THE SYNTHESIS AND PHOTOCHEMISTRY OF 2,7,7-TRIMETHYL-2, 4-CYCLOHEPTADIENONE AND 2,6,6,7-TETRAMETHYL-2, 4-CYCLOHEPTADIENONE

Thesis for the Degree of Ph. D.
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ANTHONY F. NAPLES
1973

This is to certify that the

thesis entitled

The Synthesis and Photochemistry of 2,7,7-Trimethyl-2,4-Cycloheptadienone and 2,6,6,7-Tetramethyl-2,4-Cycloheptadienone

presented by

Anthony F. Naples

has been accepted towards fulfillment
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Harold Hart
Major professor

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ABSTRACT

THE SYNTHESIS AND PHOTOCHEMISTRY OF

2,7,7-TRIMETHYL-2,4-CYCLOHEPTADIENONE

AND

2,6,6,7-TETRAMETHYL-2,4-CYCLOHEPTADIENONE

By

Anthony F. Naples

This thesis describes the synthesis and photochemistry in various media of 2,7,7-trimethyl-2,4-cycloheptadienone (14) and 2,6,6,7-tetramethyl-2,4-cycloheptadienone (19).

Compound 14 was synthesized from cycloheptanone in approximately 10% overall yield. Irradiation in cyclohexane of the $n\pi^*$ band (350 nm) gave a trace amount of 1,3,3-trimethylbicyclo[3.2.0]hept-6-en-2-one (15a) as the only volatile product. Irradiation through Pyrex in cyclohexane or TFE solution gave, in addition to 15a and its photoisomer 3,3,6-trimethylbicyclo[3.2.1]hept-6-en-2-one (15b), 2,5,5-trimethyl-4-vinyl-2-cyclopentenone (16) as the major product. Compound 16 arises from a rearrangement previously unobserved with any other cycloheptadienone. The excited state of 14 from which this major product arises is undoubtedly $\pi\pi^*$, since irradiation (>330 nm) of protonated 14 ($14\text{-}H^+$)

in FSO_3H solution gave 16-H^+ as the exclusive photoproduct.

Compound 19 was synthesized from eucarvone (4) in about 35% yield by reacting 4 with methyl iodide in THF using lithium bis(trimethylsilyl) amide (LiHMDS) as the base. Preferential excitation of the $n\pi^*$ band (350 nm) of 19 gave 1,3,4,4-tetramethylbicyclo[3.2.0]hept-6-en-2-one as the exclusive product. Photolysis of 19 in cyclohexane using 3000 Å light resulted in the formation of cis and trans - 2,5-dimethyl-4-(2-methyl-1-propenyl)-2-cyclopentenones 22 and 23 respectively in addition to 21. Compounds 22 and 23 are clearly analogous to 16 and are considered to arise via a $\pi\pi^*$ excited state of 19. When the solvent was changed to the highly polar 1,1,1-trifluoroethanol (TFE), the photolysis of 19 through Pyrex gave 2,4,7,7-tetramethylbicyclo-[4.1.0]hept-4-en-3-one (24) as the major product, in addition to 21, 22, 23 and secondary photolysis products. That 24 also arises from a $\pi\pi^*$ excited state of 19 was demonstrated by irradiation of 19-H^+ (in FSO_3H), which can only react via a $\pi\pi^*$ state. Under these conditions 24-H^+ was the exclusive product.

Compound 21 undergoes the familiar photochemical 1,3-acyl shift when irradiated through Pyrex in TFE to give 3,4,4,6-tetramethylbicyclo-[3.2.0]hept-6-en-2-one (34) apparently via an $n\pi^*$ singlet excited state. However, irradiation of 21 in cyclohexane resulted in a triplet reaction to 1,4,5,5-tetramethyltricyclo[4.1.0.$0^{2,7}$]heptan-3-one (36).

THE SYNTHESIS AND PHOTOCHEMISTRY OF 2,7,7-TRIMETHYL-2,4-CYCLOHEPTADIENONE AND 2,6,6,7-TETRAMETHYL-2,4-CYCLOHEPTADIENONE

By

Anthony F. Naples

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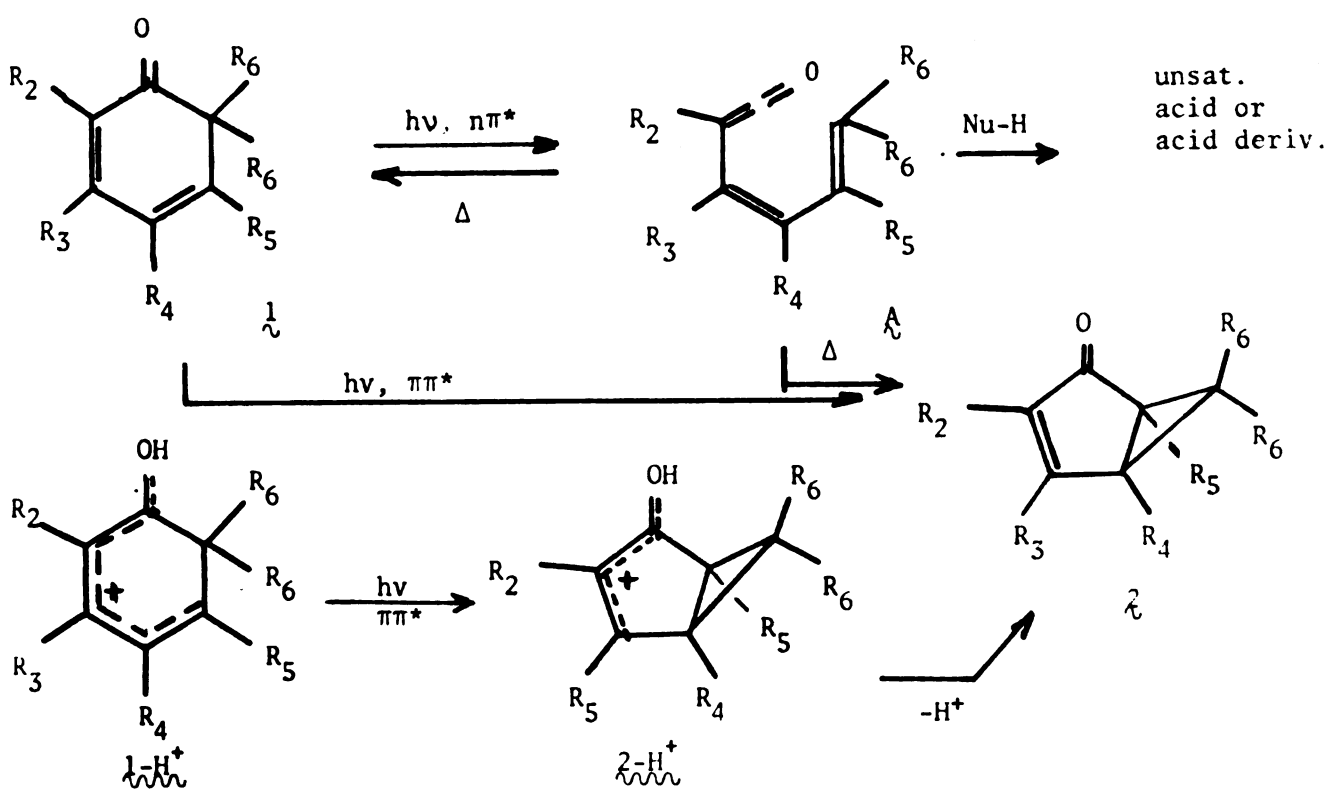
R4


OH
R4

INTRODUCTION

Highly polar media alter the spectra and normal photoisomerization path of 2,4-cyclohexadienones 1.[1] Most conjugated cyclohexadienones show weak $n\pi^*$ absorption at about 350 nm and a much more intense $\pi\pi^*$ band at about 290-310 nm; when irradiated in ether, hexane, methanol or other common solvents, they produce ketenes,[2,3] probably from the $n\pi^*$ singlet state.[3] Depending on the solvent and the substitution pattern, the ketene may recyclize to the starting dienone 1, react with a nucleophile to give unsaturated acids or their derivatives, or in the case of highly substituted ketenes (e.g. $R_2 - R_6 = CH_3$) cyclize via a $(\pi^4_a + \pi^2_a)$ reaction[4] to bicyclo[3.1.0]hexenones 2.



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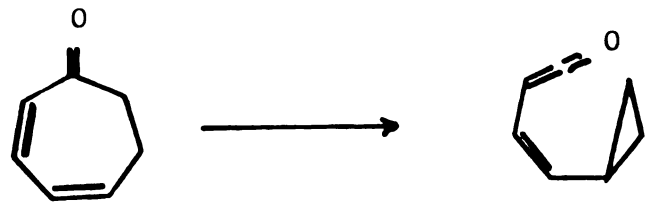
Dissolution of the dienones in trifluoroethanol (TFE) or adsorption on silica gel causes a large (10-40 nm, depending on substituents) bathochromic shift of the $\pi\pi^*$ band. The band also broadens considerably, and because of its greater intensity it usually completely obscures the $n\pi^*$ absorption band. When irradiated under these conditions, the dienones isomerize directly to bicyclo[3.1.0]hexenones via the $\pi\pi^*$ state,[1] rather than to ketenes.

At least two explanations for this phenomenon are plausible. Since the $\pi\pi^*$ state is more polar than the ground state, whereas the reverse is true for the $n\pi^*$ state, polar solvents lower the energy of the former and raise that of the latter.[5] Exceedingly polar solvents such as trifluoroethanol or the silica gel surface may reverse the relative energies of the two states. Whereas ring opening to a ketene occurs from the $n\pi^*$ state,[3] isomerization to the bicyclo[3.1.0]hexenone may be a $\pi\pi^*$ singlet reaction of the dienone. If the $n\pi^*$ and $\pi\pi^*$ states of a molecule are not too far apart in energy (say 50 nm), such reversals by highly polar media may be general, and useful in altering the customary photochemistry of such molecules. Alternatively, trifluoroethanol or silica gel may be functioning as proton donors and one may be witnessing a $\pi\pi^*$ photoisomerization of the protonated dienone $\underset{\sim}{1}\text{-}H^+$ (a hydroxybenzenonium ion). Indeed, protonated dienones (e.g. $R_2 - R_5 = H$, $R_6 = CH_3$ or $R_2 - R_6 = CH_3$) in HSO_3F solution which of necessity react by a $\pi\pi^*$ state give only $\underset{\sim}{2}\text{-}H^+$ upon photolysis.[6]

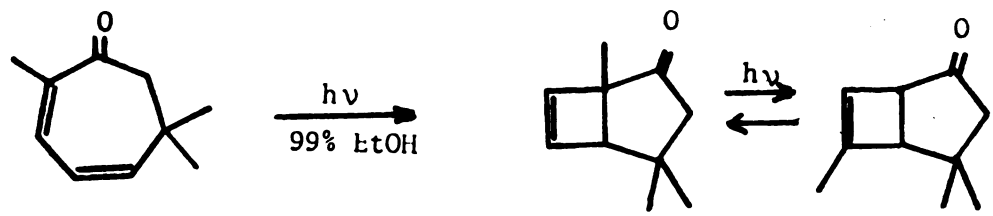
The counterpart of the photoisomerization $\underset{\sim}{1} \rightarrow \underset{\sim}{2}$ could conceivably be realized from 2,4-cycloheptadienones, but in fact no example of the reaction $\underset{\sim}{3} \rightarrow \underset{\sim}{8}$ is known. 2,4-Cycloheptadienones exhibit great



3 B_2

variety in their photochemical behavior depending on the presence and location of substituents, the solvent and the particular excited state from which the reaction occurs.

Eucarvone 4 was the first and most studied compound of this type, because of its accessibility from carvone.[7] Its uv spectrum in cyclohexane has a $\pi\pi^*$ maximum at 298 nm (ε5500) and an $n\pi^*$ maximum at 350 nm (ε40). In polar solvents, the $\pi\pi^*$ band shifts to longer wavelengths as expected (303 nm in EtOH, 310 nm in TFE, and 318 nm for eucarvone adsorbed on silica gel suspended in cyclohexane.[8] In sulfuric acid, where the dienone is fully protonated, this maximum is shifted to 400 nm.[9] Therefore it is not surprising that the product structure depends upon the solvent polarity. The photoisomerization 4→5a studied initially by Büchi and Burgess[10] is historically important, since it was the first example of a photolytic 1,3-acyl migration in β,γ-unsaturated ketones (5a⇄5b). The photoisomerization to 5a is a relatively inefficient process (Φbenzene .0025) which is thought to occur from



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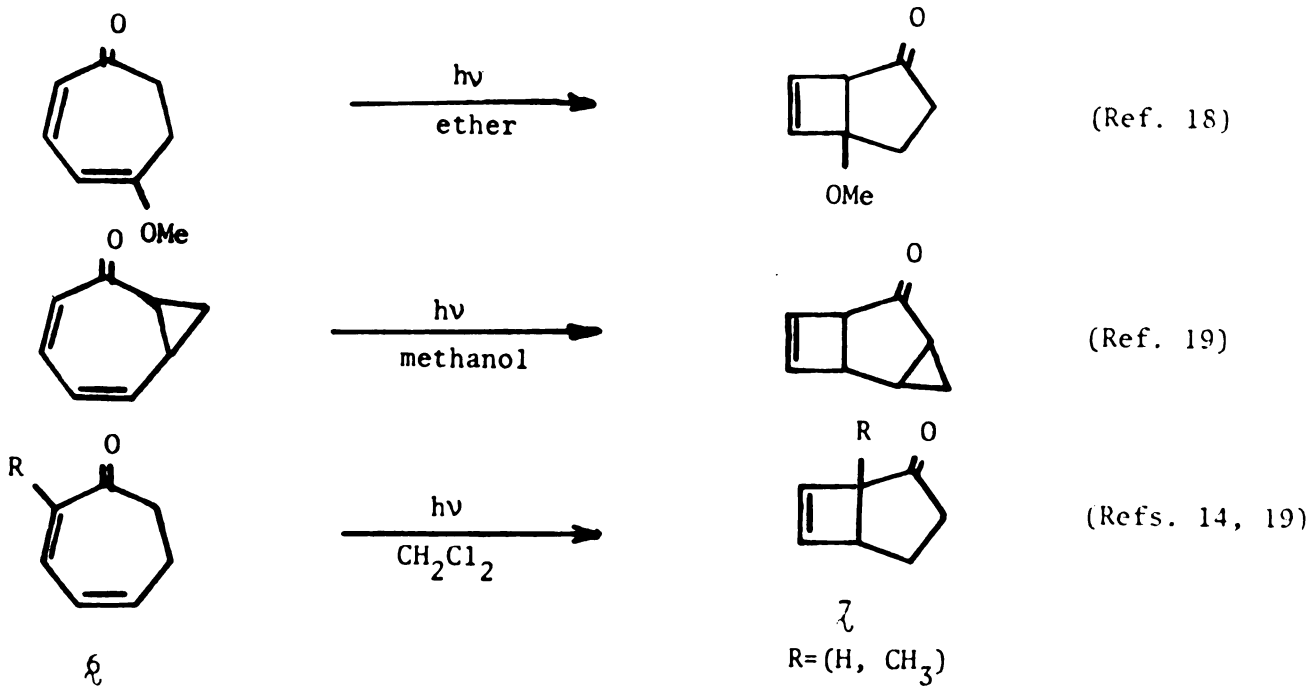
both the singlet and the triplet states[11] of 4. This type of photoisomerization has been observed for several 2,4-cycloheptadienones:



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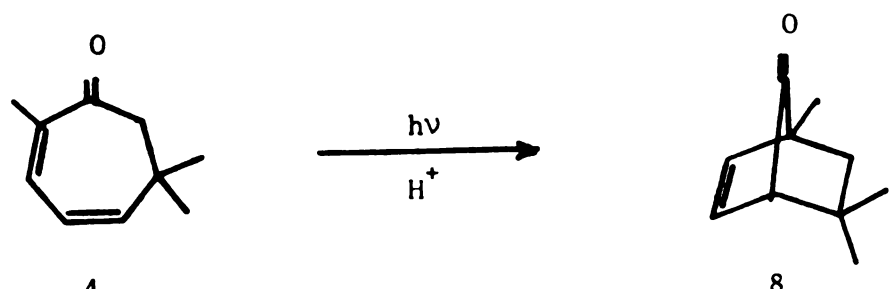
R=(H, CH_3)

A second type of photoisomerization, to the trimethyl 7-norbornenone 8, was observed when eucarvone was irradiated in aqueous acid[12] and in other acidic media[8,9,13].



4 8

Although this type of product is formed in relatively minor amounts from eucarvone, it is the exclusive photoproduct of protonated 2,4-cycloheptadienone or its 2-methyl derivative 6-H^+.[14]

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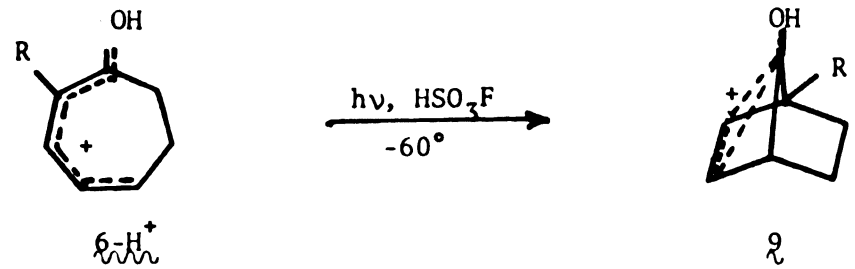
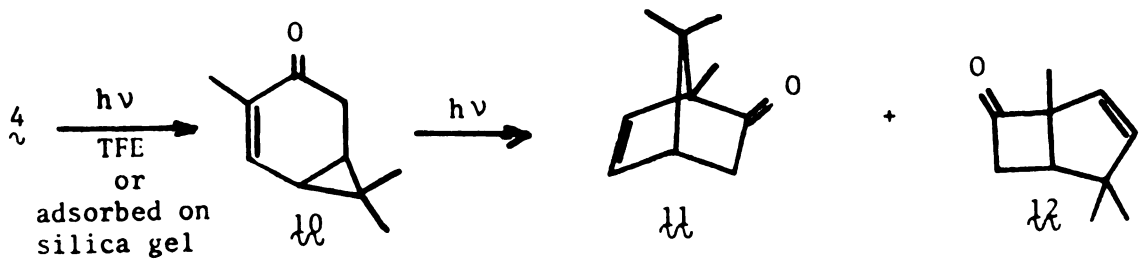


6-H+ 9

A third type of photoisomerism of eucarvone occurs in highly polar solvents, where a major primary product is the bicyclo[4.1.0]hept-2-en-4-one 10.[8] Dehydrocamphor 11[13] and the cyclobutanone 12[8] arise from the photolysis of 10 and have also been detected among the isolable products of the photolysis of eucarvone.



10 11 12

Mechanisms

Quenching and sensitization experiments[11,15] indicate that the formation of bicyclo[3.2.0]hex-6-en-2-ones such as 5a and 7 from 2,4-cycloheptadienones in neutral solvents probably arises from the lowest nπ* singlet and triplet states. Orbital symmetry-allowed disrotatory ring closures could account for the products.

The ππ* process 4→10 (and its protonated analog) is more interesting since it involves cleavage of a carbon-carbon bond beta to the carbonyl group. Since this pathway is favored by polar solvents, it may best be represented by dipolar intermediates (or in the case of the protonated ketones, carbonium ions). This interpretation accounts for

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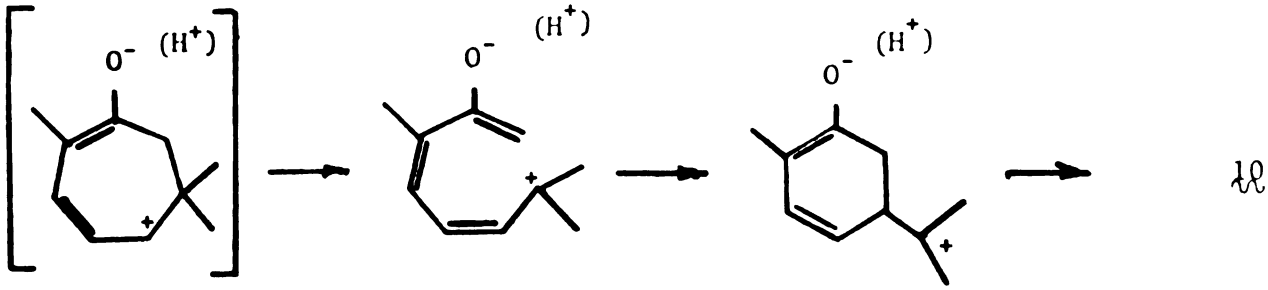
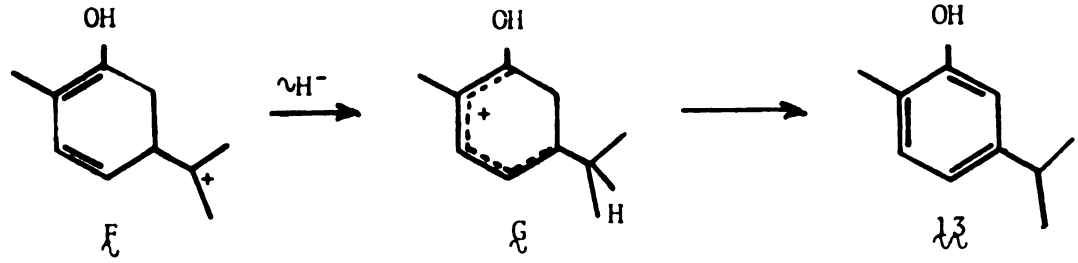
the observed substituent effects more satisfactorily than does the alternative view of the reaction as an allowed $[\sigma 2_a + \pi 2_a]$ concerted reaction.[16] If the $\pi\pi^*$ state is represented as the dipolar structure C, then an electrocyclic ring opening to D can lead to the observed



C D E

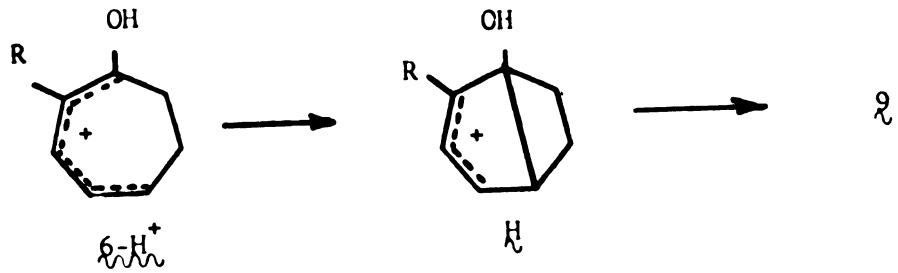
product either directly or through the intermediate E. Since Hine and Childs,[9] in their irradiation of 4-H^+, found the phenol 13 among the



F G 13

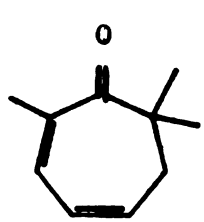
products after quenching, the stepwise path via E seems the more likely.[17] The ion E partitions between the paths which lead to 10 and 13. We recognized early[17] that the formation of 10 (or 10-H^+) through the ring opening of C might be aided by the presence of the gem dimethyl substituents on the carbon bearing positive charge in intermediates such as D and E. It seemed possible that 10 and related products were therefore not necessarily characteristic of all cycloheptadienones, but only of those with such substituents at C6. In fact, it has

recently been observed[14] that the absence of these substituents causes the reaction to take an alternate path.

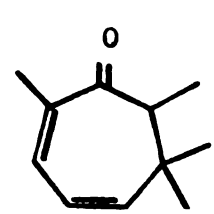


6-H$^+$ H 9

The protonated dienone, reacting from a $\pi\pi^*$ state, undergoes a photochemically allowed ring closure[20] of the pentadienyl cation 6-H$^+$ to the allyl cation H; a thermal 1,2 alkyl shift leads to the observed protonated 7-norbornenone 9. In the case of eucarvone this path (leading to 8) competes rather poorly with the ring opening (to D). It also seemed to us that the ring opening reaction should occur equally well whether the gem dimethyl group is at C6 or C7 in the original dienone since the methyl groups can stabilize the positive charge by being at either end of the heptatrienyl cation. However, since the conversion of D to E should be strongly disfavored if methyls are absent from C6, the ion corresponding to D, but having the methyls at the other end of the carbonium ion system might be expected to react in a different manner. To test these ideas, we synthesized and irradiated 14[17] and 18.[21] Our results are the subject of this thesis.



14



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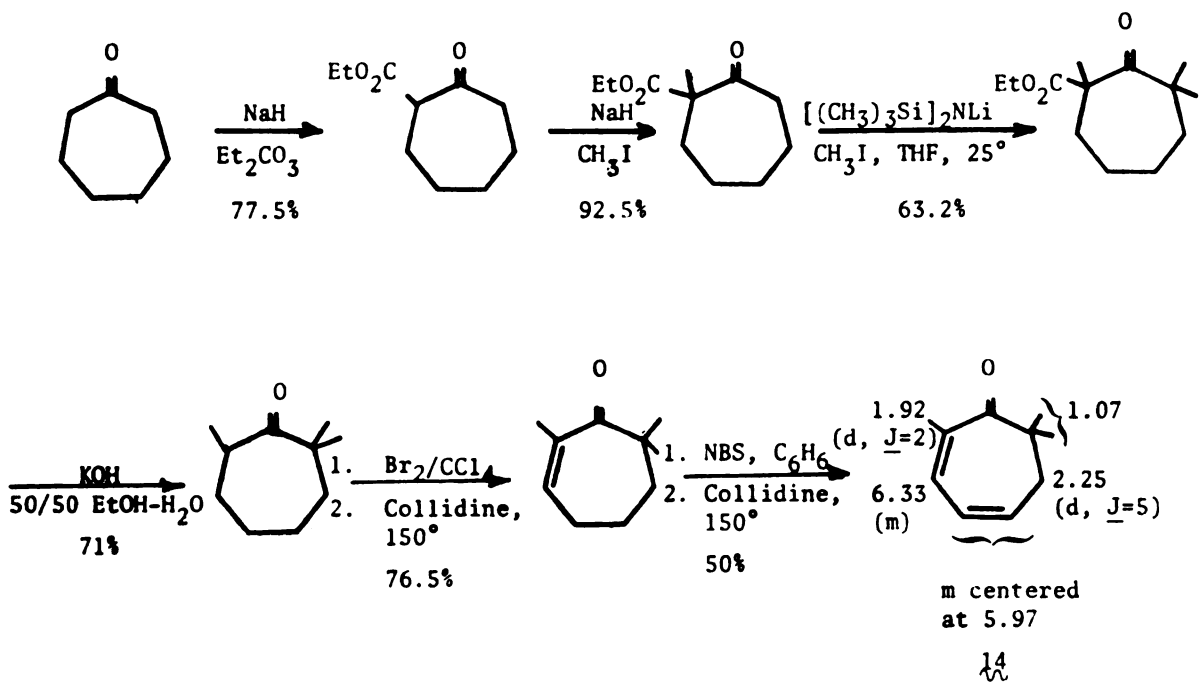
RESULTS AND DISCUSSION

A. The Synthesis and Irradiation of 2,7,7-Trimethyl-2,4-cycloheptadienone, 14.

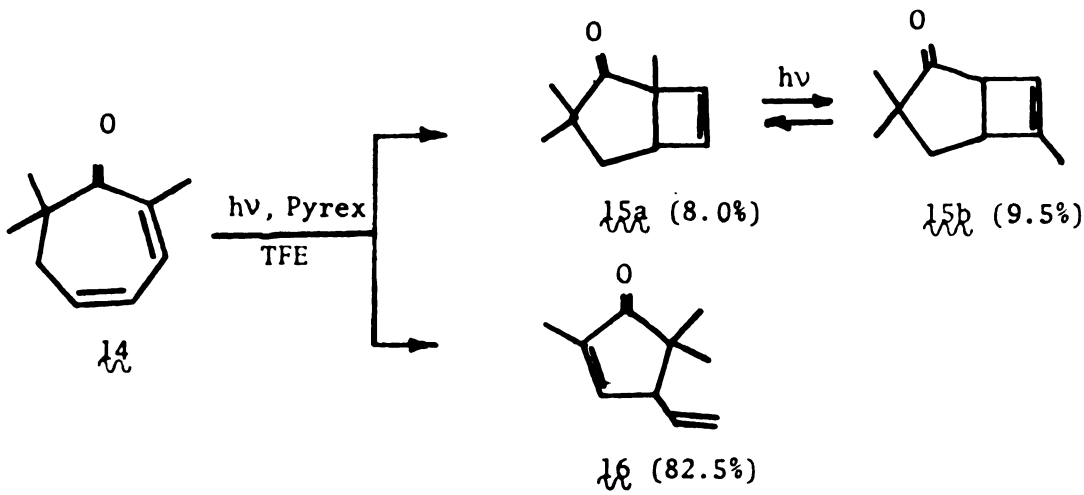
Compound 14 was synthesized from cycloheptanone in about 10% overall yield by the sequence shown. The dienone displayed an nπ* band



($\lambda_{max}^{cyclohexane}$ 350 nm, ε75) as a shoulder of the more intense ππ* absorption at 290 nm (ε5650). In TFE the ππ* band was shifted to longer wavelength (302 nm, ε4650), completely obscuring the nπ* band.

