks at m/e (relative intensity), 198 (4), 170 (99), 155 (100), 128 (20); uv (cyclohexane), λ max 238 nm (ε = 50,400), 267 (22,700), 325 (sh, 2830);

Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12

Found: D, 85.20; H, 7.08

Some other minor products where formed in this reaction, but were not characterized.

E. THE DEHYDROGENATION OF 2,3-DIHYDRO-2,3,7-TRIMETHYL-4,5-BENZOTROPONE (20) WITH SULFUR

Sulfur (0.040 g, 1.25 mmole) and 20 (0.200 g, 1 mmole) were placed in a flask and heated at 270° for three hours using a sand bath. The smell of hydrogen sulfide gas was apparent. The flask contents were cooled. The material was distilled at 110° and 0.1 mm to yield a yellow oil and a black residue. Purification of the oil was accomplished by gas chromatography (SE-30, 20%, 5' x ¼" column at 165°). Five major peaks were obtained.

Peak one (17%) was due to 22 as identified above.

Peak two was due to a mixture of starting material, 20, and trimethylnaphthalenes 23 and 24.

Peak three was caused by impure starting material, 20.

Peak four (23%) was produced by a new product, a dimethylnaphthol, 25 (compare experimental section J) which was not positively identified. Compound 25, although not completely pure had the following characteristics: mp 82-84°; ir (CCl_4), 3670 cm^{-1} (m), 2940 (m), 1732 (w), 1660 (w), 1634 (m), 1520 (w), 1472 (m), 1410 (m), 1257 (s), 1199 (s), 1110 (m), 1032 (m), 890 (m); nmr (CCl_4), δ 2.32 (broad s, 3H), 2.42 (broad s, 3H), 4.67 (broad, 1H), 6.87-7.67 (5H); mass spectrum, m/e (relative intensity), 174 (1), 173 (14), 172 (100), 157 (36), 153 (12), 143 (14), 141 (9), 129 (28), 128 (35), 115 (15); uv (cyclohexane), λ max 231 nm (ε = 61,500), 259 (sh, 2620), 270 (sh, 3770), 280 (4500), 291 (3680), 315 (1640), 328 (2050).

Peak five (6%) was due to 21.

F. PREPARATION OF 2,3-DIHYDRO-2-BROMO-2,3,7-TRIMETHYL-4,5-BENZOTROPONE (26)

Ketone 20 (4.00 g, 20 mmoles) was dissolved in 40 ml of carbon tetrachloride. To this solution, 100 ml of glacial acetic acid was added. The flask contents were stirred at room temperature. Bromine (3.20 g, 20 mmoles) in 50 ml of acetic acid was added dropwise until the color of bromine was faintly retained by the liquid and was not discharged within 15 minutes. Reaction completion was tested with silica gel thin layer chromatography eluted with chloroform. The mixture was stirred for an additional hour, and 5% sodium bisulfate solution was added until the bromine color was discharged. The solution was extracted three times with carbon tetrachloride, the CCl_4 portions were combined, washed twice with 1N sodium hydroxide, and twice with water. The CCl_4 solution was dried (anhydrous magnesium sulfate), filtered, and evaporated to a dark oil which crystallized. Repeated recrystallizations from methanol gave colorless crystals of 26, (3.68 g, 71%) mp 81-82°. Alternatively, 26 was purified by chromatography over basic alumina eluted with 10% ether in petroleum ether, followed by recrystallization from methanol or hexanes. Ir (neat oil) 2995 cm^{-1} (m), 2950 (m), 1684 (m), 1652 (s), 1627 (m), 1450 (m), 1390 (m), 1218 (m), 1080 (m), 1040 (m), 800 (m), 768 (s); nmr (CCl_4), δ 1.27 (d, J = 7 Hz, 3H), 1.95 (s, 3H), 2.15 (d, J = 2 Hz, 3H), 3.45 (q, J = 7 Hz, 1H), 6.93 (q, J = 2 Hz, 1H), 7.23 (sharp, 4H); nmr Eu shift (CCl_4), δ (normalized shift), 1.27 (1.19), 1.95 (2.29), 2.15 (2.29), 3.45 (1.15), 6.93 (1.00); mass spectrum, m/e (relative intensity), 280 (13), 278 (13), 199 (100), 185 (13), 171 (72), 156 (62), 155 (48), 141 (47), 128 (40), 115 (34); uv (cyclohexane), λ max 233 nm

(ε = 12,700), 306 (9700), 326 (sh, 5900).

Anal. Calcd for $C_{14}H_{15}Br$: C, 60.23; H, 5.42

Found: C, 60.19; H, 5.51

G. PREPARATION OF 1,3-DIMETHYL-1-(1-BROMOETHYL)-β-NAPHTHONE (27)

Bromoketone 26 (0.030 g) was placed in a flask equipped with a nitrogen inlet and outlet and a condenser. Dimethyl formamide (1 ml) or dimethyl sulfoxide (1 ml) was added and the mixture was heated in an oil bath at 160° for 20 minutes. After cooling, water was added and the mixture was extracted three times with ether. The ether extracts were washed twice with dilute sodium bicarbonate solution and twice with water, dried (anhydrous magnesium sulfate), filtered, and evaporated to an oil of 27, 0.022 g (75%). Ir (CCl_4), 3000 cm^{-1} (w), 2940 (w), 1652 (s), 1450 (w), 1390 (w); nmr (CCl_4), δ 1.48 (d, J = 7 Hz, 3H), 1.57 (s, 3H), 1.98 (d, J = 2 Hz, 3H), 4.55 (q, J = 7 Hz, 1H), 7.23 and 7.83 (5H); nmr Eu shift (CCl_4), δ (normalized shift), 1.48 (1.08), 1.57 (1.69), 1.98 (1.77), 4.55 (2.12), 7.23 (1.00); mass spectrum, m/e (relative intensity), 280 (13), 278 (13), 199 (100), 171 (67), 156 (46), 143 (55), 141 (51), 128 (52), 115 (35); uv (cyclohexane), λ max 233 nm (ε = 16,500), 241 (17,000), 301 (sh, 8500), 311 (9600), 324 (sh, 7200).

Anal. Calcd for $C_{14}H_{15}Br$: C, 60.23; H, 5.42

Found: C, 60.21; H, 5.51

H. THE REACTION OF 2,3-DIHYDRO-2-BROMO-2,3,7-TRIMETHYL-4,5-BENZOTROPONE (26) WITH TRI-n-BUTYLTIN HYDRIDE

Bromoketone 26 (0.0278 g, 0.1 mmole) was placed in a dry flask fitted with a nitrogen inlet and outlet, a condenser, and a septum. Using a syringe, 0.5 ml of dry benzene was injected and the reaction mixture

was stirred magnetically and cooled to 10° in a dioxane-dry ice bath. Tri-n-butyltin hydride (0.0246 ml, 0.0290 g, 0.1 mmole) was added using a syringe over a period of 10 minutes. The reaction was followed by withdrawing a drop of reaction mixture and adding it to sulfuric acid in ether. The production of a gas indicated unreacted tri-n-butyltin hydride. After four hours no gas was produced. The solvent was evaporated and purification by silica gel thick layer chromatography (3:1, cyclohexane: chloroform eluent) gave two bands. The band of lower Rf value was impure 20. Further purification by gas chromatography (SE-30, 20%, 5' x ¼" column at 175°) yielded pure 20.

I. REACTION OF 1,3-DIMETHYL-1-(1-BROMOETHYL)-8-NAPHTHONE (27) WITH TRI-n-BUTYLTIN HYDRIDE

In a 25-ml three-necked flask were placed 0.0392 g (0.42 mmole) of 27 and 0.5 ml of dry benzene. The flask contents were stirred with a magnetic stirring bar and a slow stream of nitrogen was passed through the flask. After cooling the mixture to 10° in a dioxane-dry ice bath, 0.0372 ml (0.142 mmole = 0.0408 g) of tri-n-butyltin hydride was added using a syringe. Addition required several minutes. The reaction was followed by removing a drop of reaction mixture using a syringe and adding it to a solution of sulfuric acid in ether. If unreacted tri-n-butyltin hydride remained, gas was evolved. After 6.5 hours no gas was evolved when the reaction mixture was tested. The solvent was evaporated and purification was accomplished by silica gel thick layer chromatography eluted with a 3:1 mixture of cyclohexane and chloroform. The plate was eluted three times. Three bands were produced; that of highest Rf value was found to be due to 27. The next band was due to 20, some 22, and some impurities. The material from band two was

injected on an SE-30 column (20%, 5' x ¼" at 175°). Three peaks resulted. Peak two was due to 20. Peak three was due to an unidentified material. Peak one was found to be due to 1-ethyl-1,3-dimethyl-β-naphthone, 22.

J. THE PYROLYSIS OF 1,3-DIMETHYL-1-(1-BROMOETHYL)-β-NAPHTHONE (27)

A vaporizer bulb containing 0.0504 g of 27 was attached to an unpacked vycor tube heated to 440°. A collector, cooled in a dry ice-acetone bath was also attached. The apparatus was evacuated to 0.1 mm Hg and the material was pyrolyzed by heating the vaporizer bulb with an oven. After all the material had been passed through the hot tube, the apparatus was cooled and the tube and collector were washed with methylene chloride. The solvent was evaporated and the oil obtained was purified by gas chromatography (SE-30, 20%, 5' x ¼", 180°). Three peaks were obtained and the corresponding products collected. That of shortest retention time was 1,3-dimethyl-1-vinyl-β-naphthone, 31, (an oil, 0.0040 g, 7% yield). Ir (CCl_4), cm^{-1}, 2950 (m), 1660 (s), 1628 (m), 1455 (m), 1380 (m), 1270 (m), 1205 (m), 940 (m); nmr (CCl_4), δ 1.57 (s, 3H), 1.95 (d, J = 2 Hz, 3H), 4.80 (d of d, J_1 = 2 Hz, J_2 = 18 Hz, 1H), 5.04 (d of d, J_1 = 2 Hz, J_3 = 11 Hz, 1H), 5.84 (d of d, J_2 = 18 Hz, J_3 = 11 Hz, 1H), 7.15 (q, J = 2 Hz, 1H), 7.27 and 7.32 (4H); mass spectrum, m/e (relative intensity), 198 (17), 183 (18), 170 (37), 156 (48), 155 (100); uv (cyclohexane), λ max 232 nm (ε = 14,000), 238 (12,800), 297 (sh, 8300), 306 (9100), 319 (sh, 6400).

The second peak was due to 1,3-dimethyl-2-naphthol, 32 (0.0047 g, 9.6%), colorless crystals, mp 88.5-89.5° (lit.[36] 89-90°). Ir (CCl_4), 3645 cm^{-1} (m), 3030 (w), 2930 (w), 1630 (w), 1470 (w), 1440 (w), 1408

(w), 1255 (m), 1194 (s), 1180 (m), 1155 (w), 1108 (m), 1030 (w), 890 (w), 855 (w); nmr (CCl_4), δ 2.37 (broad s; 3H), 2.45 (s, 3H), 4.58 (broad s, 1H), 7.03-7.73 (5H); mass spectrum, m/e (relative intensity), 172 (100), 157 (30), 128 (30); uv (cyclohexane), λ max 270 nm (ε = 4800), 279 (6400), 291 (4800), 314 (1800), 328 (2500).

The peak at longest retention time was due to unreacted 27; 0.0048 g (9.6%) was recovered.

K. PREPARATION OF 1,3-DIMETHYL-1-(1-ACETOXYETHYL)-β-NAPHTHONE (33)

In a 50-ml flask were placed 0.4 g of 26, 10 ml of acetic acid, 0.4 g of silver acetate, and 1 ml of water. The solution was stirred at room temperature for 18 hours. The reaction mixture was extracted with carbon tetrachloride three times, the carbon tetrachloride portions were combined and washed three times with water. After being dried over anhydrous magnesium sulfate and filtered, the solvent was evaporated to leave a yellow oil of 33. Recrystallization from hexanes gave colorless crystals, mp 68-69°. Purification may also be done by gas chromatography (SE-30, 20%, 5' x ¼", 175°). (On FFAP 33 was partially converted to 34.) Alternatively column chromatography over florisil eluted with 10% ether in hexanes gave pure 33. Ir (CCl_4), 3000 cm^{-1} (w), 2950 (w), 1738 (s), 1656 (s), 1450 (w), 1380 (m), 1240 (s), 1205 (w), 1090 (w), 1030 (w), 980 (w), 960 (w); nmr (CCl_4), δ 0.93 (d, J = 7 Hz, 3H), 1.45 (s, 3H), 1.93 (s, 3H), 1.95 (d, J = 2 Hz, 3H), 5.29 (q, J = 7 Hz, 1H), 7.23, 7.38, 7.50, 7.62 (Ar-H, 5H); nmr europium shift values, δ (normalized shift), 0.93 (1.11), 1.45 (1.28), 1.93 (1.79), 1.95 (1.00), 5.29 (3.96); mass spectrum, m/e (relative intensity), 215 (1), 214 (10), 172 (100), 157 (20), 143 (6), 141 (9), 128 (18), 115

(10), 43 (68), (this spectrum is very similar to that of 24 with the exception of the m/e 43 peak); uv (CH_3CN), λ max, 233 nm (sh, ε = 31,000), 238 (32,600), 321 (16,900).

Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.40 H, 7.02

Found: C, 74.60 H, 6.91

L. THE THERMAL CONVERSION OF 1,3-DIMETHYL-1-(1-ACETOXYETHYL)-β-NAPHTHONE, 33, to 1,3-DIMETHYL-2-ACETOXYNAPHTHALENE (34)

Gas chromatography of 33 on a FFAP, 20%, 3/8" x 10' column at 215° gave a broadened peak. The peak was collected and found to be due to 33 plus a new material, 34. Reinjection twice gave pure 34, 1,3-dimethyl-2-acetoxynaphthalene. Ir (neat), 2900 cm^{-1} (w), 1750 (s), 1378 (m), 1210-1204 (s), 1175 (s), 1155 (m), 1100 (m), 925 (w), 895 (w), 720 (m); nmr (CCl_4), δ 2.30 (broad s, 3H), 2.35 (s, 3H), 2.45 (broad s, 3H), 7.10-8.05 (5H); mass spectrum, m/e (relative intensity), 214 (10), 172 (100), 157 (23), 143 (11), 141 (13), 128 (34), 115 (18), 63 (5), 51 (5), 43 (7); uv (cyclohexane) λ max 233 nm (ε = 17,000), 261 (sh, 990), 270 (1290), 280 (1480), 291 (1090).

M. THE VACUUM PYROLYSIS OF 1,3-DIMETHYL-1-(1-ACETOXYETHYL)-β-NAPHTHONE (33)

Compound 33 (23.3 mg) was vacuum pyrolyzed through an unpacked vycor tube heated to 450°. The pyrolysis apparatus was evacuated to a pressure of 0.1 mm. The vaporization bulb was heated to 90° with an oven. The collector was cooled to -78°. After pyrolysis all the material had collected in the end of the pyrolysis tube. The tube was washed with methylene chloride and the solvent evaporated. Purification of the residue by gas chromatography (SE-30, 20%, 5' x ¼" column at 180°)

gave 8.7 mg (56% yield) of colorless crystals of 1,3-dimethyl-2-naphthol, 32, mp 89-90°.[36]

N. PREPARATION OF 1,3-DIMETHYL-1-VINYL-8-NAPHTHONE (31)

Bromoketone 26 (1.00 g) was placed in a flask equipped with a condenser and benzene (2 ml) was added. Silver oxide (Ag_2O, 1.00 g) was added and the solution was refluxed overnight. However, the solvent was entirely lost and the flask became dry. A partial silver mirror was deposited on the flask. After the mixture was cooled, benzene was added and the solution was filtered to remove the Ag_2O. Evaporation yielded an oil containing two components which were separated by gas chromatography (SE-30, 20%, 10' x ¼", 190°).

Peak one was due to product 31.

The material of peak two was identified as 33 by comparison of nmr spectra. The origin of 33 in this reaction has not been explained.

Repetition of this reaction, but without allowing the reaction mixture to go to dryness, gave 27.

O. THE PYROLYSIS OF 2,3-DIHYDRO-2-BROMO-2,3,7-TRIMETHYL-4,5-BENZOTROPONE (26)

Pyrolysis of 0.278 g (1 mmole) of 26 was accomplished through an unpacked vycor tube heated to 450° and evacuated to 0.1 mm pressure. The collector was cooled to -78°. A liquid condensed in the end of the pyrolysis tube, most of which was transferred to the collector by gentle heating with a heat gun. The collector was rinsed with CCl_4 and evaporated to give impure 2,3,7-trimethyl-4,5-benzotropone, 21. Thick layer alumina chromatography eluted with 10% ether in petroleum ether

yielded pure 21, (55 mg, 28%). The other isolable product from the chromatography was 1,2,3-trimethylnaphthalene, 23, (12 mg, 7% yield). A further 26 mg of unidentified by-products were also obtained.

A CCl_4 rinse of the pyrolysis tube yielded a small amount of yellow oil of inconstant composition from experiment to experiment. These products were not identified.

P. PREPARATION OF 2,3,6,7-TETRAMETHYL-2,3,6,7-TETRAHYDRO-4,5-BENZOTROPONE (35)

The same procedure used to prepare 20 was followed. Cuprous iodide, (1.1430 g, 6 mmoles), 0.264 g (0.12 mmoles) of methyllithium in ether solution, and 0.600 g of 20 reacted to give an essentially quantitative yield (0.648 g) of an oil which was a mixture of isomers of 35. Purification without separation of the isomers was accomplished by gas chromatography (SE-30, 20%, 5' x ¼" column at 180°) to give 35 as a colorless oil; ir (neat) 2990 cm^{-1} (s), 1703 (s), 1490 (m), 1460 (s), 1380 (m), 765 (s); mass spectrum, m/e (relative intensity), 217 (14), 216 (78), 201 (8), 189 (11), 188 (16), 174 (21), 160 (42), 159 (59), 145 (70), 132 (100), 131 (100), 129 (33), 128 (30), 117 (86), 115 (43), 91 (46); uv (cyclohexane), a shoulder at 234 nm (ε = 725), λ max 256 nm (ε = 380), 264 (430), 268 (390), 271.5 (400), 289 (295).

Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32

Found: C, 83.28; H, 9.42

Injection of the mixture of isomers of 35 on a FFAP, 20%, 10' x ¼" column at 215° and 150 ml/min He flow gave two peaks. Peak one was due to a single isomer of 35, nmr (CCl_4), δ 0.94 (d, J = 7 Hz, 6H), 1.25 (d, J = 7 Hz, 6H), 3.04 (m, 4H), 7.13 (sharp, 4H). Peak two contained

the remainder of the mixture; nmr (CCl_4), δ 0.72 (d, J = 7 Hz), 1.17 (d, J = 7 Hz), 1.40 (d, J = 7 Hz), 1.37 (d, J = 7 Hz), 2.92 (m), 4.08 (m), 7.07 and 7.16 (Ar-H).

Q. THE DEHYDROGENATION OF 2,3,6,7-TETRAMETHYL-2,3,6,7-TETRAHYDRO-4,5-BENZOTROPONE (35) WITH PALLADIUM ON CHARCOAL

To ketone 35 (0.20 g) was added 2 g of trichlorobenzene and 0.150 g of 10% palladium on charcoal. Nitrogen was bubbled through the solution. The flask was fitted with a thermometer and the contents were heated in a sand bath to 205° (bath temperature 250°). The reaction was followed by gas chromatography (SE-30, 20%, 5' x ¼", 165°) for four days. Aliquots were removed, filtered with benzene, and evaporated. The resulting oil was then injected on the above column. Two major peaks were produced; the first was starting material and the second was product. After four days both peaks had roughly the same area. The reaction mixture was cooled and filtered with benzene to remove the catalyst. After evaporation of the benzene, the trichlorobenzene solvent was removed by vacuum distillation. The residue was separated by gas chromatography (above column). The two major peaks were collected; the first peak was due to unreacted 35, the second was due to the product, 1,3,4-trimethyl-1-ethyl-8-naphthone, 36 (48%); ir (CCl_4) 3000 cm^{-1} (m), 1701 (w), 1652 (s), 1620 (w), 1465 (m), 1388 (m); nmr (CCl_4), δ 0.45 (t, J = 7 Hz, 3H), 0.88 (q, J = 7 Hz, 2H), 1.33 (s, 3H), 1.97 (broad s, 3H), 2.30 (broad s, 3H), 7.15 (m, 4H); uv (cyclohexane), λ max 226 nm (ε = 7950), 233 (9660), 240.5 (9300), 298 (6250), 305 (6145), 320 (sh, 3860).

R. THE REACTION OF 2,7-DIMETHYL-4,5-BENZOTROPONE (5) WITH BROMINE

Sufficient carbon tetrachloride to dissolve 1.84 g (10 mmoles) of 5 was placed in a flask containing that amount of 5. The solution was stirred magnetically and cooled to 0^{o}. A CCl_4 solution of bromine (3.2 g, 20 mmoles, 1.09 ml) was added slowly over 1½ hours. After being stirred an additional hour, the solution was rapidly filtered by suction and a yellow solid was obtained. This was washed with a small amount of CCl_4 to remove traces of bromine. The solid melted at 133-42^{o} with decomposition to a red liquid and a white solid. The yellow solid was difficult to handle and could not be purified. Dissolution in other solvents caused reaction to other materials not investigated. Further reaction of the yellow crystals with bromine in CCl_4 with heating led to a yellow oil; ir 1665 cm^{-1} (s), which was also difficult to handle and purify.

S. THE REACTION OF 1,2,3,4-TETRAMETHYLNAPHTHALENE (38) WITH DIBROMOCARBENE GENERATED IN THE PHASE TRANSFER REACTION

1,2,3,4-Tetramethylnaphthalene, 38, synthesized by the procedure of Hausiak[38] was treated according to the procedure of Makosza[40] and optimized for the production of product 40. In a flask were placed 0.92 g (0.005 mole) of 38, 3.80 g (0.015 mole) of bromoform, and 0.05 g of benzyltriethylammonium chloride. The mixture was cooled to 0^{o} and stirred with a mechanical stirrer. Then 2.5 ml of a 50% sodium hydroxide solution was added slowly to prevent overheating. The reaction mixture was allowed to warm to room temperature and was stirred for 24 hours. Water and chloroform were added and the mixture was stirred

until it was no longer viscous. The resulting mixture was transferred to a separatory funnel, the organic layer was separated and the aqueous phase further extracted twice with chloroform. The organic extracts were combined and washed twice with sodium chloride brine which minimized emulsion formation. (If emulsions formed, separations were performed as well as possible, or the solution was filtered). The chloroform solution was then dried over anhydrous magnesium sulfate, filtered, and evaporated to give an oil. The yields by nmr peak area ratios were 54% of 40, 18% of 38 and 28% of 41. Purification was accomplished by silica gel column chromatography using a 2.5 foot column eluted with petroleum ether. The first product to elute from the column was 4,6,7-trimethyl-5-bromo-2,3-benzoheptafulvene, 40, an oil. Ir (CCl_4), 2940 cm^{-1} (m), 1645 (w), 1608 (w), 1490 (s), 1455 (s), 1394 (m), 1130 (w), 995 (w), 940 (s), 924 (s), 728 (m); nmr (CCl_4), δ 1.92 (broad s, 3H), 2.02 (broad s, 3H), 2.43 (s, 3H), 5.05 (d, J = 2 Hz, 1H), 5.11 (d, J = 2 Hz,1H), 6.93-7.40 (4H); mass spectrum, m/e (relative intensity), 276 (28), 274 (29), 195 (100), 180 (94), 165 (95), 153 (18), 152 (20), 141 (23), 128 (9), 115 (17), 89 (33), 76 (26), 63 (13); uv (cyclohexane), λ max 231 nm (sh, ε = 21,000), 241 (17,300), 247 (15,000), 253 (12,800), 259 (10,500), 267 (8300).