Irradiation of a .01 M solution of 14 in TFE through Pyrex with a Hanovia 450 watt mercury lamp gave a fast and clean (90%) conversion to three photoproducts, 15a (8.0%), 16 (82.5%), and 15b (9.5%). In cyclohexane, under identical photolysis conditions, the reaction gave 27% 15a, 66% 16 and 7% 15b. It is noteworthy that no α cleavage occurs with 14 despite the fact that one can envisage several plausible reaction

products from such a reaction path. The photoproducts and starting

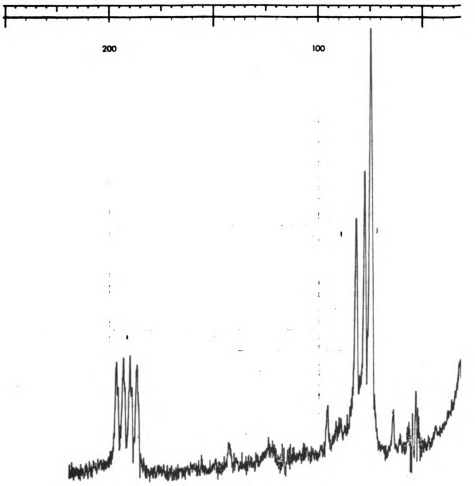


dienone were stable to heat. Therefore, vapor phase chromatography (vpc) was used to monitor the reaction and to separate the products for analysis.

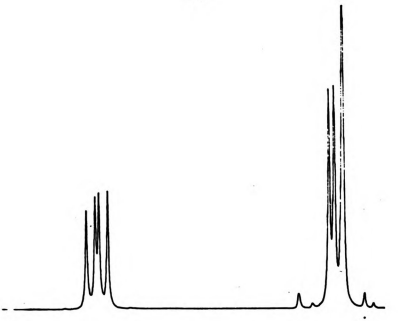
1,3,3-Trimethylbicyclo[3.2.0]hept-6-en-2-one, 15a had the shortest retention time of the four compounds and its mass spectrum (M=150) showed that it was an isomer of 14. The ir spectrum (CCl_4) showed carbonyl absorption at 1722 cm^{-1}, characteristic of a cyclopentanone. The nmr spectrum revealed three 3H singlets (δ1.03, 1.22, 1.27) having high and approximately equal europium shift numbers (methyls α to the carbonyl group). The two vinyl proton doublets (J=6.0) at δ6.38 and 6.12 were characteristic of C6 and C7 protons respectively in a bicyclo[3.2.0]hept-6-en-2-one system.[22] The C6 proton doublet had the smallest shift number in the spectrum and showed additional coupling ($J\tilde{}$1) with the C5 proton. The C5 proton appeared at δ2.95 as a quartet or doublet of doublets due to coupling (J=6.5, J'=3.5) with the geminal protons at C4. Each peak of this quartet was split further into a doublet due to a small (J=1) interaction with the C6 vinyl proton. The C4 geminal protons gave rise to a complex pattern of 5 apparent

lines between δ1.60 and δ2.10, which was not satisfactorily simplified by spin decoupling with the C5 proton. However, a computer simulation (Figure 1b) of the ABX system formed by the C4 and C5 protons gave a close approximation of the observed (Figure 1a) 100 MHz spectrum. The simulated spectrum showed 8 lines for the C4 geminal protons. Two of these lines overlapped to give the peak of highest intensity. Further details are included in the experimental section of this thesis.

3,3,6-Trimethylbicyclo[3.2.0]hept-6-en-2-one, 15b had the longest retention time of the photoproducts. The mass spectrum (M=150) showed that it was an isomer of 14. The ir spectrum (CCl_4) displayed a carbonyl band at 1722 cm^{-1} (cyclopentanone). The nmr spectrum showed two 3H singlets of a gem dimethyl group (δ1.00 and 1.15) having high and approximately equal shift numbers (alpha to a carbonyl function). The third methyl appeared as a 3H multiplet at δ1.75 (allylic) having the lowest shift number in the spectrum, which suggested its location at C6. The C1 alpha proton (δ3.15, m) had the largest shift number in the spectrum. Also observed was a 1H vinyl multiplet at δ5.80, a 1H C5 proton signal (≈q, $\underline{J}$≈5) at δ3.13, and a sharp doublet for the C3 protons which were unexpectedly equivalent and were coupled to the C5 proton ($\underline{J}$=5). Spin decoupling of a 100 MHz spectrum verified the interaction between the C5 and C3 protons. Compound 15a is undoubtedly formed from 14 via the well known photoisomerization first reported for eucarvone, (4)[10] and later for other 2,4-cycloheptadienones.[14,18,19] In addition to the spectral data for 15a and 15b further evidence for their assigned structures was obtained from their facile interconversion via a photochemical 1,3-acyl shift. Thus, irradiation of 15a in cyclohexane or TFE gave mixtures of 15a and 15b whose compositions



(a)



(b)

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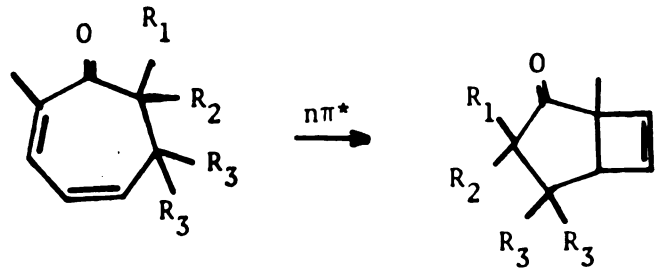
became constant after the times indicated in the experimental portion of this thesis. The photostationary state for the reaction in TFE (47% 15a, 53% 15b) was established in about 1/3 the time necessary for a similar state to be reached in cyclohexane. In the latter case, a steady state ratio of 68% 15a to 32% 15b was established. As pointed out by Büchi, the relative amounts of the two photoisomers obtained in this reaction reflect merely the absorbances of the two compounds at the wavelength of incident light and not their relative thermodynamic stabilities. Therefore, although the uv spectra of 15a and 15b were not examined, the observed change in product ratio with solvent polarity was not unexpected.

The exact nature of the excited state(s) of 14 from which 15a arises is still unclear. Attempts to isolate the $n\pi^*$ band by irradiating 14 in cyclohexane through a Corning #3718 uranium glass filter (>330 nm) have thus far been only partially successful. Irradiation at such wavelengths would be expected to cause preferential excitation of the $n\pi^*$ band at 350 nm while eliminating reactions that result from $\pi\pi^*$ excitation. The main reaction, however, appeared to be the formation of nonvolatile material. A single volatile product having the same retention time as 15a did appear in the vpc chromatograms of the photolysis mixture. Its formation accounted for about 1% of the converted starting material. Similar experiments with 4 and its methyl analog 19 were much more successful. Thus, only 5a and 21 were obtained from 4 and 19 respectively when each was irradiated in cyclohexane with wavelengths longer than 330 nm (vide infra). These reactions were considerably slower than the corresponding reactions



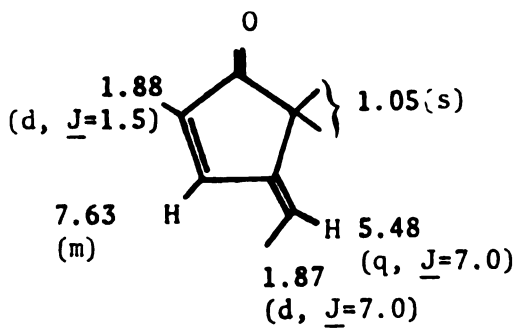
14	$R_1=R_2=CH_3$, $R_3=H$	15a	$R_1=R_2=CH_3$, $R_3=H$
4	$R_1=R_2=H$, $R_3=CH_3$	5a	$R_1=R_2=H$, $R_3=CH_3$
19	$R_1=H$, $R_2=R_3=CH_3$	21	$R_1=H$, $R_2=R_3=CH_3$

through Pyrex due to the decreased light intensity.

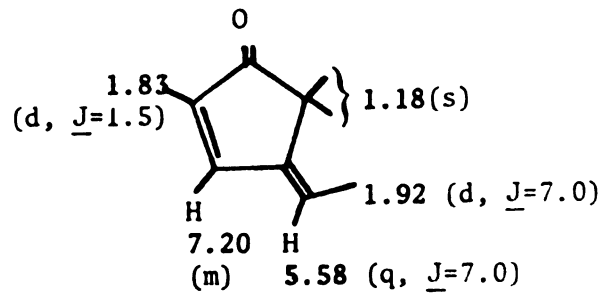
The photoproduct of 14 which deserves the greatest interest was 2,5,5-trimethyl-4-vinylcyclopent-2-enone (16) which resulted from a rearrangement previously unobserved with any other cycloheptadienone. It had the second longest retention time of the photoproducts (appearing between 15a and 15b) and its mass spectrum (M=150) showed that it was also an isomer of 14. The ir spectrum (CCl_4) showed absorption at 1705, 1640 (cyclopentenone) and 930 cm^{-1} (terminal methylene). The uv spectrum (cyclohexane) with maxima at 344 nm (ε45), 330 (60), 317 (50) and 225 (9,370) was indicative of an α,β-unsaturated ketone. In the nmr spectrum, the gem dimethyl singlets appeared at δ.87 and 1.07 while the third methyl group was seen as a doublet of doublets at δ1.75 due to coupling with the C3 (J=1.8) and C4 (J=2.5) protons. The C4 proton resonance at δ3.03 was a doublet (J=8.0) due to coupling with the adjacent proton of the C4 vinyl group. Each peak of this doublet was split further into a quintet as a result of interaction with the C3 vinyl proton (J=2.5) and with the protons of the methyl group at C2 (J=2.5). The low field position of the C3 vinyl proton

(δ6.98) suggested its location on the β carbon of an α,β-unsaturated ketone system. The remaining three vinyl protons of the C4 vinyl group gave rise to a complex group of signals between δ4.60 and δ6.00 corresponding to an ABC system further perturbed by the adjacent C4 proton. The splittings given above were verified by decoupling.

Treatment of 16 with base (a 5-fold excess of $NaOCH_3$ in methanol) caused isomerization to the fully conjugated dienones 17a and 17b. After three hours at room temperature, only 17a was formed but 25 hours at reflux gave a mixture of the two isomers with 17b predominating (52:48).



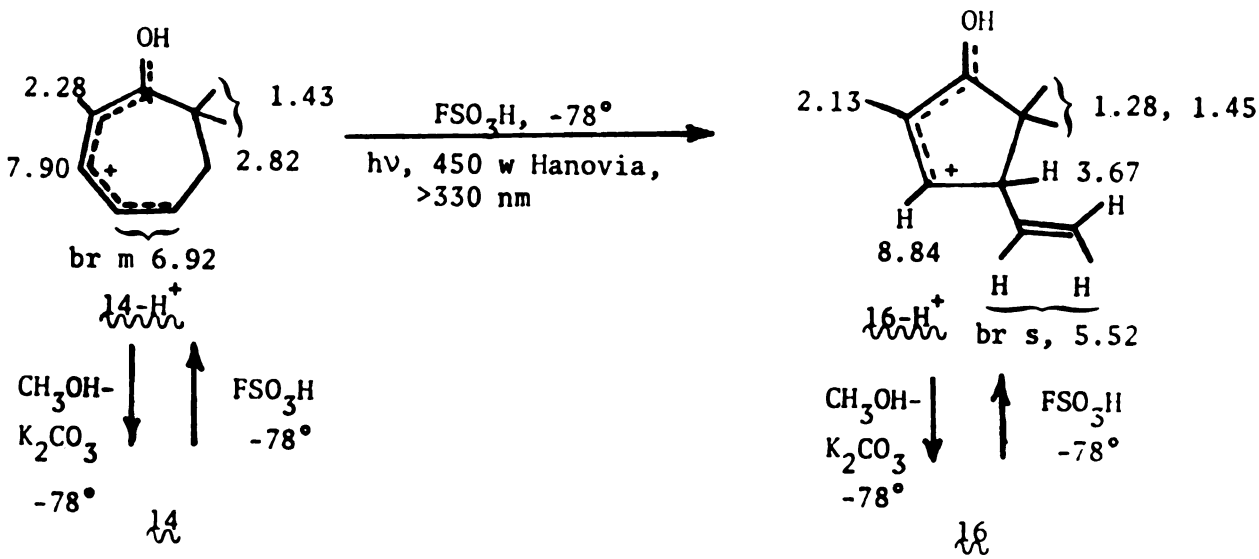
17b



17a

Geometry is tentatively assigned on the basis of observations that (a) the chemical shifts of the C3 vinyl protons differ as expected,[23] and (b) interaction between the gem dimethyls at C5 with the ethylidene methyl should make 17b the thermodynamically more stable isomer. The mass spectra of the isomers (M=150) showed that they were isomeric with 16. The ir spectra of the neat liquids (1698, 1610 cm^{-1}) and uv spectra [$\lambda_{max}^{cyclohexane}$ 355 nm (ε60), 340 (90), 328 (90), 288 (14,300), 277 (22,600), 268 (16,400) for 17a and 369 (60), 350 (94), 336 (100), 298 (8,100), 285 (12,800), 276 (11,550) for 17b] show that the exocyclic double bond in 16 has moved into full conjugation in 17.

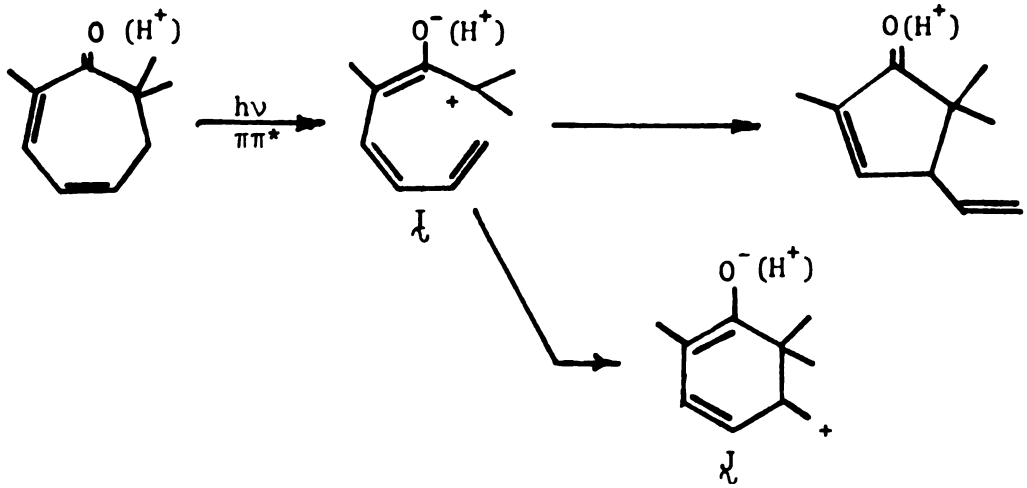
Since its formation is favored in polar solvents, the vinylcyclopentenone 16 is thought to arise from a ππ* state of 14. To test this possibility, 14-H$^+$, which can only react via a ππ* state, was irradiated in FSO_3H at -78° using a 450 watt Hanovia mercury lamp with a Corning #3718 filter. Under these conditions, the long wavelength band of 14-H$^+$ ($\lambda_{max}^{H_2SO_4}$ 399 nm ε4730) was preferentially excited, resulting in a clean isomerization to one product 16-H$^+$.



The photoproduct was identified by its nmr spectrum (-46°) in the FSO_3H photolysis mixture and by quenching the cation product in a methanol-carbonate suspension at -78°, which gave 16 in about 50% isolated yield (based on the amount of 14 used in the experiment). A 90% conversion of 14 was observed upon quenching of the photolysis mixture after 6 hours of irradiation and subsequent examination of the crude product by nmr. The relative yield of 16 was approximately 75%. The remaining 25% of the product mixture consisted of 17a, 17b and 18. However, the relative amounts of these minor products is not precisely known and further investigation of this matter is in progress.

Reprotonation of 16 by the method described gave back 16-H^+.

The structure of 18 is yet unknown. However, 18 (like 17a and 17b) is undoubtedly formed by an acid rearrangement of the photoproduct 16. To demonstrate this, 16 was protonated by the method described and kept at -78° for 7 hr. Quenching of this mixture, followed by nmr analysis of the recovered material, revealed a 70% conversion of 16 to 55.5% 17b, 25% 17a and 19.3% 18. It is noteworthy that this experiment, in contrast to the isomerization of 16 in base, gave 17b as the predominant isomer of the 17a - 17b pair. The results can be rationalized using an intermediate such as I (analogous to D). In contrast with D, I



will have the greatest positive charge density at the other end of the unsaturated system because of the different location of the gem dimethyl group. Cyclization to J (analog of D→E) is highly unfavorable because it would lead to a primary cation, whereas cyclopentenone formation encounters no difficulties.

One can generalize these results thus far as follows. In reactions from the ππ* state of 2,4-cycloheptadienones (or their protonated forms), substituents which stabilize a positive charge will favor

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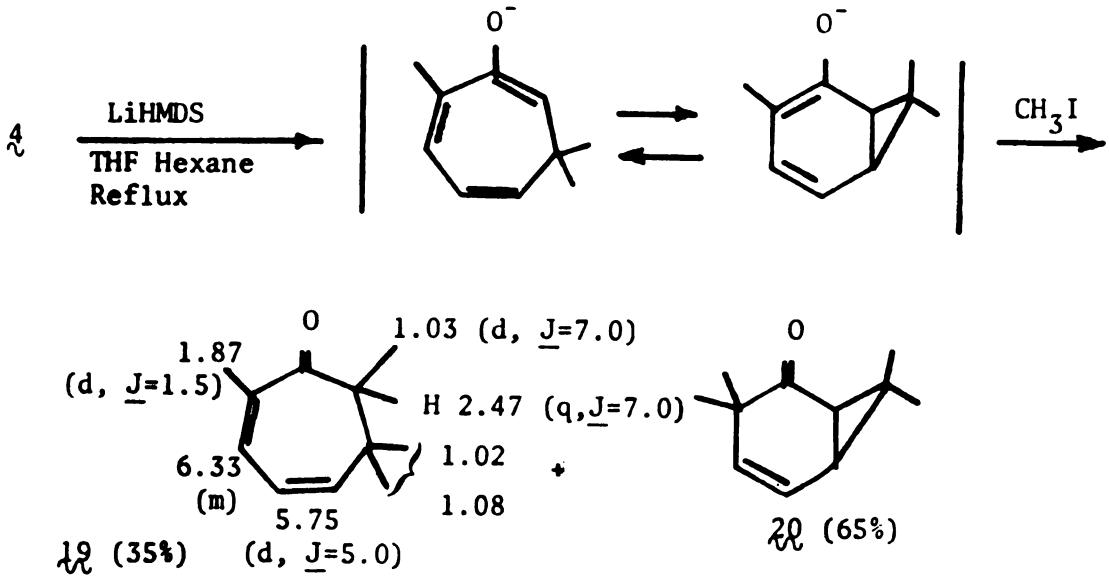
products of the type 10 if located at C6, and of the type 16 if located at C7. To explore the generality of this proposal, 7-methyleucarvone (2,6,6,7-tetramethyl-2,4-cycloheptadienone) was synthesized and irradiated.

B. The Synthesis and Irradiation of 2,6,6,7-Tetramethyl-2,4-cycloheptadienone (19).

Compound 19 was prepared from eucarvone by the method shown below.



The result of this methylation procedure, in which lithium bis(trimethylsilyl)amide (henceforth referred to as LiHMDS) was utilized as the base, was in marked contrast to the results reported by Corey and Burke.[7] Using a different base and solvent system, these workers failed to observe the formation of 19 from eucarvone. While the present work was in progress, a paper describing an alternate synthesis of 19 from

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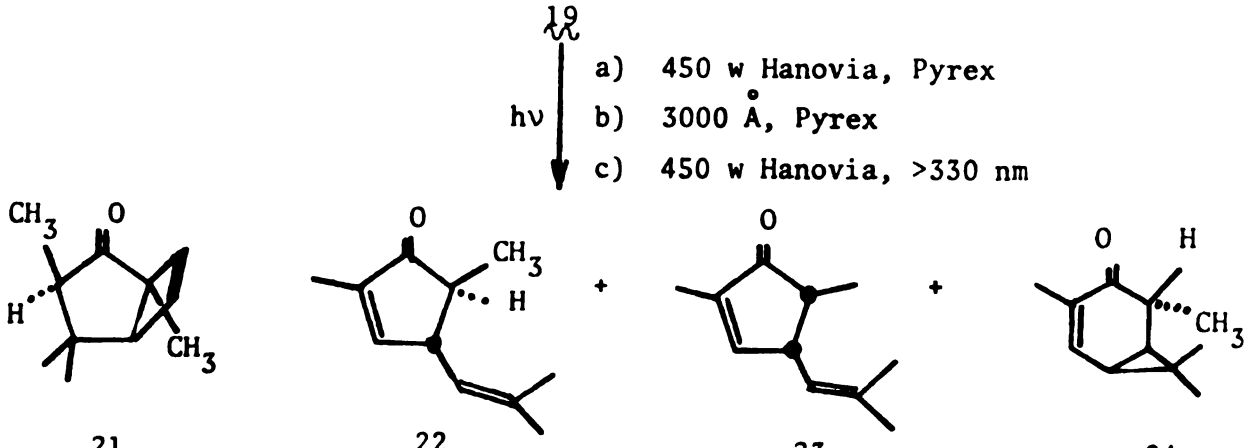
eucarvone appeared in the literature.[24] Like its analogs 4 and 14, 19 displayed an nπ* band ($\lambda_{max}^{cyclohexane}$ 350 nm ε100) as a shoulder of its more intense ππ* band (315 sh (ε4,500), 300 (6,200), 216 sh (5,900)). In TFE the ππ* band was also shifted to longer wavelength (312 (5,600)) and completely obscured the nπ* band. In a nonpolar solvent such as cyclohexane, the photochemistry of 19 displayed much the same behavior toward changes of incident light wavelength as did 14. Thus, irradiation of 19 in cyclohexane through Pyrex using a 450 watt Hanovia mercury lamp gave 91% 21, 3% 22 and 6% 23, whereas a similar photolysis of 19 using a Rayonet reactor with 3000Å lamps gave 38% 21, 8.3% 22 and 48.7% 23. In each case, the reaction was stopped at 50-60% conversion of 19,



	21	22	23	24
a)	91%	3%	6%	--
b)	38%	8.3%	48.7%	5%
c)	100%	--	--	--

at which time the vpc fraction corresponding to the remaining 19 in the photolysis mixture was collected. The nmr spectrum of this fraction

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from the 450 watt lamp photolysis showed that the material was pure 19. A similar spectrum of the fraction from the 3000Å photolysis, however, showed that the sample contained a small amount (<5%) of 24 (vide infra). In addition, traces of the secondary photoproducts arising from 24 were detected in the analytical vpc chromatogram of the 3000Å photolysis mixture. In neither the 450 watt lamp nor 3000Å photolysis did this starting material fraction show the presence of compound 35, a secondary photoproduct arising from 21 (vide infra).

Since the relative yield of 21 was nearly doubled when the incident light was polychromatic above the Pyrex cutoff (≈280 nm), an $n\pi^*$ reaction was implicated in the formation of this product. This supposition was verified upon irradiation of a cyclohexane solution of 19 with a 450 watt lamp through a Corning #3718 uranium glass filter, whence the exclusive product was 21 after 95% conversion of the dienone. By analogy, 21 is presumed to be formed via the same mechanism that gives rise to 5a and 15a. Only one of the two possible epimers of 21 was obtained from the photolyses of 19 or from direct synthesis of 21 from 5a. The tentatively assigned structure(s) for compound 21 shown on page 18 was arrived at by a circuitous route and resulted in some chemistry that has little to do with the main topic of this thesis. For this reason, the evidence for structure 21 and the related work are presented in Part C of this portion of the thesis.

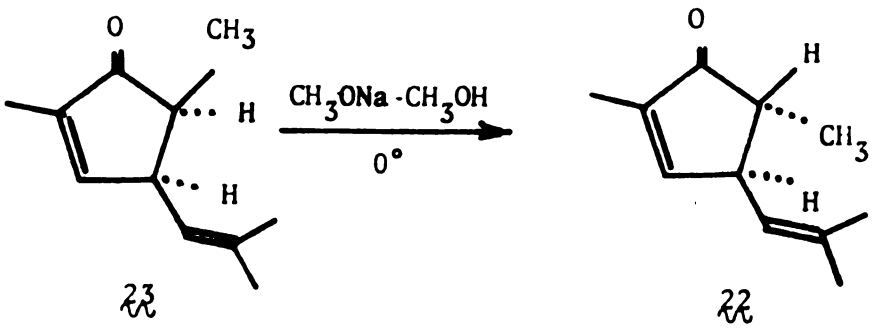
Trans-2,5-dimethyl-4-(2-methyl-1-propenyl)-2-cyclopentenone (22) and cis-2,5-dimethyl-4-(2-methyl-1-propenyl)-2-cyclopentenone (23) are clearly analogous to 16 in structure and in the mechanism by which they are formed. The mass spectra of the two isomers showed (M=164) that they were both isomeric with 19. Compound 22 displayed bands in

the infrared (neat) at 1700, 1665 (w) and 1640 (w) cm^{-1} and uv (cyclohexane) maxima at 356 nm (ε16), 342 (40), 328 (52), 316 (48) and 219 (9,800) indicating a conjugated cyclopentenone with an α-alkyl substituent. The calculated wavelength for the most intense maximum was 217 nm with solvent correction. In the nmr spectrum, the C5 methyl doublet ($\underline{J}$=7.5) at δ1.18 had the highest shift number of the four methyl signals present. The three remaining methyls were allylic (chemical shift). The C2 methyl with a slightly smaller europium shift number appeared at δ1.77 as a triplet ($\underline{J}$=2) apparently through coupling with the C3 and C4 protons, while the butylidene methyl doublets at δ1.72 had the lowest shift numbers in the spectrum and were coupled equally ($\underline{J}$=1.5) with the butylidene proton. The C5 proton at δ1.90 had the largest shift number in the spectrum and appeared as a quartet of doublets due to coupling with the protons of the C5 methyl ($\underline{J}$=7.5) and with the C4 proton ($\underline{J}$=3.0). The C4 proton at δ3.12 had the appearance of a doublet (large coupling ($\underline{J}$=9.5) with the butylidene proton) which was broadened by interactions with the C3, C5 and butylidene protons. Finally, the spectrum showed two vinyl protons, i.e. the butylidene proton doublet ($\underline{J}$=9.5) at δ4.93 and the C3 vinyl proton multiplet at δ6.98.

The spectra of 23 were quite similar to the above with ir (CCl_4) absorptions at 1700, 1665 (w) and 1640 (w) cm^{-1} and uv (cyclohexane) maxima at 358 (ε16), 342 (42), 327 (68), 315 (116), 281 (200) and 219 (9000). As in 22, these data are consistent with a conjugated cyclopentenone with an α methyl substituent. The nmr spectrum showed a C5 methyl doublet having the highest shift number of the methyls. The remaining three methyls were allylic. The C2 methyl had a slightly smaller shift number than the one at C5 and appeared at δ1.78 as a

triplet (J=1.5) due to coupling with the C3 and C4 protons, while the butylidene methyl doublets at δ1.73 had the lowest shift numbers in the spectrum and were coupled equally (J=1.5) with the butylidene proton. The C5 proton, having the largest shift number in the spectrum, appeared at δ2.43 as a quintet (J=7.5), with apparently equal interactions with the C4 and C5 methyl protons. The C4 proton signal had the appearance of a broad triplet (J≈7-10). The spectrum showed two vinyl protons, i.e. the butylidene proton doublet (J=10.0) with each peak split into a septet (J=1.5) due to further coupling with the butylidene methyls and, lastly, the multiplet (J=1.5) for the C3 proton at δ6.92. The splittings for 3 were verified by decoupling of a 100 MHz spectrum.