Next, a mixture of minor products which were not identified was eluted, followed by unreacted tetramethylnaphthalene. The next compound eluted was produced in only tiny amounts. It was identified as 4,6,7-trimethyl-5-bromo-6,7-(dibromocyclopropyl)-2,3-benzoheptafulvene, 53; ir (CCl_4), 2980 cm^{-1} (w), 1632 (m), 1496 (m), 1452 (s), 1397 (m), 1128 (m), 957 (s), 934 (s), 840 (s), 810 (s), 777 (s), 724 (m), 678 (m); nmr (CCl_4), δ 1.60 (s, 6H), 2.25 (s, 3H), 5.38 (s, 1H), 5.55 (1H), 7.22 (4H);

mass spectrum, m/e (relative intensity), 448 (1), 446 (1), 367 (5), 288 (19), 286 (19), 273 (7), 271 (8), 249 (3), 247 (3), 207 (100), 192 (38), 178 (12), 165 (18), 152 (9), 141 (6), 128 (4), 115 (8), 108 (8), 101 (8), 96 (8), 95 (8), 94.5 (10), 89 (15), 80 (20), 76 (8), 63 (9), 51 (8); uv (cyclohexane), λ max 227 nm (ε = 7550), 274 (2000).

The last compound to be eluted was 41; recrystallized from hexanes, mp 105-107°, ir (CCl_4), 2940 cm^{-1} (m), 1490 (m), 715 (s); nmr (CCl_4) δ 1.78 (broad s, 3H), 1.94 (broad s, 3H), 2.14 (s, 1H), 2.20 (s, 1H), 2.54 (s, 3H), 7.28 (center of m from 6.90-7.63, 4H); mass spectrum, m/e (relative intensity), 446 (6), 444 (6), 367 (67), 287 (25), 273 (66), 271 (67), 207 (85), 191 (62), 178 (43), 165 (100), 152 (48), 141 (22), 128 (15), 115 (24), 101 (15), 95 (17), 89 (22), 76 (15), 69 (13), 63 (20); uv (cyclohexane), λ max 266 nm (ε = 8,460), 237 (sh, 14,700).

Anal. Calcd for $C_{16}H_{15}Br_3$: C, 42.99; H, 3.38

Found: C, 43.32; H, 3.22

T. THE REACTION OF 1,2,3,4-TETRAMETHYLNAPHTHALENE (38) WITH POTASSIUM t-BUTOXIDE-GENERATED DIBROMOCARBENE

The reaction was optimized for production of product 40 over product 39. A 500-ml flask was fitted with a condenser, a dropping funnel, and an inlet and outlet for nitrogen. A slow stream of nitrogen was passed through the flask and the flask was flamed dry, then cooled. To the flask were added 7.36 g (0.04 mole) of 38, 200 ml of dry benzene, and 6.72 g (0.06 mole) of potassium t-butoxide. The flask contents were cooled to 0° and stirred magnetically. Bromoform (10.12 g, 0.04 mole) in 25 ml of dry benzene was slowly added (4 hr) from the dropping funnel. After the addition was complete, the reaction mixture was stirred for an additional four hours. Water was then slowly added to

quench the reaction. The solution was transferred to a separatory funnel, an equal volume of water was added and the organic layer was separated. The aqueous layer was extracted twice with benzene and the benzene portions were combined. These were washed twice with water, dried over anhydrous magnesium sulfate, filtered and evaporated to a semi-solid. Separation was accomplished using a two-foot silica gel column eluted with petroleum ether.

The first compound eluted was 4,6,7-trimethyl-5-bromo-2,3-benzoheptafulvene, 40, 2.05 g (18%), identified as above.

The second compound eluted was unreacted 38, 4.72 g (64%) recovered.

The third compound eluted was 5,6-benzo-1,2,4,7-tetramethyl-3,3,8,8-tetrabromotricyclo[5.1.0.$0^{2,4}$]octane, 39; recrystallized from hexanes, mp 125-126°; ir (CCl_4), 2960 cm^{-1} (m), 1565 (w), 1510 (w), 1480 (w), 1400 (s), 988 (w), 850 (s); nmr (CCl_4), δ 1.60 (s, 6H), 1.70 (s, 6H), 7.33 (m, 4H); mass spectrum, m/e (relative intensity), 532 (15), 530 (1), 528 (2), 526 (1), 524 (5), 449 (6), 447 (6), 378 (30), 289 (35), 287 (35), 208 (100), 193 (29), 178 (30), 165 (26), 152 (14), 142 (11), 141 (11), 128 (7), 115 (7), 103 (15), 95 (10), 89 (21), 82 (30), 80 (22), 76 (14); uv (cyclohexane), λ max 272 (sh, ε = 1110), 282 (690).

Anal. Calcd for $C_{16}H_{16}Br_4$: C, 36.40; H, 3.06

Found: C, 36.44; H, 2.93

Compound 39 can be made the predominant reaction product by appropriately changing the reaction conditions.

Other products formed in low yield were not characterized.

U. THE THERMAL REARRANGEMENT OF 4,6,7-TRIMETHYL-5-BROMO-2,3-BENZOHEPTAFULVENE (40)

Compound 40 isolated from the carbene reaction, was injected on a FFAP, 20%, 3/8" x 10' column at 190°. Two peaks were obtained; peak one, at shorter retention time, tailed into peak two. Reinjection of the material from peak one gave only peak one. Reinjection of the material collected from peak two gave both peaks. The material of peak two was thus partially rearranged to that of peak one which was stable to the column conditions. Peak two was due to the material originally injected, assigned structure 40. The infrared and nmr spectra of this and the original material were the same, and their uv spectra were similar. The material of peak one appeared to have similar spectra, but closer scrutiny showed them to be different. This material was assigned structure 43; infrared (CCl_4), 2900 (m), 1642 (w), 1608 (w), 1490 (m), 1452 (m), 1388 (m), 995 (m), 943 (m), 921 (s); nmr (CCl_4), δ 1.89 (broad, 3H), 2.03 (broad, 3H), 2.37 (sharp, 3H), 5.05 (d, J = 3 Hz, 1H), 5.10 (d, J = 3 Hz, 1H), 7.17, 7.27, 7.30 (4H); uv (cyclohexane), λ max 262 nm (sh, ε = 4560), 220 (sh, 12,200).

V. THE ACID-CATALYZED REARRANGEMENT OF 4,6,7-TRIMETHYL-5-BROMO-2,3-BENZOHEPTAFULVENE (40)

Benzoheptafulvene 40 (0.155 g), isolated from the carbene reaction, was dissolved in trifluoroacetic acid (TFA). The solution became dark brown. After five minutes the reaction was quenched in aqueous sodium hydroxide solution; the mixture obtained was extracted with CCl_4, dried over magnesium sulfate, and evaporated. Nmr analysis showed a mixture of compounds which appeared to be the same substances produced in the

thermal rearrangement of 40 and assigned as structures 40 and 43. The new isomer either decomposed or rearranged back to 40 slowly at room temperature.

W. THE PREPARATION 4,5,6,7-TETRAMETHYL-2,3-BENZOHEPTAFULVENE (59)[41]

A three-necked flask was flame-dried, fitted with a condenser, an inlet and outlet for nitrogen, a mechanical stirrer, and a septum. Cuprous iodide (7.1 g, 37.5 mmoles) and 30 ml of anhydrous ether were added to the flask. The flask contents were cooled to 0^{o} and stirred. Methyllithium (1.575 g) in ether solution was added using a syringe, and the solution was stirred for three hours. An additional 30 mg of methyllithium in ether was added and the solution was stirred for another hour. A solution of 1.75 g (6.38 mmoles) of 40 in 25 ml of anhydrous ether was then added using a syringe, the ice bath was removed and the solution was stirred for three hours at room temperature. The solution was poured with stirring into dilute ammonium chloride solution, the ether layer was separated and the aqueous layer was extracted twice with ether. The ether extracts were combined, washed with water and sodium chloride solution, dried over anhydrous magnesium sulfate, and evaporated to yield 1.33 g (100%) of 4,5,6,7-tetramethyl-2,3-benzoheptafulvene, 59 as a yellow oil which was purified on a silica gel column eluted with petroleum ether. Ir (neat) 2950 cm^{-1} (s), 1495 (m), 1460 (m), 1390 (m), 1120 (m), 910 (m), 770 (s); nmr (CCl_4), δ 1.75 (broad s, 3H), 1.95 (broad s, 6H), 2.17 (broad s, 3H), 4.97 (sharp, 2H), 7.10-7.30 (4H); mass spectrum, m/e (relative intensity), 211 (17), 210 (82), 195 (95), 180 (52), 170 (44), 165 (70), 155 (86), 141 (100), 128 (23), 115 (43), 89 (43), 76 (45).

X. THE FORMATION OF 2,3,6,7-TETRAMETHYL-4,5-BENZOHEPTAFULVENE (60)

Product 59 (0.102 g), isolated from the reaction of 40 with dimethylcopper lithium, was placed in 1 ml methylene chloride and 0.5 ml of trifluoroacetic acid was added. The reaction mixture immediately became dark, indicative of benzotropylium ion formation. After five minutes the reaction was quenched by adding the mixture to aqueous sodium hydroxide. The organic layer was separated and the aqueous layer was extracted three times with carbon tetrachloride. The organic layers were combined and washed once with aqueous base and three times with water, dried over magnesium sulfate, filtered and evaporated to a yellow oil. Nmr analysis indicated that it was a mixture of 59 and 60 in a ratio of about 2:1. Repetition of the reaction for longer times did not change this ratio. The product was separated on a silica gel thick layer plate eluted with petroleum ether. The band with the highest Rf value was an impurity of 40. The second band was 59. The third band was 60, obtained as an oil; infrared (CCl_4), 2960 cm^{-1} (s), 1495-1450 (broad, w), 1395 (w), 1180 (m), 915 (m); nmr (CCl_4), δ 2.10 (broad, 12H), 4.78 (2H), 7.17 (4H); mass spectrum, m/e (relative intensity), 210 (97), 195 (76), 180 (33), 165 (38), 157 (100), 142 (42), 141 (40), 129 (29), 115 (16), 89 (28).

The injection of 59 on a FFAP column (20%, 3/8" x 10') at 180° gave one principal peak, a mixture of 59, 60, and other materials not identified. An attempted preparation of the Diels-Alder adduct of 59 and maleic anhydride (by heating the mixture in xylene) also led to a mixture of 59, 60 and decomposition products.

Y. THE FORMATION OF 1a,7a-DIHYDRO-1a,2,7,7a-TETRAMETHYL-1H-CYCLOPROPA[b]NAPHTHALENE-2,7-DIOL (65)

Compound 64, 2,3-dimethyl-2,3-methano-1,4-naphthoquinone,[42,43] (1 g, 5 mmole) was dissolved in 50 ml of anhydrous ether and the mixture was stirred under a nitrogen atmosphere. The solution was cooled to 0^{o} in an ice bath and 0.33 g (15 mmole) of methyllithium in ether solution was added using a syringe. Gas evolution occurred and the color of the mixture changed to green, then yellow-orange. The cooling bath was removed and the solution was allowed to stir at room temperature for two hours. Ammonium chloride solution was added to quench the reaction. The solution was extracted with ether, washed with water, dried (anhydrous magnesium sulfate), filtered and evaporated to give an oil which was 65 obtained as a mixture of isomers (calculated crude yield 100%); ir (CCl_4) 3625 cm^{-1} (s), 3500 (s), 3090 (m), 3000 (s), 1460 (s), 1380 (s), 1310 (s), 1080 (s), 925 (s); nmr (CCl_4) one isomer, δ -0.02 (d, J = 5 Hz, 1H), 0.30 (d, J = 5 Hz, 1H), 1.33 (broad s, 6H), 1.42 (s, 3H), 1.65 (s, 3H), 6.87-2.60 (4H), other isomer, δ -0.10 (d, J = 5 Hz, 1H), 0.48 (d, J = 5 Hz, 1H), 1.33 (s, 12H), 6.87-2.60 (4H); the hydroxyl protons appeared at 1.70-2.00 as shown by disappearance of these absorptions after shaking 65 with methanol-d_1.

Z. THE REACTION OF 1a,7a-DIHYDRO-1a,2,7,7a-TETRAMETHYL-1H-CYCLOPROPA[b]NAPHTHALENE-2,7-DIOL (65) WITH DIPHOSPHOROUS TETRAIODIDE

Diphosphorous tetraiodide[48] (570 mg, 2 mmole) was placed in a flask equipped with a reflux condenser. Benzene (5 ml) was added and the solution was stirred magnetically at room temperature. A solution of 232 mg (1 mmole) of 65 in 5 ml of pyridine was added and the reaction mixture was refluxed for two hours. The reaction was checked by withdrawing a sample, recording the nmr spectrum, then replacing the sample. After two hours the reaction mixture was cooled and the organic phase was decanted from the precipitate in the flask into a separatory funnel. The precipitate was washed with ether and the wash added to the separatory funnel. The organic solution was washed with 2N sodium hydroxide solution and with 12% sodium bisulfite solution. The color of the organic phase became clear yellow. The ether solution was further washed with salt brine and water. A white precipitate (which formed during the washings) was filtered and the solution was dried over sodium sulfate, filtered and evaporated to an oil of 1a,7a-dihydro-1a,2,7a-trimethyl-7-methylene-1H-cyclopropa[b]naphthalene-2-ol, 67; ir (CCl_4), 3630 cm^{-1} (w), 3500 (w), 3090 (m), 2940 (s), 1620 (s), 1600 (s), 1450 (s), 1315 (s), 1080 (s), 895 (s), 710 (s); nmr (CCl_4), δ 0.23 (d, J = 5 Hz, 1H), 0.77 (d, J = 5 Hz, 1H), 1.20 (s, 3H), 1.38 (s, 6H), 4.97 (broad s, 1H), 5.17 (broad s, 1H), 6.60-7.60, (4H). The hydroxyl proton was not identified.

AA. THE REACTION OF 2,3-DIMETHYL-1,4-NAPHTHOQUINONE (61) WITH DICHLOROCARBENE

Naphthoquinone 61 (0.368 g, 2 mmole), 0.02 g of benzyltriethylammonium chloride, and 0.720 g (6 mmole) of chloroform were placed in a round-bottomed flask and stirred with a mechanical stirrer. A 50% sodium hydroxide solution (1 ml) was added slowly and the mixture was stirred for 48 hours.[40] Chloroform was added dropwise periodically to give a less viscous solution. At the end of the reaction chloroform was added until the material all went into solution; the mixture obtained was transferred to a separatory funnel and diluted with water. The organic phase was separated and the aqueous phase was extracted twice with chloroform. The organic portions were combined and washed three times with water or brine, dried over anhydrous magnesium sulfate, filtered and evaporated to an oil which crystallized. Recrystallization was not successful. Small amounts were injected on an SE-30, 5' x ⅛", 20% column at 200°. The major peak was a mixture of starting material and product 68 (X = Cl). Ir (CCl_4) 1682 cm^{-1} (s); nmr (CCl_4), δ 1.62 (s, 6H), 7.35-8.00 (4H).

BB. THE REACTION OF 2,3-DIMETHYL-1,4-NAPHTHOQUINONE (61) WITH DIBROMOCARBENE

Naphthoquinone 61 (0.368 g, 2 mmole), 0.02 g of benzyltriethylammonium chloride, 1.52 g (6 mmole) of bromoform and 1 ml of 50% sodium hydroxide were combined and stirred mechanically. Five drops of ethanol were added.[40] The reaction mixture was stirred for 48 hours. Enough methylene chloride was added during this time to

keep the mixture from becoming semi-solid. The mixture was diluted with water, extracted with dichloromethane, washed with water, dilute hydrochloric acid, and water. The solution was dried over anhydrous magnesium sulfate, filtered, and evaporated. Purification over basic alumina eluted with 10% ether in cyclohexane gave an almost colorless oil of 69 (X = Br) which slowly crystallized. Nmr (CCl_4), δ 1.60 (s, 6H), 7.42-7.97 (4H).

CC. PREPARATION OF 1,2,3,4-TETRAMETHYL-1,4-DIHYDRONAPHTHALENE-1,4-ENDOXIDE (76)

Tetramethylfuran[52] (14 g, 0.113 mole) was placed in a three-necked flask fitted with a reflux condenser, two addition funnels, a magnetic stirring bar, and an oil bath. Glyme (55 ml) was added and the solution was stirred and heated to reflux. In one addition funnel was placed 31 g (0.226 mole) of anthranilic acid in 100 ml of glyme, in the other 26.4 g (0.226 mole) of isoamyl nitrite in 100 ml of glyme. These solutions were added dropwise simultaneously over 1.5 hours.[54] The solution was refluxed an additional 20 minutes. The flask contents were cooled, 1N sodium hydroxide was added until the solution was basic, and the solution was diluted with water and extracted three times with petroleum ether. The petroleum ether extracts were combined, washed three times with water, dried (anhydrous magnesium sulfate), filtered and evaporated to an oil. Fractional distillation at 20 mm Hg gave several ml of colorless liquid boiling at 47°; a mixture of glyme, isoamylalcohol and tetramethylfuran. The impure

product, 76, was removed from the pot; 15.5 g [calculated from nmr to be 53% (12.0g) 76] which was used in the next reaction without further purification. Purification of a sample for spectral analysis was accomplished by column chromatography (florisil) or gas chromatography (SE-30, 20%, 5' x ¼", 165°) which yielded a colorless liquid which slowly crystallized; mp 40-42° (lit. 46.6-46°);[52] ir (CCl_4), 3000 cm^{-1} (m), 2990 (m), 1460 (m), 1445 (m), 1390 (s), 1260 (m), 1150 (s); nmr (CCl_4), δ 1.57 (s, 6H), 1.67 (s, 6H), 6.93 (4H); mass spectrum, m/e (relative intensity), 200 (78), 177 (100); 157 (69); uv (cyclohexane), λ max 236 nm (ε = 600), 243 (sh, 560), 259 (432), 265 (524), 271 (680), 279 (644).

DD. THE SENSITIZED PHOTOLYSIS OF 1,2,3,4-TETRAMETHYL-1,4-DIHYDRONAPHTHALENE-1,4-ENDOXIDE (76)

A sample of 0.0492 g of 76 in 15 ml of acetone in a quartz test tube was purged with nitrogen for 15 minutes, capped with a syringe cap, and irradiated at room temperature with a high pressure mercury vapor lamp using a corex filter for 2½ hours. The reaction was followed by gas chromatography. After photolysis, the solvent was evaporated and product was collected by gas chromatography (SE-30, 20%, 5' x ¼" column at 165°). The minor products were not identified. The major product was 1,2,3-trimethyl-1-acetylindene, 81, an oil; ir (CCl_4), 2990 cm^{-1} (m), 2940 (m), 1705 (s), 1635 (w), 1610 (w), 1475 (m), 1360 (m), 1200 (m), 1100 (m); nmr (CCl_4), δ 1.28 (s, 3H), 1.38 (s, 3H), 1.80 (q, J = 1 Hz, 3H), 2.07 (q, J = 1 Hz, 3H), 7.05 (m, 4H); nmr shift experiment, δ (normalized Eu shift), 1.28 (4.2), 1.38 (5.2), 1.80 (2.2), 2.07 (1.0); mass spectrum, m/e (relative intensity), 201 (4), 200 (22), 157 (100), 142 (50), 141 (33), 129 (31), 115 (24), 43

(50); uv (cyclohexane), λ max 222 nm (ε = 13,000), 229 (sh, 12,000), 261 (7100), 285 (sh, 2200).

EE. PREPARATION OF 2,2,3,4-TETRAMETHYL-1,2-DIHYDRONAPHTHALENE-1-ONE (78)

To a solution of 0.056 g of 76 in 1 ml of CH_2Cl_2 was added 0.25 ml of trifluoroacetic acid. The mixture was stirred at room temperature for 15 minutes, then quenched in aqueous sodium hydroxide. Carbon tetrachloride was used to extract the aqueous solution three times. The organic extracts were combined and washed several times with water, dried over anhydrous magnesium sulfate, filtered, and evaporated to an oil. No yield was determined; however, no starting material was recovered and some tar was produced. The product, 2,2,3,4-tetramethyl-1,2-dihydronaphthalene-1-one,[55] 78, was purified by gas chromatography (SE-30, 20%, 5' x ¼" column at 165°); ir (neat), 1670 cm^{-1} (s), 1630 (m), 1600 (m); nmr (CCl_4), δ 1.27 (s, 6H), 1.97 (broad s, 3H), 2.13 (broad s, 3H), 7.43 (3H), 7.97 and 8.07 (1H); uv (cyclohexane), λ max, 236 nm (ε = 31,000), 242 (sh, 25,000), 268 (34,000), 276 (3800), 285 (2800), 328 (1560), 335 (1600), 349 (sh, 1170); mass spectrum, m/e (relative intensity), 200 (73), 185 (100).

FF. THE REACTION OF 1,2,3,4-TETRAMETHYL-1,4-DIHYDRONAPHTHALENE-1,4-ENDOXIDE (76) WITH DICHLOROCARBENE

To 12.0 g of 76 was added 14.7 g (0.1250 mole) of chloroform and 0.2 g of benzyltriethylammonium chloride. The mixture was cooled to 0° and stirred with a mechanical stirrer. A 50% sodium hydroxide solution (20 ml) was added slowly to prevent overheating. After three hours, the mixture was allowed to warm to room temperature. Stirring

was continued for 21 additional hours. The resulting viscous mixture was diluted with water and extracted with petroleum ether four times. The ether portions were combined, washed with sodium chloride solution, then with water, dried (anhydrous magnesium sulfate), filtered, and evaporated to give 16.6 g of a yellow oil which was a mixture of 77, 85, and 86. Product ratios were not reproducible. Product 77 was 3,3-dichloro-1,2,4,5-tetramethyl-6,7-benzo-8-oxotricyclo[3.2.1.$0^{2,4}$]octane; nmr (CCl_4), δ 0.92 (s, 6H), 1.80 (s, 6H), 7.18 (4H). In a typical reaction only trace amounts of 77 were isolated. Only once was 77 the only product formed. In all cases 77 readily rearranged to product 85.

Product 85 was 1,7-dichloro-2,3,6,7-tetramethyl-3,6-epoxy-4,5-benzocyclohepta-1,4-diene; nmr (CCl_4), δ 1.53 (s, 3H), 1.65 (s, 3H), 1.83 (s, 6H), 7.18 (4H). Product 85 was usually the major product of this reaction; sometimes it was the sole product, but usually it was contaminated with 86 which it readily formed upon elimination of HCl. Compound 85 could be further purified by chromatography on florisil eluted with ether in hexanes.

Product 86 was 1-chloro-2,3,6-trimethyl-7-methylene-3,6-epoxy-4,5-benzocycloheptа-1,4-diene, nmr (CCl_4), δ 1.68 (s, 3H), 1.78 (s, 3H), 1.97 (s, 3H), 5.17 (s, 1H), 5.33 (s, 1H), 7.12 (4H).

The yield for all three products was close to quantitative but impossible to accurately determine. Gas chromatography of the mixture on an SE-30 column (20%, 5' x ¼", 165°) produced pure 86.

The remaining spectral data for 86 were: ir (CCl_4), 3000 cm^{-1} (m), 2950 (m), 1800 (w), 1620 (w), 1600 (m), 1460 (m), 1385 (m), 1340-1200 several bands, 990-690 several bands; mass spectrum, m/e

(relative intensity), 248 (1), 246 (3), 211 (22), 205 (40), 203 (100); uv (cyclohexane), λ max, 230 nm (sh, ε = 75,000), 270 (sh, 2,860).