Spectral and chemical evidence were used to assign the C5 geometry in the two epimers, 22 and 23. The C4H-C5H coupling constants (7.5 Hz for 23 and 3.0 for 22) are in agreement with the dihedral angles (≈0° and ≈120° respectively) observed in models of the two epimers.

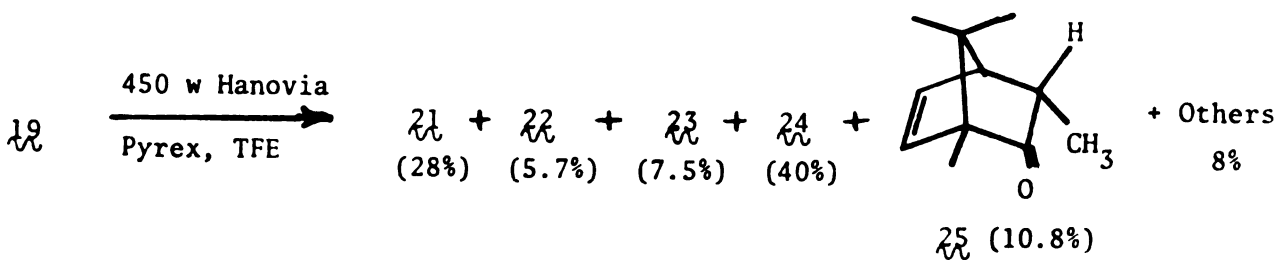


23 22

In addition, 23 was quantitatively converted to 22 in sodium methoxide-methanol at 0°, using conditions which did not bring the double bonds into conjugation. This result is quite reasonable considering the expected greater thermodynamic stability of 22.

Given the observations on eucarvone, it was not surprising that

the methyl analog 19 also displayed a marked alteration in photochemistry with increasing solvent polarity. Thus, when a .06 M solution of 19 in TFE was irradiated through Pyrex, the formation of 2,4,7,7-Tetramethylbicyclo[4.1.0]hept-4-ene-3-one (24) which had been obtained only in trace amounts in cyclohexane now accounted for nearly 60% of the reaction products. In addition, the rate of disappearance of the starting material was greatly accelerated (relative to the cyclohexane reaction), giving an 85% conversion in 1 hour. The bicyclic enone 24

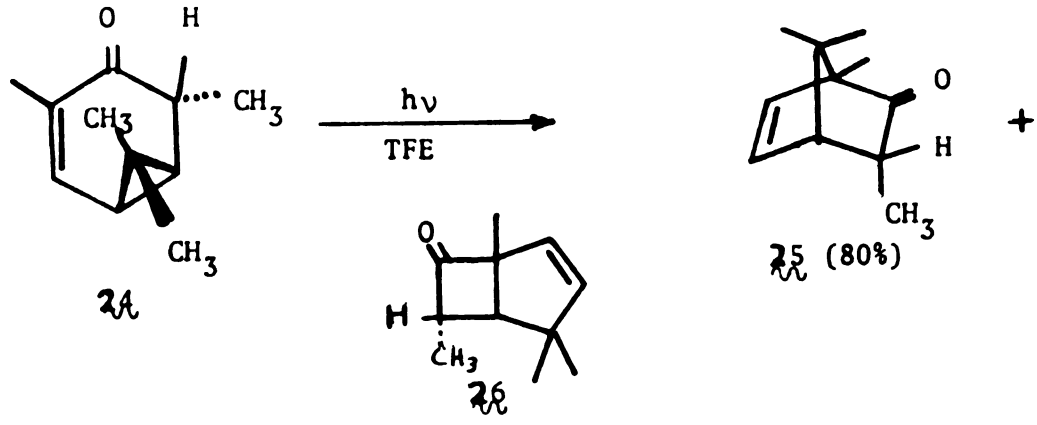


is the methyl analog of 10. All photoproducts were separable from the starting material by preparative vpc except 24. Identical retention times were recorded for 19 and 24; however, pure samples of 24 were obtained for analysis from another route (vide infra). The ir spectrum of 24 showed carbonyl absorption at 1660 cm^{-1} and the uv (cyclohexane) spectrum had maxima at 346 nm (ε88), 317 sh (270), 268 (3,700) and 244 (4,660), consistent with an α,β-unsaturated ketone having additional conjugation with a cyclopropane ring. The mass spectrum (M=164) showed that 24 was an isomer of 19. The nmr spectrum revealed a single vinyl proton at low field (δ6.72), probably at the end of an α,β-unsaturated ketone system. This signal appeared as a doublet (J=5.5) of quartets (J=1.5) due to coupling with the C6 proton and allylic methyl protons

respectively. Of the gem dimethyl singlets, the one at δ1.22 had the lower shift number (lowest in the spectrum) and was assigned exo stereochemistry. The endo methyl singlet appeared at high field (δ.80), being directly over the π system. The spectrum showed two additional methyl signals, one allylic (δ1.45, d, J=1.5) and the other at C2 (δ1.15, d, J=7.5) with exo stereochemistry. The C2 proton had the largest shift number and appeared as a quartet (J=7.5) broadened by further slight coupling with the C1 proton. The signals of the two cyclopropyl protons, which could not be adequately shifted from the methyls, appeared in the δ.90-1.50 region of the spectrum. The exo geometry assigned to the C2 methyl group has not been verified by comparison with the corresponding endo isomer, since an attempt to epimerize 24 in base (≈5-fold excess of $NaOCH_3$ in methanol) at 25° resulted in rapid decomposition to tarry material. Examination of a model of 24 in a preferred conformation (π system approximately planar) reveals a dihedral angle of about 90° between the C1 and C2 protons. A model of the endo isomer of 24 shows this angle to be about 60° which would also give rise to a very small coupling constant for the C1-C2 proton interaction. However, in the endo model, the C2 and C7 endo methyl groups experience serious crowding that would make this epimer an unlikely choice for the structure of 24.

Although quantitative measurements were not performed, it is clear that 24 is photolytically labile with its maximum concentration occurring at about 60% conversion of 19 in the preceding photolysis. At 85% conversion of 19, 24 was itself about half converted to endo-1,3,7,7-tetramethylbicyclo[2.2.1]hept-5-en-2-one 25 and two minor products of shorter retention time. The minor products, formed in an approximately

1:1 molar ratio, accounted for a total of 8% of the product yield of the TFE photolysis of 19 and were left unidentified. That 25 is a secondary product arising from 24[25] (an example of the photochemical vinylcyclopropane-cyclopentene rearrangement)[26] was confirmed by the observation that 25 was not formed in the photolysis of 19 in cyclohexane.[27] Also, irradiation of a solution of 24 in TFE through Pyrex



resulted in a rapid conversion to 25 (80%) and two minor products (≈10% each) having retention times identical to the minor products mentioned above in the TFE photolysis of 19. One of these unidentified products could be 26, resulting from the alternative vinylcyclopropane-cyclopentene rearrangement pathway. The stereochemistry at C3 in 25 was assigned with the assumption that this center (C2 in 24) is not altered during the transformation of 24 to 25. Although the ir (neat) carbonyl frequency of 25 (1730 cm^{-1}) differed somewhat from the carbonyl absorption of its analog (lacking the C3 methyl group) reported by Schuster, et al.,[13] the uv spectrum ($\lambda_{max}^{cyclohexane}$ 319 nm (ε179), 307 (256), 296 (230), 280 sh (180) and 214 (2,410)) was in good agreement. The structural assignment is based on the nmr spectrum and $Eu(fod)_3$ shift data which appear in the experimental part of this thesis.

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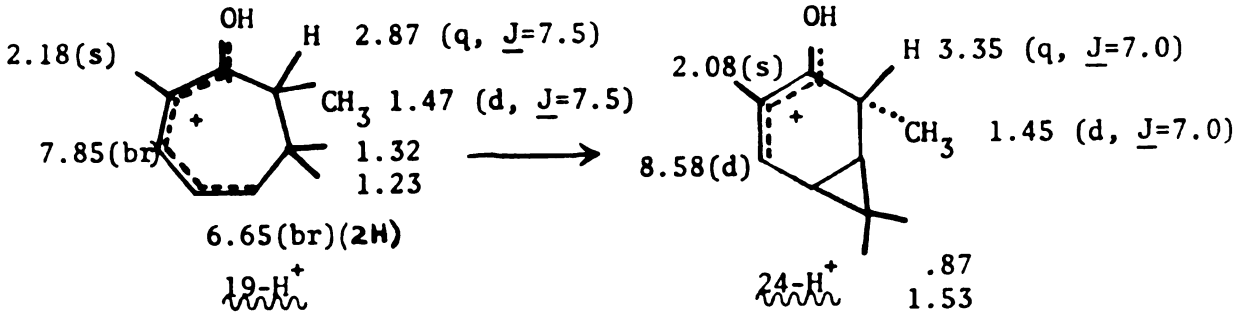
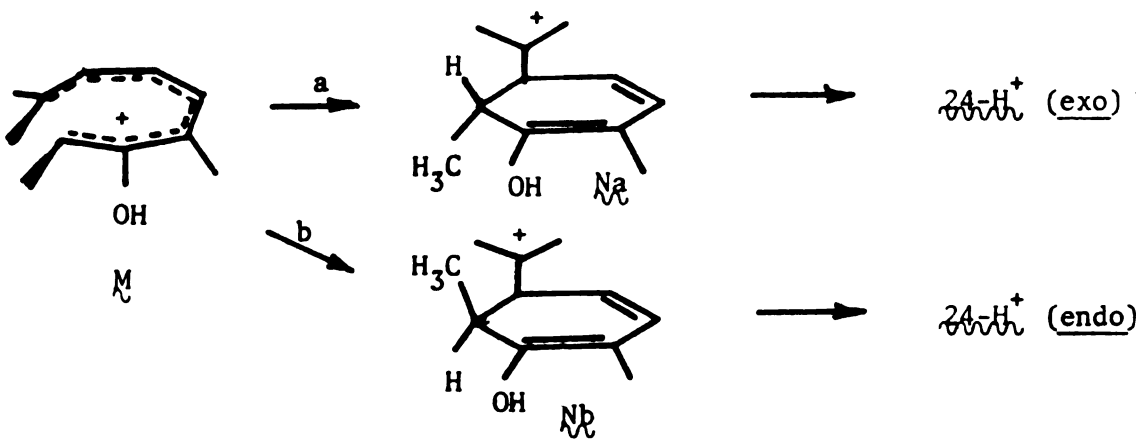
It remained to be shown that 24 is formed via a ππ* excited state of 19. This was demonstrated in the photolysis of protonated 19 (19-H$^+$) which, like 14-H$^+$ and 4-H$^+$, can only react from its ππ* state. Irradiation of the long wavelength band of 19-H$^+$ [$\lambda_{max}^{H_2SO_4}$ 405 nm (ε5,450)] resulted in a clean transformation to 24-H$^+$, the only species observable in the nmr spectrum (-46°) after 6 hours.

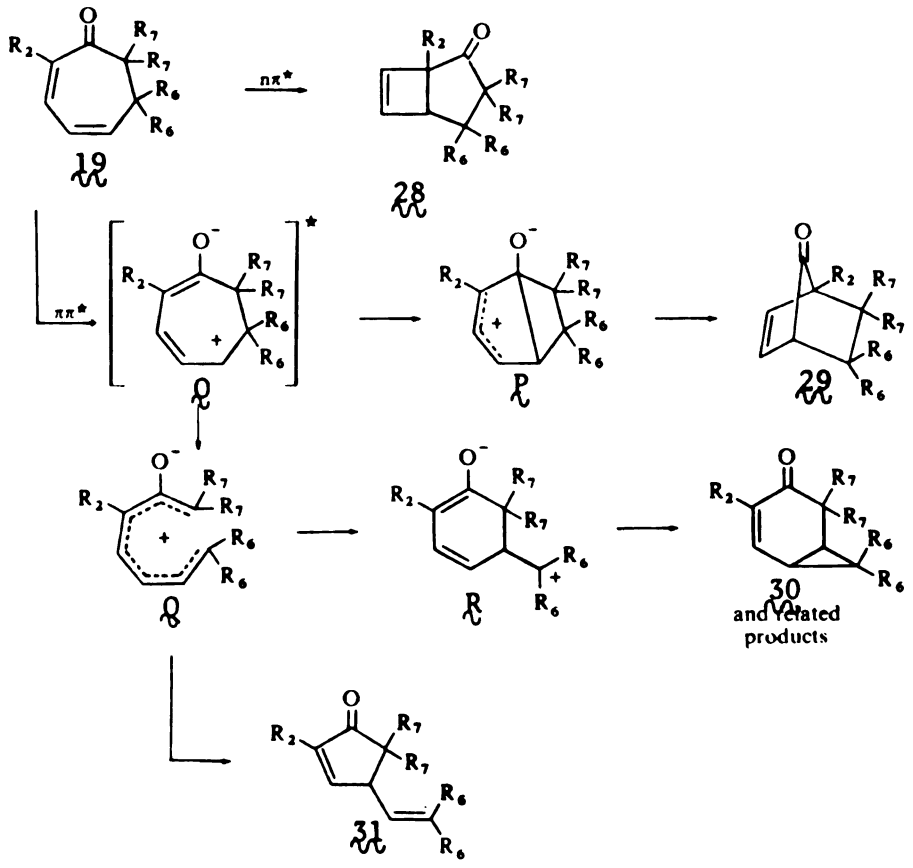


Quenching of the product cation gave pure 24 in good yield. The purity of the product was verified by its nmr spectrum and vpc chromatogram. Reprotonation of 24 gave 24-H$^+$. Experiments showed 19 to be stable in FSO_3H in the absence of irradiation for at least 48 hours at -78°. As noted previously, only one epimer (exo) of 24 was produced from

photolysis of 19 in TFE or cyclohexane. The same result was observed for the reaction in acid, where one would suspect epimerization of the ketone to be more likely. Using the mechanism (invoking intermediates M and N) proposed for the formation of 24 (or $24\text{-}H^+$) it must be concluded that path a in the Figure below is energetically favored over path b, and that structure 24 is indeed the <u>exo</u> form.