Anal. Calcd for $C_{15}H_{15}OCl$: C, 73.02; H, 6.13

Found: C, 73.05; H, 6.20

The addition of MeOH to 77 caused it to crystallize, but an attempt to recrystallize 77 caused rearrangement to 85 and solvolysis to 87, 1-chloro-2,3,6,7-tetramethyl-7-methoxy-3,6-epoxy-4,5-benzocycloheptа-1,4-diene which was purified by gas chromatography (SE-30, 20%, 5' x ¼" column at 165°); nmr (CCl_4), δ 1.02 (s, 3H), 1.63 (s, 6H), 1.88 (s, 3H), 3.42 (s, 3H), 7.17 (4H); mass spectrum, m/e (relative intensity), 280 (7), 278 (20), 200 (100).

GG. REACTION OF 1,7-DICHLORO-2,3,6,7-TETRAMETHYL-3,6-EPOXY-4,5-BENZOCYCLOHEPTA-1,4-DIENE (85) WITH SODIUM BOROHYDRIDE [59]

Sodium hydroxide (0.04 g, 0.001 mole) was placed in a flask previously fitted with a stirrer and a condenser. A mixture of 80% diglyme-water (0.5 ml) was added. The mixture was heated to 50° and stirred. After the sodium hydroxide was completely dissolved, 0.151 g (0.004 mole) of sodium borohydride was added, followed by 0.148 g (0.5 mmole) of 69 in 0.5 ml of 80% diglyme-water. The solution was stirred at 50° for 20 hours. The flask contents were cooled, and extracted with petroleum ether four times. After combination of the extracts, they were washed with water, dried over anhydrous magnesium sulfate, filtered, and evaporated. The mixture obtained contained 24% 85, 38% 89, and 16% 86, 7% 87 and 5% 90 as determined by nmr integration. Purification by gas chromatography on an SE-30 column (20%, 5' x ¼", at 165°) yielded two principal peaks. The peak with the shortest retention time gave 0.020 g (16%) of 89 and the second peak

gave 85. Compound 89 was 1-chloro-2,3,6,7-tetramethyl-3,6-epoxy-4,5-benzocyclohepta-1,4-diene; colorless crystals, mp 78-79.5°; ir (CCl_4), 3000 cm^{-1} (s), 1645 (w), 1464 (m), 1390 (s), 1355 (w), 1250 (w), 1175 (w); nmr (CCl_4), δ 0.90 (d, J = 7.5 Hz, 3H), 1.60 (s, 3H), 1.62 (s, 3H), 1.82 (d, J = 2 Hz, 3H), 2.70 (q of d, J = 7.5 Hz, J = 2 Hz, 1H), 7.13 (4H); mass spectrum, m/e (relative intensity), 250 (3), 248 (8), 213 (100), 205 (58), 170 (60); uv (cyclohexane), λ max 228 nm (sh, ε = 5100), 259 (600), 265 (780), 273 (760);

Anal. Calcd for $C_{15}H_{17}OCl$: C, 72.86; H, 6.52

Found: C, 72.68; H, 6.66

Following the two major peaks were two minor peaks. Peak three was identified to be due to 87 by spectral comparison. Peak four was assigned to 90, 1-chloro-2,3,6,7-tetramethyl-7-hydroxy-3,6-epoxy-4,5-benzocyclohepta-1,4-diene, mp 140-144°: ir (CCl_4), 3610 cm^{-1} (m), 3500 (m), 3010 (m), 2960 (m), 1637 (w), 1461 (m), 1388 (s), 1338 (s), 1108 (s); nmr (CCl_4), δ 1.13 (s, 3H), 1.63 (s, 3H), 1.68 (s, 3H), 1.80 (s, 3H), 2.37 (broad s, 1H), 7.07, 7.17, 7.23 (4H); mass spectrum, m/e (relative intensity), 246 (1) p - 18, 231 (3), 221 (3), 211 (11), 206 (33), 205 (22), 204 (100), 185 (31), 169 (33), 146 (63); uv (cyclohexane), λ max 234 nm (sh, ε = 4610), 259 (803), 266 (975), 273 (923).

HH. THE FORMATION OF 1-CHLORO-2,3,6-TRIMETHYL-7-METHYLENE-3,6-EPOXY-4,5-BENZOCYCLOHEPTA-1,4-DIENE (86) FROM 1,7-DICHLORO-2,3,6,7-TETRAMETHYL-3,6-EPOXY-4,5-BENZOCYCLOHEPTA-1,4-DIENE (85)

1. By Reaction with Potassium Hydroxide in Ethanol

A solution of 0.51 mg (0.18 mmole) of 85, 2 ml of absolute ethanol, and 14 mg of potassium hydroxide was refluxed for three hours, then poured into 15 ml of water and extracted with chloroform. The chloroform extracts were washed with water, dried over magnesium sulfate, filtered, and evaporated to give a mixture of 86 (37%) and 1-chloro-2,3,6,7-tetramethyl-7-ethoxy-3,6-epoxy-4,5-benzocyclohepta-1,4-diene, 91 (63%). The mixture was purified on an SE-30, 20%, 5' x ¼" column at 170° to yield two principal peaks. The first was due to 86. The second was due to 91, a colorless crystalline compound: mp 83-84.5°, infrared (neat liquid), 3000 cm^{-1} (m), 1638 (w), 1460 (s), 1382 (s), 1337 (w), 1283 (w), 1239 (s), 1212 (m), 1125 (s), 1090 (s), 1078 (s), 1025 (m), 975 (s), 950 (s), 892 (w), 872 (w), 765 (s), 734 (m), 692 (s); nmr (CCl_4), δ 1.00 (s, 3H), 1.13 (d of d, appeared as a triplet, J_1 = 7 Hz, J_2 = 7 Hz, 3H), 1.58 (s, 6H), 1.82 (s, 3H), 3.39 (d of q, J_1 = 7 Hz, J_3 = 10 Hz, 1H), 3.83 (d of q, J_2 = 7 Hz, J_3 = 10 Hz, 1H), 6.88, 6.97, and 7.00 (4H); nmr Eu shift values (CCl_4), δ (normalized shift), 1.00 (4.3), 1.13 (4.0), 1.58 (4.3), 1.58 (1.0), 1.82 (1.7), 3.39 (5.7), 3.83 (5.7); mass spectrum, m/e (relative intensity), 294 (7), 292 (18), 279 (1), 277 (3), 274 (1), 263 (1), 257 (11), 256 (15), 249 (7), 247 (5), 246 (5), 245 (13), 231 (7), 227 (7), 214 (100), 204 (33), 185 (47), 169 (25), 157 (35), 146 (40), 115 (30), 43 (90); uv (cyclohexane), λ max 225 nm (sh, ε = 6000), 236 (sh, 4800),

260 (670), 267 (890), 274 (885). A 100 MHz spectrum with decoupling was obtained. Irradiation between the δ 3.39 and δ 3.83 multiplets caused the peaks at δ 1.13 to collapse toward a singlet, although a sharp singlet was never obtained. Irradiation of either the δ 3.39 multiplet or the δ 3.83 multiplet caused the δ 1.13 peaks to become a doublet. Irradiation of the δ 1.13 peaks influenced both the δ 3.39 and the δ 3.83 multiplets. If the second radio frequency was properly adjusted a doublet (J = 10 Hz) was obtained in place of each doublet of quartets. Otherwise each doublet of quartets became a singlet and a quartet of altered coupling constant; with proper adjustment either the right or left quartet in each set became a singlet while the other remained a quartet.

Anal. Calcd for $C_{17}H_{21}O_2Cl$: C, 69.73; H, 7.23

Found: C, 70.07; H, 7.23

2. By Pyrolysis

Compound 85 (0.236 g) in 4 ml of benzene was dropped slowly onto a pyrex column packed with pyrex beads and heated to 450°. A slow stream of nitrogen was passed through the hot tube and the pyrolyzed material was condensed in a flask at -78°. After all the material had been collected, it was warmed to room temperature, dried over anhydrous magnesium sulfate, filtered, and evaporated to give 0.1711 g of 86 containing 5% of unreacted 85.

3. By Alumina Chromatography

Compound 85 was placed on a three-inch basic alumina column and eluted with cyclohexane. Evaporation of the cyclohexane yielded 86 plus a small amount of 88 (vide infra). Compound 86 could be further

purified by column or gas chromatography as previously described, but was usually used in the following reaction without further purification.

II. REACTION OF 1,7-DICHLORO-2,3,6,7-TETRAMETHYL-3,6-EPOXY-4,5-BENZOCYCLOHEPTA-1,4-DIENE (85) WITH SULFURIC ACID

Diene 85, (30 mg) was placed in a flask and 1 ml of concentrated sulfuric acid was added. The reaction mixture was stirred for 10 minutes at room temperature, then quenched in ice-water. The aqueous solution obtained was extracted three times with carbon tetrachloride. The organic extracts were combined and washed three times with water, dried (anhydrous magnesium sulfate), filtered, and evaporated to give colorless crystals. No yield was calculated. Purification was accomplished by gas chromatography (SE-20%, 5' x ¼" column at 165°) giving 85 and 88 in a ratio of 1:12. Product 88 was identified as 3-chloro-1,2,4-trimethylnaphthalene,[58] colorless crystals, mp 108-109°, (lit.[58] 111°): ir (CCl_4), 3100 cm^{-1} (m), 2940 (s), 1580 (m), 1510 (m), 1460 (s), 1390 (s), 1370 (s), 1180 (s), 1010 (s), 920 (s); nmr (CCl_4), δ 2.55 (s, 3H), 2.62 (s, 3H), 2.75 (s, 3H), 7.25-7.57 (2H), 7.80-8.08 (2H); mass spectrum, m/e (relative intensity), 206 (33), 204 (100), 189 (31), 169 (73); uv (MeOH), λ max, 227 nm (sh, ε = 73,000), 233 (90,000), 270 (sh, 3900), 279 (5600), 289 (6500), 299 (sh, 4600).

JJ. REACTION OF 1-CHLORO-2,3,6-TRIMETHYL-7-METHYLENE-3,6-EPOXY-4,5-BENZOCYCLOHEPTA-1,4-DIENE (86) WITH SULFURIC ACID

Benzodiene 86 (30 mg) was placed in a flask and 1 ml of concentrated sulfuric acid was added. The mixture was stirred at room temperature for 10 minutes; then the reaction was quenched in ice-water. Extraction of the resulting solution with carbon tetrachloride

gave an emulsion that did not separate. Filtration yielded a reddish solid that was not soluble in water, pentane, chloroform, or methanol. This solid was not further investigated. The organic layer of the filtrate was separated from the aqueous layer, dried over anhydrous magnesium sulfate, filtered and evaporated to give a yellow solid. Purification by gas chromatography (SE-30, 20%, 5' x ¼" column at 165°) gave one peak. The retention time and spectra showed it to be 88, 3-chloro-1,2,4-trimethylnaphthalene.[42]

KK. THE HYDROGENATION OF 1-CHLORO-2,3,6-TRIMETHYL-7-METHYLENE-3,6-EPOXY-4,5-BENZOCYCLOHEPTA-1,4-DIENE (86)

To a two-necked flask equipped with a serum cap was added 400 mg of 10% palladium on charcoal. The flask was alternately evacuated and flushed with hydrogen three times. Cyclohexane (2 ml) was injected into the flask and the suspension was stirred magnetically at room temperature. Into the flask was injected 0.92 g of 86 in 15 ml of cyclohexane. The uptake of hydrogen was plotted vs reaction time. When the hydrogen uptake leveled off at approximately one equivalent of hydrogen, the flask was removed from the hydrogenation apparatus, the solution was filtered to remove the catalyst, and the solvent was evaporated. Purification by gas chromatography (SE-30, 20%, 5' x ¼" column at 165°) gave two peaks. The peak at shorter retention time was 1,2,4,5-tetramethyl-6,7-benzo-8-oxobicyclo[3.2.1]octane, 92 (25%) obtained as crystals, mp 85-86°; ir (CCl_4) 3000 cm^{-1} (m), 1470 (m), 1390 (s); nmr (CCl_4), δ 0.70 (d, J = 7 Hz, 6H), 1.46 (s, 6H), 1.12 to 2.05 (m, 4H), 7.10 (4H); mass spectrum, m/e (relative intensity), 206 (8), 173 (43), 159 (100); uv (cyclohexane), λ max 269 nm (ε = 910),

262 (800), 256 (520), 250 (sh, 300).

Anal. Calcd for $C_{15}H_{22}O$: C, 83.29; H, 9.32

Found: C, 83.22; H, 9.27

The peak at longer retention time was 89, 74% yield. Compound 89 was normally used in the following reaction without purification.

LL. THE PREPARATION OF 4,5,7-TRIMETHYL-6-CHLORO-2,3-BENZOHEPTAFULVENE (94)

The following apparatus was assembled. A small three-necked flask was fitted with a nitrogen inlet and a Dewar condenser. The condenser was attached to a tube leading to the top rear of the hood. A stirring bar was placed in the flask, which was placed in a water bath on a stirring plate. The temperature of the water bath was kept below 30° throughout the reaction by the addition of ice. A capillary gas inlet tube with the top end bent over was placed in a neoprene gasket, so that it could be easily slid up and down. This gasket and tube assembly was placed in the third neck of the flask. The tube was attached to a trap constructed of a small filter flask which was attached to the outlet of a cold trap constructed from a graduated tube. The inlet of the graduated tube was attached to another trap which was connected to a boron trifluoride (BF_3) cylinder. In the reaction flask was placed 1 g of 89 in 10 ml of glacial acetic acid. The solution was cooled in the water bath, stirred, a slow stream of nitrogen was passed through the flask, and a dry-ice methanol bath was made in the Dewar condenser. The capillary inlet tube was slid up out of the acid solution to prevent suck-back into the traps. The BF_3 cylinder could then be opened to allow a slow stream of BF_3 gas to pass into the reaction vessel.

The reaction could be carried out in two ways from this point. First, if a measured amount of BF_3 gas was to be used, a liquid nitrogen dewar was placed around the graduated tube and BF_3 was condensed in the graduated tube until the required amount condensed. The BF_3 cylinder was closed, the liquid nitrogen bath was removed and a liquid nitrogen-methanol slush was substituted in its place. This bath allowed the slow evolution of BF_3 gas into the reaction vessel. After the evolution was started the capillary inlet tube was pushed into the reaction mixture. When sufficient BF_3 was added, the capillary was first removed from the reaction mixture to prevent suck-back, and then the liquid nitrogen bath was replaced on the graduated tube. About 8 - 10 ml of condensed BF_3 gas was usually sufficient to completely convert the starting material. By the time 10 ml of BF_3 was added, the reaction mixture was almost always a solid mass (BF_3-acetic acid complex).

The second method for carrying out the reaction involved starting a slow flow of BF_3 through the system, pushing the gas capillary into the reaction mixture and letting the BF_3 bubble until the reaction mixture became solid. The capillary was then pulled out of the mixture and the BF_3 gas supply turned off.

In all cases the reaction progress was followed by quickly removing the nitrogen inlet, inserting a disposable pipet into the flask, quickly withdrawing a small amount of the reaction mixture, and replacing the nitrogen inlet. The aliquot removed was added to a 5 ml pear-shaped flask containing 2-3 drops of water and 2-3 drops of ether. The flask contents were shaken and the ether was withdrawn by syringe and injected on an analytical gas chromatograph

using an SE-30, 5%, 5' x 1/8" column at 190°. The product had a longer retention time than the starting material and since the reaction was usually carried out using impure starting material it was best to have authentic samples of 89 and 94 to check the gc results.

When complete, the reaction was quenched using the following procedure. The hose on the gas inlet capillary tube was removed and the tube was pushed into the reaction mixture. A flask containing 200 ml of ether and 100 ml of a saturated solution of sodium carbonate in water was placed under the bent end of the capillary tube. If the reaction mixture was liquid, a stopper was momentarily placed in the outlet of the Dewar condenser and the material was slowly ejected through the capillary tube into the rapidly stirred solution of base. The flask was then rinsed with ether and the rinse was ejected. The ether rinse was repeated. If the mixture was a solid, ether was added in portions to the flask and ejected and the solid was thus slowly dissolved and quenched.

The resulting ether solution was stirred until bubbles ceased to form. The aqueous layer was removed, the ether layer was washed with a sodium carbonate solution twice and then with water. The ether was dried over anhydrous calcium chloride, filtered, and evaporated to give 4,5,7-trimethyl-6-chloro-2,3-benzoheptafulvene, 94 as a yellow oil. The yield of 94 was usually about 20 to 30% of theoretical. Compound 94 was somewhat unstable and slowly darkened on standing at room temperature. It was purified by gas chromatography on a 20% SE-30, 5' x ¼" column at 165° or by column chromatography over basic alumina eluted with petroleum ether. Ir (CCl_4), 2940 cm^{-1} (s), 1680 (m), 1490 (m), 1460 (m), 1390 (m), 1000 (w), 920 (s); nmr (CCl_4), δ 2.10

(broad s, 3H), 2.17 (s, 3H), 2.23 (broad s, 3H), 5.13 (m, 2H), 7.17 and 7.33 (4H); mass spectrum, m/e (relative intensity), 232 (35), 230 (90), 215 (34), 195 (100), 180 (80), 165 (62), 147 (55); uv (cyclohexane), λ max 262 nm (sh, ϵ = 5800), 282 (sh, 4700).

Anal. Calcd for $C_{15}H_{15}Cl$: C, 78.08; H, 6.55

Found: C, 78.35; H, 6.56

A second compound, 93, was also isolated in very low yield by gc or column chromatography. The structure of 93 was not certain. The spectral data pertaining to it were: ir (CCl_4), 1702 cm^{-1} (s); nmr (CCl_4), δ 1.35 (s, 3H), 1.73 (s, 3H), 1.87 (broad s, 3H), 1.95 (broad s, 3H), and 7.07 (4H); mass spectrum, m/e (relative intensity), 214 (8), 186 (10), 171 (100), 156 (67), 141 (29), 128 (26), 115 (22).

MM. THE REACTION OF 1-CHLORO-2,3,6,7-TETRAMETHYL-3,6-EPOXY-4,5-BENZOCYCLOHEPTA-1,4-DIENE (89) WITH FLUOROSULFONIC ACID

A sample of 89 in an nmr tube was dissolved in methylene chloride. Fluorosulfonyl chloride was condensed in a layer on top of the methylene chloride solution and fluorosulfonic acid was added in a further layer. The tube contents were mixed while the solution was kept at -78°. The nmr spectrum was taken to determine when reaction occurred, first at low temperatures and then as the acid solution was warmed up in ten degree steps. Reaction first occurred at about -10°. Before the material was completely reacted the solution was cooled to -78° and the reaction was quenched by adding the mixture to a solution of potassium hydroxide in methanol and water at -78°. Purification by gas chromatography (FFAP, 20%, 5' x ¼", 195°) yielded small amounts of 93 and 94 identified as above.

NN. THE PREPARATION OF 2,3,6,7-TETRAMETHYL-4,5-BENZOTROPONE (1)

In a 100-ml flask were combined 1.3 g of 94, 10 ml of methylene chloride, 15 ml of methanol, and 1 ml of water. The mixture was stirred magnetically and cooled in an ice bath. Concentrated sulfuric acid was added dropwise until a deep yellow color was obtained. This required about 18 ml of H_2SO_4. The flask contents were allowed to warm to room temperature and were stirred overnight. The reaction was quenched by adding ice to the solution until the yellow color was dissipated. The solution was then poured into a separatory funnel and extracted three times with methylene chloride. The extracts were washed with a saturated sodium carbonate solution twice, then with water, dried over magnesium sulfate, filtered, and evaporated. The crystals so obtained were placed on a florisil column and eluted with 10% ether in hexane. The product obtained by evaporation of the fractions containing product was a crystalline solid which could be further purified by recrystallization from MeOH (80% yield) or by gas chromatography on an SE-30 column (20%, 5' x ⅛" at 165°). The product 2,3,6,7-tetramethyl-4,5-benzotropone, 1, was produced pure in 4% overall yield from compound 76. Compound 1 was obtained as colorless prismatic crystals, mp 104-105°; infrared, (KBr) 2930 cm^{-1} (w) 1622 (s), 1490 (w), 1450 (w), 1380 (m), 1340 (m), 1166 (w), 1037 (w), 788 (w) and 770 (m); nmr (CCl_4), δ 2.03 (broad, 6H) 2.23 (broad, 6H), 7.22 (4H); nmr Eu shift (CCl_4) δ (normalized shift), 2.03 (12.0), 2.23 (4.14), 7.30 (2.4), 7.13 (1.0); mass spectrum, m/e (relative intensity), 212 (1), 184 (100), 169 (98); uv cyclohexane, λ max 232 nm (ε = 30,600), 237 (sh, 30,000), 271 (sh, 8600), 314 (sh, 2100).

Anal. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60
Found: C, 84.94; H, 7.67

OO. THE VACUUM PYROLYSIS OF 2,3,7-TRIMETHYL-4,5-BENZOTROPONE (21)

Benzotropone 21 (0.023 g) was pyrolyzed at 0.5 mm Hg and 700° through an unpacked vycor tube. The collector was cooled to -78° and the sample was sublimed using an oven. After all the material had passed through the tube, the tube and collector were washed with methylene chloride and the solvent was evaporated. Purification by gas chromatography (SE-30, 20%, 5' x ¼" column at 180°) yielded 6 mg (28%) of 1,2,3-trimethylnaphthalene, 23.[34]

PP. THE VACUUM PYROLYSIS OF 2,3,6,7-TETRAMETHYL-4,5-BENZOTROPONE (1)

Benzotropone 1 was vacuum pyrolyzed at 600° and 0.5 mm Hg using an unpacked vycor tube. The collector was cooled to -78°, and the sample was vaporized using an oven. After completion of the pyrolysis, the tube and collector were washed with methylene chloride and the solvent was evaporated. Purification of the residue by gas chromatography (SE-30, 20% 5' x ¼" column at 180°) yielded three small peaks of unidentified materials at short retention times and two major peaks at longer retention time, which were 1,2,3,4-tetramethylnaphthalene (38), 0.0036 g (12%) and at longest retention time, unreacted 1 (0.0024 g, 7%). Both 1 and 38 were identified by comparison of retention times and spectra with authentic samples.

QQ. THE PHOTOLYSIS OF 2,3,6,7-TETRAMETHYL-4,5-BENZOTROPONE (1)

Benzotropone 1 was dissolved in 50 ml of cyclohexane ($\sim 5 \times 10^{-3}$ M solution). Nitrogen was bubbled through the solution for 1 hour before

irradiation and slowly during irradiation. The solution was irradiated using a high pressure mercury lamp and a corex filter. The reaction was followed by analytical gc using an SE-30, 5' x 1/8", 3% column at 170°. No reaction was apparent in the first two hours; after 9 hours, no new peaks were obtained by gc analysis. The solution was evaporated and purified by alumina thick layer chromatography eluted with petroleum ether. The only identifiable compound was a few milligrams of 1,2,3,4-tetramethylnaphthalene, 38, identified by spectral comparison.

RR. THE REACTION OF 2,7-DIMETHYL-4,5-BENZOTROPONE (5) WITH meta-CHLOROPERBENZOIC ACID

Benzotropone 5 (2.208 g, 12 mmoles) was placed in 10 ml of methylene chloride and 3.10 g (18 mmoles) of 99% meta-chloroperbenzoic acid in 10 ml of methylene chloride was added. The reaction mixture was stirred at room temperature. The reaction was followed by withdrawing aliquots, obtaining nmr spectra, and replacing the aliquots. The reaction was allowed to continue for nine days. Two additional grams of meta-chloroperbenzoic acid were added during that time. The reaction mixture was worked up by washing twice with 5% sodium bisulfite solution, twice with 5% sodium bicarbonate solution, and twice with water. The organic phase was dried over magnesium sulfate and evaporated. The material obtained was placed on a florisil column and eluted with 5% ether in hexanes. The first product to be eluted was 2,3-dimethylnaphthalene, 62, of which a small amount was produced and identified by comparison with authentic spectra. The second was the mono-epoxide 95 (0.177 g, 7%) obtained as crystals after recrystallization from carbon tetrachloride. Unreacted 5 was then eluted,

followed by diepoxide 96 (0.2161 g, 8%) obtained as colorless crystals after recrystallization from carbon tetrachloride. Several other minor products were produced which were not characterized.