In summary, 2,4-cycloheptadienones react photochemically by two paths depending on whether an $n\pi^*$ or $\pi\pi^*$ excited state is produced. The $n\pi^*$ state leads to bicyclo[3.2.0]hex-6-en-2-ones 28, possibly from both singlet and lowest triplet states. The $\pi\pi^*$ state Q (possibly singlet) undergoes one of two electrocyclic processes, depending on the substitution pattern. When neither R_6 nor R_7 are carbonium ion stabilizing groups (e.g. R_6=R_7=H), ring closure followed by an alkyl shift occurs, leading via P to a 7-norbornenone 29. Protonation may be required since such reactions have been observed only in acidic media. When either R_6 or R_7 can stabilize a positive charge, electrocyclic ring opening competes favorably with this path to give Q which



cyclizes to R if the stabilizing substituents are at C6 or to 31 if they are at C7. When substituents are present at both positions, the cyclization of Q is partitioned along both paths apparently according to the degree of substitution at each site. Compounds such as 14 with two methyls at C7 and one methyl, one hydrogen at C6 or one methyl, one hydrogen at both C7 and C6 might be expected to react accordingly, but this prediction remains to be tested experimentally.

The reasons for the significant solvent effect on the partitioning of Q in the case of the cycloheptadienone 19 remain unclear. This question awaits further information on the relative energetics of

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C. The Structural Determination and Photochemistry of 21

One expects a pair of epimeric structures for compound 21 (exo and endo C3 methyl) to be formed from the electrocyclic ring closure of the butadiene moiety in 19. In fact, only one epimer was observed. Of all the photoproducts of 19, 21 had the shortest retention time. The mass spectrum (M=164) showed that 21 was isomeric with 19 and the ir spectrum (1725 cm^{-1} for the neat liquid) and uv spectrum [$\lambda_{max}^{cyclohexane}$ 320 nm (ε108), 309 (156), 299 (133), 290 (94) and 210 (1,700)] were consistent with a bicyclo[3.2.0]hept-6-en-2-one structure.[10] Except for the expected absence of nπ* band fine structure, the uv spectrum of 21 in TFE 300 nm (ε230), 219 (1,100) was similar to the spectrum in cyclohexane. Salient features of the nmr spectrum are shown in Figures 2 and 3 and the complete data appear in the experimental part of this thesis. Nmr data and the chemical evidence that follow are the basis for the assignment of endo stereochemistry about the C3 carbon.

It is noted that the two C3 proton signals in 5a (δ1.77 and 2.85) are over 1 ppm apart with the endo proton presumably at higher field due to its position over the π system of the cyclobutene moiety. Similar values would be expected for the C3 protons in the two epimeric forms of 21. The observed chemical shift (δ2.90) tends to favor an exo orientation for the C3 proton and thus an endo methyl group.

Although 21 underwent rapid exchange of the C3 proton in CH_3OD-CH_3OHa at 25° (to give 21-d), it was impossible to epimerize 21 in

refluxing NaOEt-ethanol or in LiHMDS-THF. In the latter case, enolate formation was assured. Only 21 was recovered, in quantitative yield, after quenching such solutions with cold water or dilute HCl.

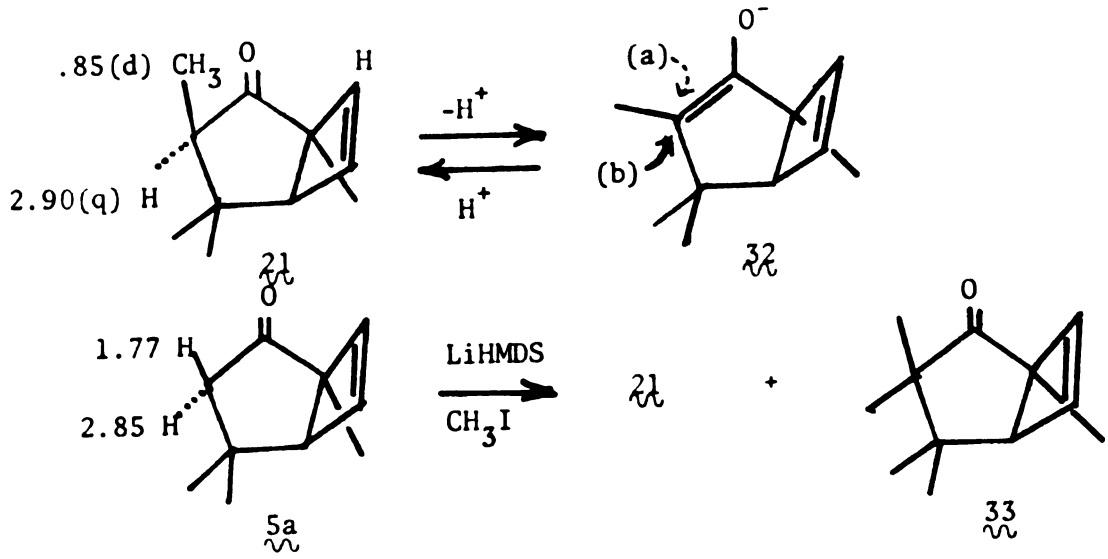

Figure 2

The greater thermodynamic stability of 21 relative to its epimer (in which a serious steric interaction between the C1 and C3 methyls is obvious) could be the determining factor in these observations. Arguments invoking a favored direction of protonation of enolate 32 seem unconvincing. From that standpoint, direction a seems to be favored resulting in the formation of the presumably less stable, exo epimer. If the less stable epimer is formed first, then there must follow a rapid and complete isomerization to the observed product. In a related experiment, 21 was the only monomethylated product of the reaction of 5a with methyl iodide in base. (This constitutes an independent synthesis of 21 and confirms its gross structure.)

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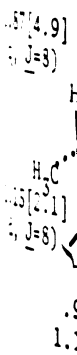
When a .1 M solution of 21 in TFE was irradiated through Pyrex, with a 450 watt Hanovia Lamp, an expected photostationary state between 21 and its photoisomer 34 was reached after 4 hours. At this time, vpc and nmr analysis of the isomer mixture showed a 7:3 ratio of 21 to 34. Compound 34 was epimerized to 35 (partially or completely, depending on column temperature) during all attempts to purify it by vpc. Thus, when the peak corresponding to 34 was collected from a preparative column and re-analyzed using an analytical column at a lower temperature, two peaks of very similar retention time (shoulders of the same peak) were observed. Nmr analysis of the collected fraction showed a mixture of 34 and 35.

It was also observed that both 34 and 35 have approximately the same retention time as 19. For this reason, recovered starting material from the TFE and cyclohexane photolyses of 19 was examined by nmr for the presence of 34 and 35. No evidence for these compounds was obtained from the spectrum, however. This indicates that 19 (and 24 in TFE) was absorbing most of the incident light.

Irradiation of 21 in cyclohexane through Pyrex using either a 450 watt lamp of Rayonet 3000 Å lamps resulted in its rapid and complete transformation to 1,4,5,5-tetramethyltricyclo[4.1.0.$0^{2,7}$]heptan-3-one (36) (Figure 3). The ir spectrum (CCl_4) displayed a carbonyl band at 1705 cm^{-1} and the mass spectrum (M=164) showed that it was an isomer of 21. In the nmr spectrum, one of the four methyl signals present appeared at a considerably lower field (δ1.68, s) than the others, consistent with a bridgehead methyl in a bicyclobutane system.[28] This methyl signal also had the lowest shift number in the spectrum. The

remaining three methyl signals were the gem dimethyl singlets (δ.73, 1.05) and the C4 methyl (δ.80, d), the latter being coupled (J=7.3) with the C4 proton (δ1.85, q). Of the bicyclobutyl protons the one at C2 (δ2.47, d of d, J=4.3, J'=2.0) had the highest shift number (highest in the spectrum) indicating a position α to the carbonyl function. The C7 proton appeared at δ1.82 as a doublet of doublets due to coupling with both the C2 (J=2.0) and C6 (J=2.7) protons. Lastly, the C6 proton (δ2.19, d of d) was coupled to both C7 (J=2.7) and C2 (J=4.3) protons. The coupling through four bonds between the C6 and C2 protons is characteristic of nuclei arranged in a W-shaped configuration within a strained ring system such as bicyclobutane.[29]

Compound 36 may be considered a product of a di-π-methane rearrangement of 21, since examples of such rearrangements are abundant in the photochemistry of β,γ-unsaturated ketones. A preliminary review of the literature[30,31,32,33] indicates that this reaction probably proceeds through a triplet excited state (nπ*) of the ketone, whereas the alternative pathway, a 1,3-acyl shift is probably a singlet reaction. The observation that 21 when irradiated through Pyrex gives only 36 in cyclohexane but only 34 in TFE suggests that nπ* triplet and nπ* singlet states respectively are operative. A qualitative quenching study, in which 21 was irradiated in cyclohexane solutions containing increasing amounts of cis-1,3-pentadiene, showed that the rate of formation of 36 was substantially decreased with increasing triplet quencher concentration. On the other hand, the formation of 34 in the TFE photolysis of 21 was apparently unaffected by the presence of cis-1,3-pentadiene. Attempts to purify 36 by preparative vpc resulted in its complete rearrangement to 34 and 35 (Figure 3) within



the column (FFAP or Carbowax 20M on Chromosorb W at a minimum temperature of 140°). Higher temperatures (160-170°) gave only 35. Collection

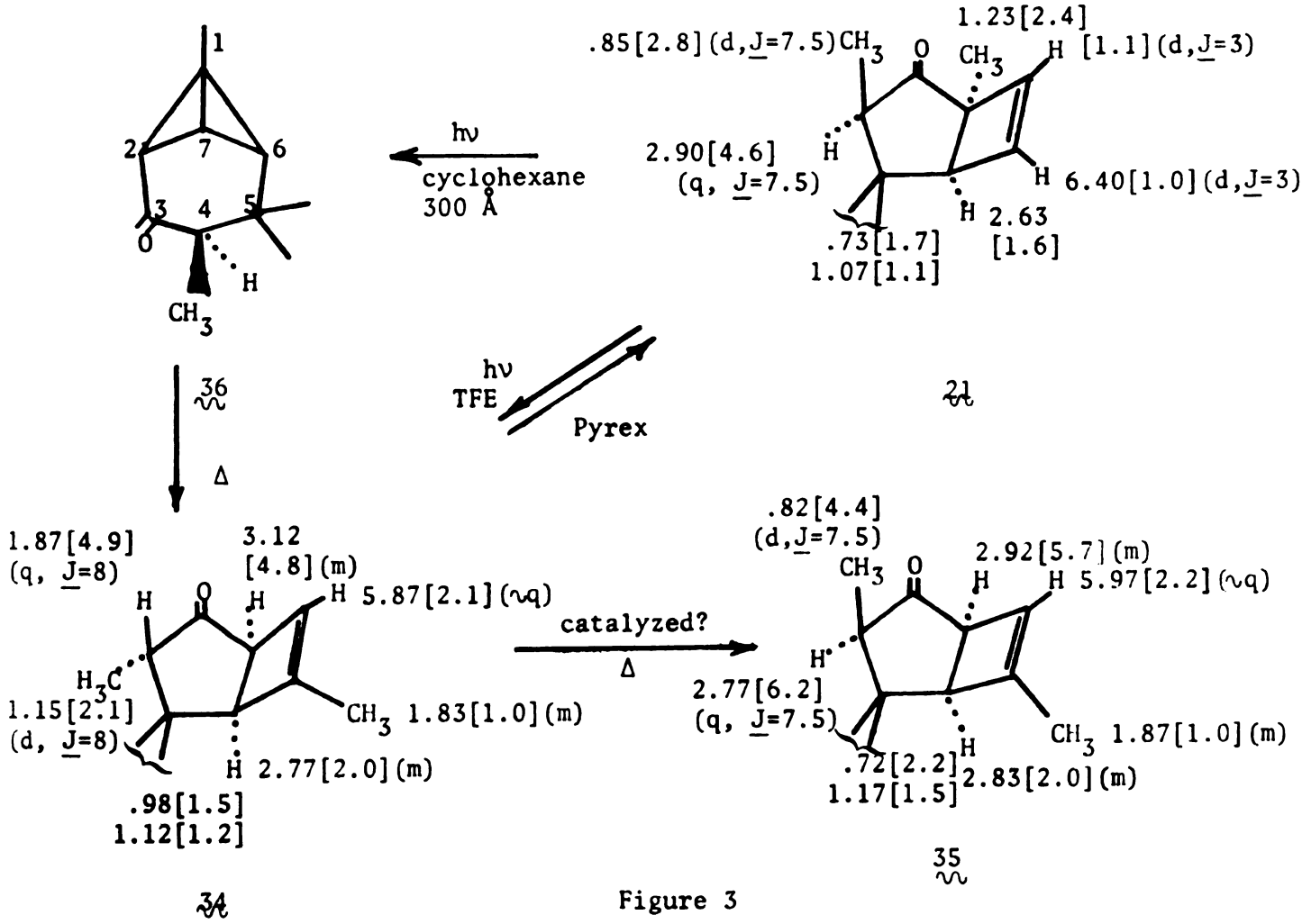


Figure 3

of the single fraction corresponding to the mixture of 34 and 35 was followed by nmr analysis which verified the presence of the two isomers. Compound 36 is apparently isomerized first to 34, which then undergoes

(possibly catalyzed) epimerization to 35. This was demonstrated by heating 36 at 145° in CCl_4 solution in a sealed nmr tube. Nmr spectra taken at 15 min intervals showed a rapid transformation to 34, the only observable compound in the spectrum after 1 hour. The spectrum was identical to that of 34 formed (but not isolated) in the TFE photolysis of 21. Continued heating of the CCl_4 solution at 145° resulted in complete conversion of 34 to 35 after 8 additional hours. At this time only 35 was observed (in addition to impurity peaks) in the nmr spectrum of the sample. Compound 35 was stable to further heating and to the vpc conditions mentioned above. Additional structural data for 34 and 35 appear in the experimental part of this thesis.

The preceding observations may be rationalized by the scheme illustrated below in Figure 4. However, although there is ample precedent for catalyzed[34] and uncatalyzed[35] bicyclobutane rearrangements of this type, little can be said concerning the mechanism of the preceding example in the absence of a careful gas phase pyrolysis of 36. The relatively low temperature required above for its rearrangement suggests a catalyzed reaction. Compound 36 rapidly decomposed (or rearranged) in the presence of a small amount of $Eu(fod)_3$ shift reagent in CCl_4 to products with olefinic protons (signals similar in shape and chemical shift to those of 34 or 35).

If one considers the thermolysis of 36 as a concerted ($\sigma 2_s + \sigma 2_a$) process, then a contradiction with the stereochemical assignment in 34 (and therefore in 21) becomes apparent. Since 34 and 35 (the observed thermolysis products) both contain C6 (instead of C7) methyls, it was assumed that only path a (illustrated below) of the two possible ($\sigma 2_s + \sigma 2_a$) processes is operative. Then only path d of the two

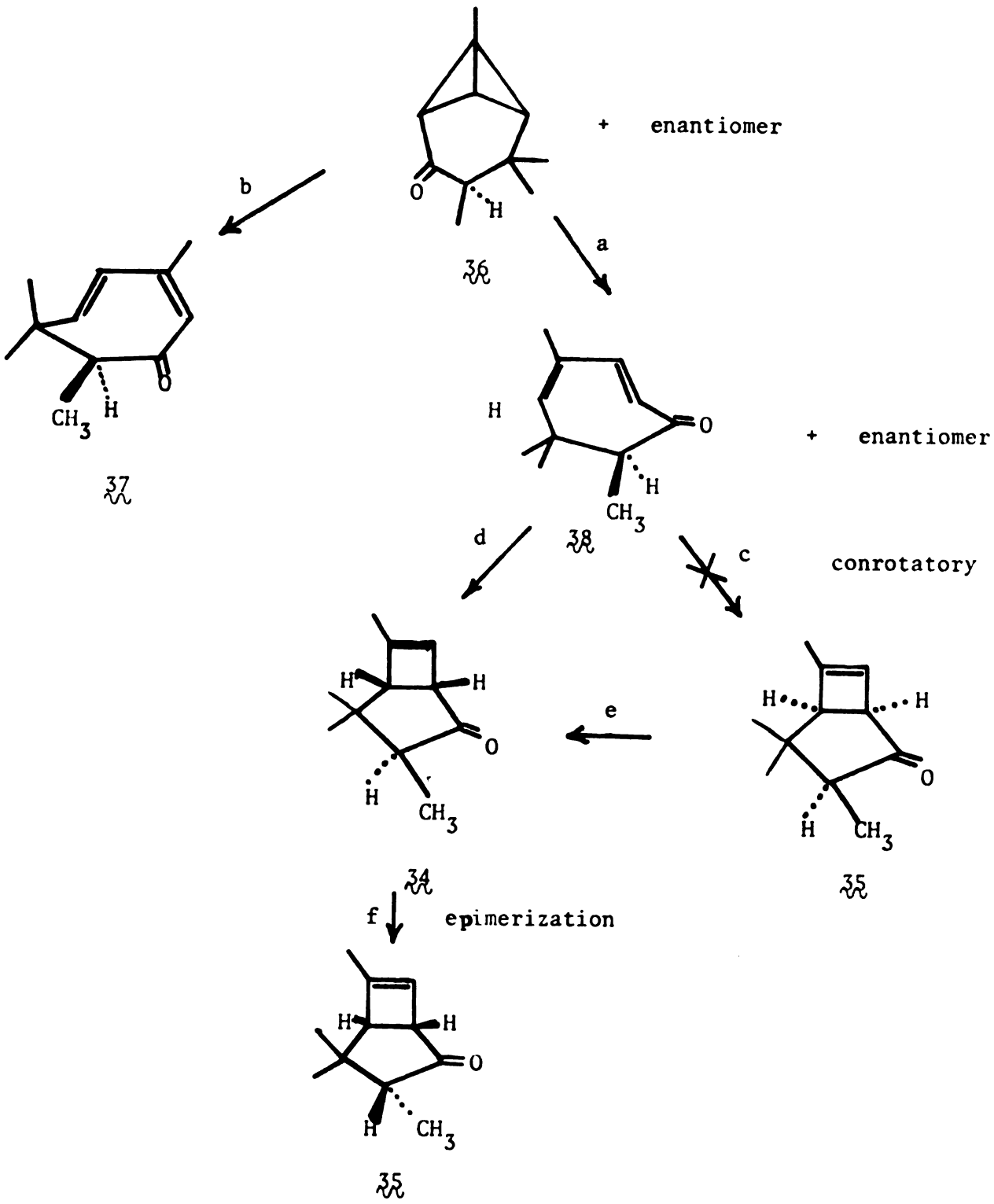
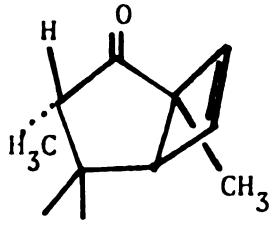


Figure 4

possible conrotatory ring closures is operative (since the product formed, 34, has an nmr spectrum identical to the Büchi photoisomer of 21 obtained in the TFE photolysis). Compound 34, arising from the

conrotatory closure, must then undergo epimerization (since that is what is observed above upon heating 34) to 35, hitherto presumed to be the less thermodynamically stable epimer of the 34-35 pair.

The limitations of nmr spectra in the assignment of C3 stereochemistry in 21 are well realized. It is possible that the compound thus far presumed to have structure 21 is actually the exo epimer illustrated below as 39. In that case, changes in structures 34 (to 40), 35 (to 41) and 36 (to 42) are necessary.



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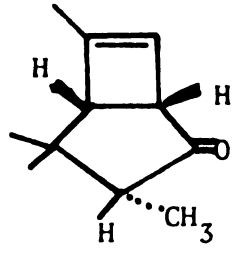

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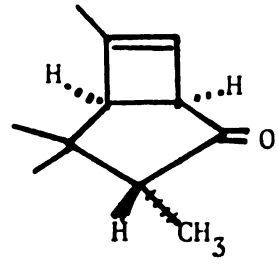

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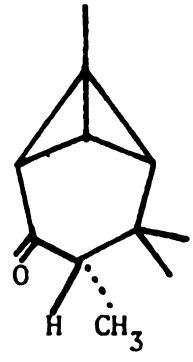

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EXPERIMENTAL

General Procedures

Except where otherwise noted, all nmr spectra were measured in CCl_4 solutions with TMS as an internal standard. The 60 MHz spectra were recorded on a Varian T-60 or A56/60 spectrometer and the 100 MHz spectra were recorded on a Varian HA100 spectrometer operated by Mr. Erich Roach. Simulated nmr spectra were obtained from a Nicolet Instrument Corporation 1082 Computer operated by Mr. Erich Roach. Spectra are recorded in units of delta. Numbers placed next to protons in structures in the discussion section refer to chemical shifts of those protons. Numbers in brackets beside chemical shifts in the discussion and experimental sections are "europium shift numbers" obtained by adding small increments of tris(1,1,1,2,2,3,3,-heptafluoro-7,7-dimethyl-4,6-octanedione)Eu(III) to the CCl_4 solution being investigated. After each addition the nmr spectrum was scanned and the new frequency of each absorption was recorded. The shift for each absorption is the difference between the frequency of the shifted absorption and the original one. Shift numbers are ratios obtained by dividing the shift of each signal in the spectrum by the shift of the least shifted signal. Infrared spectra were recorded on a Unicam SP-200 spectrophotometer in units of cm^{-1}. Ultraviolet spectra were recorded on a Unicam SP-800 spectrophotometer in cyclohexane, unless otherwise noted. Mass spectra were obtained from a Hitachi-Perkin Elmer RMU-6 operated by Mrs. Ralph Guile. Elemental analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Michigan.

General Photolysis Procedures

Solutions of the compounds to be irradiated were placed in septum-capped Pyrex tubes and purged of oxygen by bubbling dry, oxygen-free nitrogen through them for 30 minutes prior to photolysis. Irradiations were carried out with a 450 watt Hanovia Type L medium pressure mercury vapor lamp with the appropriate filter. The tubes were fastened to an immersion well apparatus which was immersed in water at ambient temperature. Alternatively, a Rayonet Photochemical Chamber Reactor or Type RS Preparative Photochemical Reactor was used. Photolyses were monitored by withdrawing small (<1μl) aliquots and injecting them into a Varian Aerograph Series 1400 analytical gas chromatograph.

2-Carbomethoxycycloheptanone. By the method of Krapcho, et al,[36] 33.7 g (.3 mol) of cycloheptanone, 100 g (.88 mol) of dimethyl carbonate and 35 g (.85 mol) of powdered NaH yielded a crude oily product, which was distilled at .5 mm Hg using a 6" Vigreux column. After a small runoff, the fraction boiling at 54° was collected. The yield of colorless product was 39.5 g (.23 mol, 77.5%). Ir (neat) 1735, 1705 (keto C=0), 1640, 1615 (enol C=0), 1320, 1280, 1250, 1225, 1205 cm^{-1}; nmr (CCl_4) spectrum reveals keto-enol mixture in a 1.6:1 ratio, δ1.4-2.8 (10H, broad with maxima at δ1.67 and δ2.38), 3.42 (.615H, m, keto proton), 3.67 (.385H, s, enol proton); mass spectrum (70eV) m/e 170 (M^+), 55 (base).

2-Carbomethoxy-2-methylcycloheptanone. Twelve grams of a 50% oil dispersion of NaH (.25 mol) in a dry nitrogen-flushed three-necked flask was washed three times with petroleum ether. After addition of 200 ml of benzene and 200 ml of THF, 2-carbomethoxycycloheptanone

(36 g, .21 mol) in 50 ml of THF was added to the stirred NaH suspension over a 30 min period. After allowing the mixture to stir for another 30 min, 56.8 g (.4 mol) of methyl iodide was carefully added and the reaction mixture was allowed to stir for 2 hours. In the workup 30 ml of glacial acetic acid was added dropwise to the stirred mixture (cooled in an ice bath), followed by 200 ml of ice water. Ether was then added and the organic layer was washed several times with water and $NaHCO_3$ solution and dried over anhydrous sodium sulfate. Evaporation of the solvent yielded 35.7 g (.19 mol, 92.5%) of a clear oil, which was shown to be nearly pure by vpc analysis (5' x 1/8" 20% FFAP on DMCS Chromosorb W at 110°). Purification of a sample for a mass spectrum was accomplished by preparative vpc (5' x 3/8" 20% FFAP on 30/60 Chromosorb W at 150°). Ir (neat) 1735, 1710, 1245, 1170 cm^{-1}; nmr (CCl_4) δ1.27 (3H, s), 3.70 (3H, s), 1.4-3.0 (10H, broad with maxima at 1.62 and 2.53); mass spectrum (70 eV) m/e 184 (M^+), 55 (base).

2,7,7-Trimethyl-2-carbomethoxycycloheptanone. Under a nitrogen atmosphere, 37 ml (.23 mol) of hexamethyldisilazane (HMDS) was placed in an ice-cooled flask and to it was added 104 ml of 2.1 M n-butyllithium in hexane with stirring. THF (200 ml) was then added carefully. The ice bath was removed and to the stirred mixture was added dropwise over 30 min 35.7 g (.19 mol) of 2-methyl-2-carbomethoxycycloheptanone in 50 ml of THF. After the addition was complete, the reaction mixture was stirred at room temperature for another hour, after which time 24 ml (57 g, .4 mol) of methyl iodide was carefully added. This mixture was stirred for three hours, then poured into ice water. Ether (500 ml) was added and the organic layer was washed several times

with cold dilute HCl, cold water, and $NaHCO_3$ solution in succession. The extract was dried over anhydrous sodium sulfate and concentrated to an oil which was taken up in 50 ml of dry THF and subjected to another methylation by the above procedure. The product of the second methylation was distilled at .1 Torr using a 6" Vigreux column. After a short runoff, the fraction boiling at 70-72° was collected giving a yield of 24.7 g (.12 mol, 63.2%). The pure product (end fraction) crystallized upon standing, mp 32-3°. Ir (neat) 1735, 1695, 1240, 1225 cm^{-1}; nmr (CCl_4) δ1.12 (3H, s), 1.15 (3H, s), 1.28 (3H, s), 6.30 (3H, s), 1.2-2.2 (8H, broad, centered at 1.58); mass spectrum (70 eV) m/e 212 (M^+), 88 (base).

2,7,7-Trimethylcycloheptanone. A mixture of 2,7,7-trimethyl-2-carbomethoxycycloheptanone (24.7 g, .116 mol), 14.2 g (.23 mol) of KOH, 100 ml of ethanol and 25 ml of water was refluxed for five hours, then poured into ice water and extracted twice with ether. The extracts were dried over anhydrous sodium sulfate and concentrated to an oil under reduced pressure. Distillation of the oil using a 6" Vigreux column gave 12.6 g (.082 mol, 71%) of the pure ketone, bp 91-2°/22 Torr. Samples were purified for analysis by preparative vpc (5' x 3/8" 20% FFAP on 30/60 Chromosorb W at 140°). Ir (neat) 1705 cm^{-1}; nmr (CCl_4) δ1.03 (3H, d, J=7), 1.05 (6H, s), 1.2-2.0 (8H, broad, centered at 1.57), 2.83 (1H, m); mass spectrum (70 eV) m/e 154 (M^+), 69 (base), 56 (100% of base).

Anal. Calcd for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.93; H, 11.76.

2,7,7-Trimethyl-2-cycloheptenone. A solution of 12.4 g (.08 mol) of 2,7,7-trimethylcycloheptanone in 25 ml of CCl_4 was added dropwise over 30 min to a stirred solution of 14.1 g (.088 mol, 4.85 ml) of bromine in 25 ml of CCl_4. Solvent and excess reagent were removed under reduced pressure and the resulting oil was refluxed with 25 ml of collidine for five hours. The reaction mixture was then poured into ice water, acidified with dilute HCl and extracted twice with ether. The ether extracts were washed with $NaHCO_3$ solution till the washings remained basic, dried over anhydrous sodium sulfate and concentrated under reduced pressure to yield 9.3 g (.061 mol, 76.5%) of the nearly pure ketone. The product was purified for analysis by preparative vpc (5' x 3/8" 20% FFAP on 30/60 Chromosorb W at 140°). Ir (neat) 1675 cm^{-1}; nmr (CCl_4) δ1.10 (6H, s, gem dimethyl), 1.60 (2H, d, J=4, C6 protons), 1.67 (2H, broad, C5 protons), 1.80 (3H, d, J=2), C2 allylic methyl), 2.25 (2H, broad, C4 allylic protons), 5.87 (1H, t, J=4, each peak split into a quartet, J=2, C3 vinyl proton); uv (cyclohexane) 318 nm (ε=70), 235 (4,500), 230 (4,600); mass spectrum (70 eV) m/e 152 (M^+), 168 (base).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.58. Found: C, 78.71; H, 10.48.