Monoepoxide 95 gave colorless crystals, mp 88-89°; infrared (CCl_4) 3000 cm^{-1} (m), 1662 (s), 1453 (m), 1380 (m), 1301 (m), 1210 (m), 1065 (m), 1042 (m), 1018 (m), 958 (m), 905 (m), 850 (m), 830 (m); nmr (CCl_4), δ 1.60 (s, 3H), 2.04 (d, J = 2 Hz, 3H), 3.90 (s, 1H), 6.60 (q, J = 2 Hz, 1H), 7.00-7.43 (4H); mass spectrum, m/e (relative intensity), 200 (20), 185 (29), 158 (50), 129 (100), 128 (83), 115 (37), 43 (200); uv (cyclohexane), λ max 234 nm (sh, ε = 11,000), 289 (10,200).

Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04

Found: C, 78.13; H, 6.01

Diepoxide, 96, was crystalline, mp 135-136°; ir (KBr), 3000 cm^{-1} (w) 1674 (s), 1600 (w), 1510 (m), 1460 (m), 1390 (m), 1090 (m), 1062 (m), 1020 (m), 960 (m), 880 (s), 772 (s); nmr (CCl_4), δ 1.60 (s, 3H), 3.67 (s, 3H), 7.10-7.50 (4H); mass spectrum, m/e (relative intensity), 216 (1), 184 (9), 156 (11), 145 (100), 117 (48), 115 (40), 43 (25), and a metastable peak at 113; uv (cyclohexane), λ max 224 nm (ε = 10,300), 269 (1860), 273 (1140).

Anal. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59

Found: C, 72.11; H, 5.31

SS. GENERAL PROCEDURE FOR GENERATION OF BENZOTROPYLIUM IONS

The ion precursor was dissolved in carbon tetrachloride or methylene chloride in an nmr tube and trifluoroacetic acid (TFA) was added to the tube. The tube contents were thoroughly mixed. A color was produced,

usually dark yellow or red. The nmr spectrum was then obtained, either on this solution or on the TFA solution obtained by extraction of the precursor from the solvent. The reaction was quenched by adding the acid solution dropwise to a solution of base (usually triethylamine) in methylene chloride at 0^{o} or to ice-water. The solution thus obtained was extracted with methylene chloride, washed with water, dried, and evaporated to yield the product or regenerated ion precursor.

TT. THE FORMATION OF 1-HYDROXY-2,3,7-TRIMETHYL-4,5-BENZOTROPYLIUM ION (97)

The general procedure for formation of benzotropylium ions was followed. A sample of 21 in carbon tetrachloride was extracted with trifluoroacetic acid and the nmr spectrum of 97 was recorded: δ 2.67 (6H), 2.98 (3H), 7.88 (3H), 8.23 and 8.33 (2H). The ion solution was quenched with water to regenerate 21.

UU. THE GENERATION OF 1-HYDROXY-2,3,6,7-TETRAMETHYL-4,5-BENZOTROPYLIUM ION (98)

A sample of 1 in carbon tetrachloride was extracted into trifluoroacetic acid and the nmr spectrum (TFA) of 98 was recorded; δ 2.65 (6H), 2.88 (6H), 7.62-8.27 (m, 4H). When the solution was quenched with water, ion 98 gave 1.

VV. THE PREPARATION OF 1,2,7-TRIMETHYL-4,5-BENZOCYCLOHEPTA-2,4,6-TRIEN-1-ol (99)

A solution of 500 mg of 5 in 50 ml of anhydrous ether was placed in a dry flask under a nitrogen atmosphere. Methyllithium in ether solution was added dropwise using a syringe until the solution changed

color to green or white. Water was added and the ether layer was separated, washed twice with water, and dried over anhydrous potassium carbonate. Evaporation without heat allowed an nmr spectrum of the product, 1,2,7-trimethyl-4,5-benzocyclohepta-2,4,6-trien-1-ol, 99, to be obtained but decomposition to a white solid occurred.[30] The product could be stored as a dilute ether solution over K_2CO_3 at 0^o for several days. The nmr spectrum (CCl_4) of 99 showed absorptions at δ 0.93 (s, 3H), 1.53 (s, 1H), 2.02 (d, J = 2 Hz, 6H), 6.22 (q, J = 2 Hz, 2H), and 6.97 (4H). Double irradiation of the δ 6.22 peak caused the collapse of the δ 2.02 peak to a singlet. The ir spectrum had an absorption at 3500 cm^{-1}, indicative of an alcohol. No carbonyl absorption was present.

The white solid which was formed resisted characterization. Its nmr spectrum consisted only of broad peaks. However, addition of trifluoroacetic acid to the white solid generated ion 100, 5,6,7-trimethyl-2,3-benzotropylium ion. Compound 99 in trifluoroacetic acid also produced ion 100. Elemental analysis of this white solid was not characteristic of any discreet compound.

WW. THE GENERATION OF 1,2,4-TRIMETHYL-4,5-BENZOTROPYLIUM ION (100)

A sample of 99 in carbon tetrachloride, when mixed with trifluoroacetic acid, produced a deep red colored solution. The nmr spectrum of ion 100 was recorded in TFA as δ 2.97 (3H), 3.08 (6H), 8.28 (4H), 9.22 (2H). This solution, when quenched with water, produced only the white solid previously encountered during the decomposition of 99. Quenching with sodium methoxide in methanol produced a mixture of methyl ethers, 1-methoxy-5,6,7-trimethyl-2,3-benzocyclohepta-2,4,6-

triene, 108, and 1-methoxy-1,2,7-trimethyl-4,5-benzocyclohepta-2,4,6-triene, 109, and alcohol 99. These compounds were unstable and underwent decomposition. Compound 108 showed nmr (CCl_4) absorptions at δ 1.70 (broad, 3H), 1.77 (broad, 3H), 2.08 (d, J = 2 Hz, 3H), 3.30 (s, 3H), 6.65 (q, J = 2 Hz, 1H), 6.90-7.20 (4H). Compound 109 showed nmr (CCl_4) signals at δ 1.27 (s, 3H), 2.08 (d, J = 2 Hz, 6H), 2.95 (s, 3H), 6.28 (q, J = 2 Hz, 2H), 6.90-7.20 (4H).

XX. THE FORMATION OF 2,7-DIMETHYL-4,5-BENZOHEPTAFULVENE 101

1. By Dilute Acid Elimination of Water

A sample of 99 (approximately 20-30 mg) in 10 ml of ether was diluted with 20 ml of ether. Two drops of trifluoroacetic acid were added and the solution was stirred at room temperature for six minutes, then poured into a 5% sodium bicarbonate solution. The ether layer was separated and washed with 5% sodium bicarbonate solution, and then with water. The ether solution was dried over anhydrous potassium carbonate and evaporated without heat. Nmr analysis showed that a mixture of 99 and 101 was present in the ratio 10:30. The nmr peaks assigned to 101 were (CCl_4); δ 2.03 (d, J = 2 Hz, 6H), 4.95 (2H), 6.23 (q, J = 2 Hz, 2H), 6.87 (4H). Compound 101 was unstable and rapidly decomposed; it was best handled under nitrogen.

2. By Quenching Ion 100

A trifluoroacetic acid solution of ion 100 was quenched by addition dropwise to a solution of triethylamine in methylene chloride at 0°. The methylene chloride solution thus obtained was thoroughly washed with water several times, dried over anhydrous potassium

carbonate, filtered and evaporated to give impure 101. This solution could be purified somewhat by chromatography over alumina eluted with methylene chloride. These solutions also decomposed to materials which gave only very broad nmr absorptions; however, addition of trifluoroacetic acid to these materials regenerated ion 100.

YY. THE PREPARATION OF 1,2,3,7-TETRAMETHYL-4,5-BENZOCYCLOHEPTA-2,4,6-TRIENE-1-OL (102)

Benzotropone 21 (0.023 g) was dissolved in 10 ml of ether under nitrogen and stirred at room temperature. Excess methyllithium in ether solution was added using a syringe. The reaction was quenched by careful addition first of wet ether and then water to the flask. After quenching, an equal volume of water was added, the ether layer separated, and the aqueous layer extracted three times with ether. The ether portions were combined and washed twice with water, dried over anhydrous potassium carbonate, filtered and evaporated at room temperature to give 86 as an oil. The nmr spectrum of 102 (CCl_4) had absorptions at δ 0.87 (s, 3H), 2.00 (q, J = 1 Hz, 3H), 2.00 (d, J = 2 Hz, 3H), 2.08 (q, J = 1 Hz, 3H), 6.18 (q, J = 2 Hz, 1H), 6.92 and 6.98 (3H), 7.22 (1H). The hydroxyl proton was not identified because of impurities in the δ 1.0-1.6 region of the spectrum. Irradiation of the δ 6.18 quartet caused the peaks at δ 2.00 to partially sharpen, although the outside shoulders assigned to the quartet at δ 2.00 did not change. The infrared spectrum (CCl_4) had an absorption at 3650 cm^{-1} indicative of an alcohol. No carbonyl band was present.

ZZ. THE PREPARATION OF 1,5,6,7-TETRAMETHYL-2,3-BENZOTROPYLIUM ION (103)

An nmr sample of 102 was shaken with trifluoroacetic acid, the trifluoroacetic acid extract was put in another nmr tube and the nmr spectrum (in TFA) of ion 103 was recorded; δ 2.98 (9H), 3.32 (3H), 8.23 (3H), 8.70 (1H), 9.00 (1H).

This solution was quenched with water and extracted with methylene chloride in the normal workup. The product gave an nmr spectrum which mainly had very broad peaks. Small peaks in the δ 4.82 region suggest that a tiny amount of the expected benzoheptafulvene product was produced. The recovered material was again extracted with trifluoroacetic acid and the nmr spectrum showed that ion 103 was produced fairly cleanly. Quenching ion 103 with triethylamine in methylene chloride according to the normal workup procedure produced essentially the same results as those obtained with the water quench.

AAA. THE FORMATION OF 1,2,3,6,7-PENTAMETHYL-4,5-BENZOCYCLOHEPTA-2,4,6-TRIENE-1-OL (106)

Benzotropone 1 (100 mg, 0.47 mmole) was placed in 10 ml of anhydrous ether. The solution was stirred magnetically at room temperature under a nitrogen atmosphere. An excess of methyllithium in ether solution was added dropwise by syringe. First wet ether, then water were carefully added to quench the reaction. An equal volume of water was added, the ether layer was separated and the aqueous solution was extracted twice with ether. The ether portions were combined, washed with dilute sodium carbonate solution, filtered and evaporated at room temperature and reduced pressure. The product was 106,

obtained as a colorless solid: infrared (CCl_4) 3660 cm^{-1} indicative of an alcohol (no carbonyl absorptions were present); nmr (CCl_4), δ 0.62 (s, 3H), 1.93 (broad, 6H), 2.07 (broad, 6H), 6.80-7.27 (4H), the hydroxyl proton was not identifiable because of impurities from the reaction.

BBB. PREPARATION OF 1,4,5,6,7-PENTAMETHYL-2,3-BENZOTROPYLIUM ION (107)

A sample of 106 in carbon tetrachloride in an nmr tube was extracted with trifluoroacetic and the acid layer was transferred to another nmr tube. The nmr spectrum (in TFA) of ion 107 was recorded as δ 2.83 (9H), 3.10 (6H), 7.87-8.50 (m, 4H).

Ion 107 may also be produced by the addition of trifluoroacetic acid to solutions of 59 and/or 60.

CCC. THE PREPARATION OF 4,5,6,7-TETRAMETHYL-2,3-BENZOHEPTAFULVENE (59) AND 2,3,6,7-TETRAMETHYL-4,5-BENZOHEPTAFULVENE (60) FROM ION (107)

A solution of ion 107 in trifluoroacetic acid was poured into ice-water and shaken. The product was extracted three times with methylene chloride. The organic extracts were combined and washed with dilute sodium carbonate solution and then with water, dried (anhydrous potassium carbonate), filtered and evaporated. Nmr analysis showed the formation of 59 and 60 in a ratio of 3:2. Alternatively, quenching with triethylamine in methylene chloride and following standard workup procedures gave the same products in the ratio of 7:3.

The source of ion 107 may be either compound 106, compound 59, or compound 60 derived from the reaction of 40 with dimethylcopper lithium reagent (Section B).

BIBLIOGRAPHY

BIBLIOGRAPHY

1. For reviews see F. Pietra, *Chem. Rev.*, 73, 293 (1973); T. Nozoe, "Tropones and Tropolones" p. 339 in "Non-Benzenoid Aromatic Compounds," D. Ginsburg editor, Interscience, New York, 1959; D. Lloyd, "Carbocyclic Non-Benzenoid Aromatic Compounds," Elsevier, Amsterdam, 1966.

2. J. Thiele and J. Schneider, *Justus Liebig's Ann. Chem.*, 369, 287 (1909).

3. J. Thiele and E. Weitz, *Justus Liebig's Ann. Chem.*, 377, 1, (1910).

4. W. Davey and H. Gottfried, *J. Org. Chem.*, 26, 3699 (1961) and *J. Org. Chem.*, 26, 3705 (1961).

5. K. C. Srivastava and S. Dev, *Tetrahedron*, 28, 1083 (1972); H. Cristol and M. Y. Montet, *Bull. Soc. Chim. France*, 585 (1958).

6. D. Caunt, W. D. Crow, T. D. Haworth, and C. A. Vodoz, *J. Chem. Soc.*, 1631 (1950).

7. E. W. Collington and G. Jones, *J. Chem. Soc. C.*, 2656 (1969); other examples are: R. P. Holysz, *J. Amer. Chem. Soc.*, 75, 4432 (1953); R. Hanna, G. Maalouf, and B. Muckensturm, *Tetrahedron*, 29, 2297 (1973); H. O. House and R. W. Bashe II, *J. Org. Chem.*, 30, 2942 (1965).

8. F. G. Bordwell and M. Winn, *J. Org. Chem.*, 32, 42 (1967).

9. S. D. Saraf, *Synthesis*, 264 (1971).

10. (a) M. K. Saxena and M. M. Bodadia, *J. Indian Chem. Soc.*, 46, 855 (1969); (b) S. D. Saraf, *Can. J. Chem.*, 47, 1169 (1969); (c) W. E. Parham, D. A. Bolon, and E. E. Schweizer, *J. Amer. Chem. Soc.*, 83, 603 (1961).

11. T. Hanafusa, S. Imai, K. Ohkata, H. Suzuki, and Y. Suzuki, *Chem. Communications*, 73 (1974); also reported in *Synthesis*, 587 (1974).

12. S. Julia and Y. Bonnet, *Bull. Chim. Soc. France*, 1340 (1957).

13. H. Hart and A. Oku, *J. Org. Chem.*, 37, 4269 (1972).

14. M. Oda, R. Breslow, and J. Pecoraro, *Tetrahedron Letters*, 43, 4419 (1972)

15. P. F. Ranken, B. J. Harty, L. Kapicak, M. A. Battiste, *Synthetic Comm.*, 3, 311 (1973).

16. G. Wittig and W. Reuther, *Justus Liebig's Ann. Chem.*, 765, 47 (1972).

17. T. Mukai, T. Nakazawa, T. Shishido, *Tetrahedron Letters*, 2465 (1967).

18. D. J. Pasto, Photochemistry of Troponoid Compound," p. 155 in "Organic Photochemistry" Volume 1, O. L. Chapman, editor, Marcel Dekker, New York, 1967.

19. T. Mukai, T. Miyashi, and Y. Tanaka, *Tetrahedron Letters*, 2175 (1968).

20. O. L. Chapman, H. G. Smith, R. W. King, D. J. Pasto, and M. R. Stoner, *J. Amer. Chem. Soc.*, 85, 2031 (1963).

21. B. Foehlisch, E. Schupp, U. Dukek, and G. Schwaiger, *Justus Liebig's Ann. Chem.*, 1861 (1973); B. Foehlisch, E. Widmann, and E. Schupp, *Tetrahedron Letters*, 2355 (1969).

22. W. Reid and H. J. Schwenecke, *Chem. Ber.*, 91, 566 (1958); M. E. Vol'pin and A. F. Pate, *Dokl. Akad. Nauk S.S.S.R.*, 70, 843 (1950) through *Chem. Abstr.* 44:6846 (1950).

23. E. Weitz and A. Scheffer, *Ber.*, 54B, 2327 (1921).

24. Y. Sugimura, N. Soma, and Y. Kishida, *Tetrahedron Letters*, 91 (1971); H. A. Corver and R. F. Childs, *J. Amer. Chem. Soc.*, 94, 6201 (1972); J. Tsunetsugu, M. Sato, and S. Ebine, *JCS Chem. Comm.*, 363 (1973); R. E. Harmon, R. Suder, and S. K. Gupta, *JCS Chem. Comm.*, 472 (1972); R. E. Harmon, R. Suder and S. K. Gupta, *JCS Perkin I*, 1746 (1972); M. Franck-Neumann and D. Martina, *Tetrahedron Letters*, 1755 (1975); M. Franck-Neumann and D. Martina, *Tetrahedron Letters*, 1759 (1975); E. J. Corey and M. Jautelat, *J. Amer. Chem. Soc.*, 89, 3912 (1967).

25. C. Jutz, I. Rommel, I. Lengyel, and J. Feeney, *Tetrahedron*, 22, 1809 (1966).

26. H. J. Bestmann and J. Leinert, *Angew. Chem. Int. Ed.*, 8, 763 (1969).

27. E. O. Bergmann and R. Ikan, *J. Org. Chem.*, 28, 3341 (1963); A. C. Cope and S. W. Fenton, *J. Amer. Chem. Soc.*, 73, 1673 (1951).

28. A. Oku and K. Yagi, *J. Amer. Chem. Soc.*, 96, 1966 (1974).

29. K. Hafner and H. Schaum, *Angew Chem. Int. Ed.*, 2, 95 (1963).

30. a. D. J. Bertelli and C. C. Ong, *J. Amer. Chem. Soc.*, 87, 3719 (1965); b. D. J. Bertelli, J. T. Gerig, and J. M. Herbelin, *J. Amer. Chem. Soc.*, 90, 107 (1968).

31. G. Love, Phd. Thesis, Michigan State University, 1972.

32. K. Ibata, H. Shimanouchi, and Y. Sasada, *Chem. Lett.*, 269 (1973).

33. H. O. House and W. F. Fisher, Jr., *J. Org. Chem.*, 33, 949 (1968); H. O. House, W. L. Respess, and G. M. Whitesides, *J. Org. Chem.*, 31, 3128 (1966).

34. P. Bey and G. Ourisson, *Bull. Soc. Chim. France*, 1411 (1968).

35. F. A. Bovey, "NMR Data Tables for Organic Compounds," Vol. 1, Interscience, N.Y., 1967; K. B. Wiberg and B. J. Nist, "The Interpretation of NMR Spectra," W. A. Benjamin, Inc., N. Y. 1962.

36. W. Cocker, *J. Chem. Soc.*, 36 (1946).

37. H. Gilman, C. G. Brannen, and R. K. Ingham, *J. Amer. Chem. Soc.*, 78, 1689 (1956); J. T. Groves and B. S. Packard, *J. Amer. Chem. Soc.*, 94, 3252 (1972); P. S. Skell and S. R. Sandler, *J. Amer. Chem. Soc.*, 80, 2024 (1958); G. M. Iskander and F. Stansfield, *J. Chem. Soc.*, 1390 (1965); A. J. Birch, J. M. Brown, and F. Stansfield, *J. Chem. Soc.*, 5343 (1964).

38. D. Hausigk, *Synthetic Communications*, 307 (1971).

39. A. Oku, T. Hino, and K. Matsumoto, *J. Org. Chem.*, 40, 695 (1975).

40. M. Makosza and M. Wawrzyniewicz, *Tetrahedron Letters*, 4659 (1969); L. Skattebol, G. A. Abskharoun, and T. Greibrokk, *Tetrahedron Letters*, 1367 (1973); also see M. Makosza and M. Fedorynski, *Synthetic Comm.*, 3, 305 (1973).

41. E. J. Corey and G. H. Posner, *J. Amer. Chem. Soc.*, 89, 3911 (1967).

42. O. Kruber, *Chem. Ber.*, 62, 3046 (1929).

43. R. T. Arnold and R. Larsen, *J. Org. Chem.*, 5, 250 (1950).

44. J. A. Moore and D. E. Reed, *Organic Syntheses*, 41, 16 (1961).

45. B. Eistert, H. Fink, T. Schulz, and J. Riedinger, *Justus Liebig's Ann. Chem.*, 750, 1 (1971).

46. T. Asano, T. Nagasaki, S. Imai, K. Ohkata, and T. Hanafusa, *Nippon Kagaku Zasshi*, 92, 532 (1971) through *Chem. Abstr.*, 76:126648e (1972).

47. H. H. Inhoffen, K. Radscheit, U. Stache, and V. Koppe, *Justus Liebig's Ann. Chem.*, 684, 24 (1965); R. Kuhn and A. Winterstein, *Helv. Chim. Acta*, 11, 106 (1928).

48. F. E. E. Germann and R. N. Traxler, *J. Amer. Chem. Soc.*, 49, 307 (1927).

49. G. L. Buchanan and J. K. Sutherland, *J. Chem. Soc.*, 2620 (1956).

50. A. C. G. Gray, T. Kakihana, P. M. Collins, and H. Hart, *J. Amer. Chem. Soc.*, 89, 4556 (1967).

51. A. C. G. Gray and H. Hart, *J. Amer. Chem. Soc.*, 90, 2569 (1968).

52. E. Wolthius, B. Bossenbroeck, G. DeWall, E. Geels, and A. Leegwater, *J. Org. Chem.*, 28, 148 (1963).

53. L. Friedman and F. M. Logullo, *J. Amer. Chem. Soc.*, 85, 1549 (1963).

54. L. F. Fieser and M. J. Haddadin, *Can. J. Chem.*, 43, 1599 (1965).

55. H. Hart and R. K. Murray, Jr., *J. Org. Chem.*, 32, 2448 (1967).

56. G. R. Ziegler and G. S. Hammond, *J. Amer. Chem. Soc.*, 90, 513 (1968); H. Prinzbach, P. Wursch, P. Vogel, W. Tochtermann, and C. Franke, *Helv. Chim. Acta*, 51, 911 (1968); J. S. Swenton, J. Oberdier, and P. D. Rosso, *J. Org. Chem.*, 39, 1038 (1974).

57. H. Hart and A. Oku, *J. Org. Chem.*, 37, 4274 (1972).

58. J. Buddrus, *Chem. Ber.*, 101, 4152 (1968).

59. H. M. Bell and H. C. Brown, *J. Amer. Chem. Soc.*, 88, 1473 (1966).

60. H. M. Bell, C. W. Vanderslice and A. Spehar, *J. Org. Chem.*, 34, 3923 (1969).

61. R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," Second Edition, John Wiley and Sons, Inc., New York, 1968.

62. M. Fetizon and N. Trong, *Bull. Soc. Chim. France*, 3208 (1965); L. A. Paquette, *J. Org. Chem.*, 30, 629 (1965); D. J. Reif and H. O. House, *Org. Syn. Coll. Vol. 4*, 375 (1963); H. Heyman and L. F. Fieser, *J. Amer. Chem. Soc.*, 73, 5252 (1951); R. O. Clinton, R. G. Christiansen, H. C. Neumann, and S. C. Laskowski, *J. Amer. Chem. Soc.*, 79, 6475 (1957).

63. D. Meuche, H. Strauss, and E. Heilbronner, *Helv. Chim. Acta.*, 41, 2220 (1958).