2,7,7-Trimethyl-2,4-cycloheptadienone (14). A mixture of 9.1 g (.06 mol) of 2,7,7-trimethylcyclohept-2-enone, 12.5 g (.07 mol) of N-bromosuccinimide, and .5 g of 2,2'-azobis(2-methylpropionitrile) in 50 ml of CCl_4 was refluxed for seven hours. The cooled mixture was then filtered and the filtrate was evaporated to an oil which was refluxed with 30 ml of collidine for three hours. The reaction mixture was then poured into ice water, acidified with dilute HCl and extracted

several times with ether. The extracts were washed with $NaHCO_3$ solution until basic, dried over anhydrous sodium sulfate and concentrated to a thick brown oil. The crude product was distilled at .1 Torr using a 6" Vigreux column with a dry ice-cooled receiving vessel. The pale yellow product distilling at 30° weighed 4.6 g (.03 mol, 50%) and a vpc chromatogram (5' x 1/8" 20% FFAP on Chromosorb W DMCS at 110°) showed that it was nearly pure. The product was purified for analysis and photolysis by preparative vpc (10' x 1/4" 20% Carbowax 20M on 60/80 Chromosorb W at 140°). Ir (neat) 1655 cm^{-1}; uv (cyclohexane) 350 nm (ε=75), 290 (6250); nmr (CCl_4) δ1.07 (6H, s, gem dimethyl), 1.92 (3H, d, J=2.0, C2 methyl), 2.25 (2H, d, J=5.0, C6 protons), 5.97 (2H, m, C5 and C6 protons), 6.33 (1H, m, C3 proton); mass spectrum (70 eV) m/e 150 (M^+), 107 (base).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.32. Found: C, 79.83; H, 9.32.

2,6,6,7-Tetramethyl-2,4-cycloheptadienone (19). Under a nitrogen atmosphere, 20.3 ml (a 10% excess) of hexamethyldisilazane (HMDS) was placed in an ice-cooled flask and to it was added 56 ml (a 10% excess) of 2.1 M n-butyllithium in hexane with stirring. THF (75 ml) was added carefully and the mixture was then brought to reflux temperature. Eucarvone (16 g, .107 mol) in 25 ml of THF was added dropwise over 15 min and the mixture was refluxed for 30 minutes. Methyl iodide (15 ml, .3 mol) was added carefully and reflux was continued for another hour, after which time the mixture was poured into ice water and shaken. After addition of 200 ml of ether, the organic layer was washed several times with cold dilute (1:20) HCl and sodium bicarbonate solution, dried over anhydrous $MgSO_4$ and concentrated to an oil. Distillation

of the product at .125 Torr with a 6" Vigreux column gave 13.9 g of a pale yellow oil having a boiling range of 26-31°. Vpc analysis of the product (5' x 1/8" 10% FFAP on 80/100 DMCS Chromosorb W at 110°) showed it to be a mixture of 65% 20 and 35% 19. A steel spinning band distilling column was used to remove most of the more volatile 20. Pure 19 was obtained for analysis and photolysis by preparative vpc (10' x 3/8" 20% FFAP on 30/60 Chromosorb W at 180°). With a helium carrier gas flow rate of 110 ml/min, the retention time for 20 and 19 were 8.5 min and 13.1 min respectively. Compound 19 displayed a carbonyl absorption band in the infrared (CCl_4) at 1655 cm^{-1}; uv (cyclohexane) 350 (ε=100), 315 (sh, 4500), 300 (6200), 216 (sh, 5900); uv (TFE) 312 (5600); uv (H_2SO_4) 405 (5450); nmr (CCl_4) δ1.02 and 1.08 (3H each, s, gem dimethyl), 1.03 (3H, d, J=7.0, C7 methyl), 1.87 (3H, d, J=1.5, C2 methyl), 2.47 (1H, q, J=7.0, C7 proton), 5.75 (2H, appear as a sharp doublet, J=5.0, C4 and C5 protons), 6.33 (1H, broad multiplet, C3 proton); mass spectrum (70 eV) m/e 164 (M^+), 122 (base), 121 (94% of base).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.43; H, 9.82. Found: C, 80.37; H, 9.84.

Compound 20 had spectra consistent with 3-methyl-4-carene-2-one. Ir (CCl_4) 1690, 1650 cm^{-1}; uv (cyclohexane) 295 (ε=50), nmr (CCl_4) δ.95, 1.03, 1.07, and 1.25 (3H each, s, C3 and C7 gem dimethyl groups), 1.67 (2H, d, C1 and C6 protons), 5.47 (1H, d, J=10.0, C4 proton), 5.83 (1H, d of d, J=10.0, J'=1.5, C5 proton); mass spectrum (70 eV) m/e 164 (M^+), 136 (base), 121 (90% of base).

Irradiation of Eucarvone (4) with >330 nm Light. A solution of .4 g of 4 in 50 ml of cyclohexane (.005 M) was purged with nitrogen and irradiated using a 450 watt lamp fitted with a Corning #3718 uranium

glass filter. After 48 hr, vpc analysis (5' x 1/8" 3% FFAP on Chromosorb W at 120°) revealed a 60% conversion of the starting material to a single photoproduct having a shorter retention time than 4. The product was separated for analysis by preparative vpc (10' x 1/4" 20% FFAP on Chromosorb W at 140°) and identified as 1,4,4-trimethylbicyclo[3.2.0]-hept-6-en-2-one. Ir (CCl_4) 1725 cm^{-1}; nmr (CCl_4) δ.97, 1.10, 1.24 (3H each, s, CH_3), 1.78 (1H, d, J=16, each peak split into a doublet, J=1, endo-methylene proton), 2.85 (1H, d, J=16, each peak split into a doublet, J=1, exo-methylene proton), 2.60 (1H, s, C2 proton), 6.13 (1H, d, J=3, C6 proton), 6.35 (1H, d, J=3, C7 proton).

Irradiation of 2,7,7-Trimethyl-2,4-cycloheptadienone (14) with >330 nm Light. A solution of .084 g of 14 in 22 ml of cyclohexane (.025 M) was purged with nitrogen in a 2 cm x 15 cm Pyrex test tube, which was then sealed and placed inside a 2.5 cm x 16 cm Corning #3718 uranium glass tube. This apparatus was suspended in a Rayonet Photochemical Reactor with 3500 Å lamps and irradiated. The progress of the reaction was monitored by vpc (5' x 1/8" 10% FFAP on DMCS Chromosorb W at 112°) by withdrawing 1μl samples at 12 hr intervals. After 48 hr the area of the starting material peak was halved. Only one volatile product was seen in the chromatogram and had a retention time identical with that of an authentic sample of 15a. The volatile product peak was <5% of the peak corresponding to unconverted starting material. A similar result was obtained when a cyclohexane solution of 14 was irradiated with a uranium glass filtered 450 watt lamp.

Photolysis of 2,7,7-Trimethylcyclohepta-2,4-dienone (14) in TFE. A solution of .01 g of the dienone in 4 ml of TFE (1.4×10^{-2}M) in a

10 x 100 mm Pyrex test tube was degassed and irradiated using a 450 watt lamp with a Pyrex filter. Reaction progress was monitored by vpc (5' x 1/8" 10% FFAP on Chromosorb W DMCS 80/100 at 110°). The N_2 carrier gas flow rate was 30 ml/min. Samples of 1µl were injected into the vpc at 15 minute intervals. Approximately 90% conversion of starting material was observed at 45 minutes of irradiation. The vpc chromatogram consisted of four peaks: 15a (5.2 min), 16 (9.2 min), 15b (11.8 min), 14 (15.6 min, corresponding to the starting material). Relative yields at t=15 min photolysis time, 50% conversion: 15a 14.8%, 16 86.0%, 15b 0.0%; t=30 min, 70% conversion: 15a 14.8%, 16 82.3%, 15b 2.9%; t=45 min, 90% conversion: 15a 8.05%, 16 82.5%, 15b 9.45%. Evaporation of the solvent gave a colorless oil, which was separated into its components by preparative vpc (10' x 3/8" 20% FFAP on Chromosorb W 30/60 at 155°). The helium carrier gas flow rate was 90 ml/min. Retention times for the photoproducts were: 15a 6.7 min, 16 12.0 min, 15b 19.8 min.

Photolysis of 14 in Cyclohexane. The preceding experiment was repeated using cyclohexane as solvent. Approximately 60% conversion of starting material was observed after 5 hr of irradiation, at which time the relative yields of the photoproducts were 15a 27%, 16 66% and 15b 7%.

Characterization of 1,3,3-Trimethylbicyclo[3.2.0]hept-6-en-2-one (15a). The product was collected as a colorless liquid. Ir (CCl_4) 1722 cm^{-1}; nmr (CCl_4) δ1.03 [2.38], 1.22 [2.8] and 1.27 [2.18] (3H each, s, C1 and C3 methyls), 2.95 ([2.8], 1H, d of d, J=6.5, J'=3.5, each of the four peaks split into a doublet, J=1, C5 proton), 6.12

([1.5], 1H, d, J=6.0, C7 vinyl proton), 6.38 ([1.0], 1H, d, J=6.0, each peak split into a doublet, J=1, C6 vinyl proton). In both 60 and 100 MHz spectra, the C4 geminal protons appeared as a complex 2H multiplet (5 lines) between δ1.60 and δ2.10. Since the spacings between the peaks of this multiplet did not change significantly with successive additions of $Eu(fod)_3$ shift reagent, it was possible to assign a shift number (1.6) to the C4 protons. In decoupling experiments, irradiation at the C5 proton absorption frequency resulted in a new complex multiplet for the C4 protons instead of the expected doublet of doublets. Therefore, this ABX system (where A is the C4 endo-proton, presumably at highest field, B is the C4 exo-proton and X is the C5 proton) was simulated by computer using a trial-and-error method in which approximate values for J_{AB}, J_{AX}, J_{BX}, ν(A) and ν(B) were varied until a close approximation of the observed 100 MHz spectrum was obtained. The small coupling between the C5 and C6 protons was neglected in this simulation. A good approximation of the observed spectrum (Figure 1_a) was obtained using the values J_{AB}=14 Hz, J_{AX}=3Hz and J_{BX}=7 Hz for the coupling constants and ν(A)=δ1.76, ν(B)=δ1.82 and ν(X)=δ2.92 as the chemical shifts. All lines were assigned an arbitrary linewidth of 1 Hz. No significant change in the simulated spectrum above was observed when J_{AB}=14 Hz was replaced by J_{AB}=-14 Hz. Mass spectrum (70 eV) m/e 150 (M^+), 107 (base).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.32. Found: C, 79.78; H, 9.47.

Characterization of 2,5,5-trimethyl-4-vinylcyclopent-2-enone, (16). The product was collected as a colorless liquid. Ir (CCl_4) 1705, 1640 cm^{-1}; uv (cyclohexane) 344 nm (ε=45), 330 (60), 317 (50),

225 (9,370); nmr (CCl_4) δ0.87, 1.07 (s, 3H each, gem dimethyls at C5), 1.75 (3H, d of d, J=1.8, J'=2.5, allylic methyl at C2 split by protons at C3 and C4 respectively), 3.03 (1H, d split into quintets, J=8.0, J'=2.5 Hz, methine proton at C4 split by the adjacent proton of the C4 vinyl group and by the C2 methyl and C3 vinyl protons respectively), 4.6-6.0 (3H, m, protons of the C4 vinyl group), 6.98 (1H, m, C3 vinyl proton). Splittings were verified by decoupling of a 60 MHz spectrum. Thus, irradiation at the C2 methyl absorption frequency resulted in the appearance of the C4 proton signal as a doublet of doublets (J=8.0, J'= 2.5) and the appearance of the C3 proton signal as a doublet (J=2.5). Irradiation at the C3 proton absorption frequency resulted in the appearance of the C2 methyl signal as a doublet (J=2.5). Mass spectrum (70 eV) m/e 150 (M^+), 135 (base).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.32. Found: C, 79.89; H, 9.36.

Reaction of 16 with CH_3ONa in Methanol. The vinylcyclopentenone 16 (.052 g, 3.4×10^{-4} mol) in 5 ml of methanol containing 5 equivalents of CH_3ONa was stirred at room temperature for three hours. Five ml of water and 5 ml of hexane were added, and the organic layer was extracted with water until the washings were neutral to pH paper. The hexane layer was dried over $MgSO_4$ and concentrated under reduced pressure to a colorless oil, which was then examined by vpc (5' x 1/8" 10% FFAP on Chromosorb W DMCS 80/100 at 110°). The N_2 carrier gas flow rate was 30 ml/min. The chromatogram revealed the conversion of the starting material principally to syn-2,5,5-trimethyl-4-ethylidene-2-cyclopentenone (17a) having a retention time of 19.2 min. A trace amount (≈3%) of anti-2,5,5-trimethyl-4-ethylidene-2-cyclopentenone

(17b) was also visible with a retention time of 17.4 min. Here syn and anti refer to the orientation of the ethylidene methyl group with respect to the gem dimethyl group at C5. The main product was isolated for analysis using a 10' x 3/8" column of 20% FFAP on Chromosorb W at 170°. With the flow rate of helium carrier gas at 90 ml/min, its retention time was 34.0 min. Ir (neat) 1698, 1610 cm^{-1}; uv (cyclohexane) 355 nm (ε60), 340 (90), 328 (90), 288 (14,300), 227 (22,600), 268 (16,400); nmr (CCl_4) δ1.18 (6H, s, gem dimethyls at C5), 1.83 (3H, d, J=1.5 Hz, allylic methyl at C2), 1.92 (3H, d, J=7.0, ethylidene methyl group), 5.58 (1H, q, J=7.0, ethylidene vinyl proton), 7.10 (1H, m, vinyl proton at C3); mass spectrum (70 eV) m/e 150 (M^+), 107 (base).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.32. Found: C, 79.92; H, 9.31.

Reaction of 16 with CH_3ONa in Refluxing Methanol. The previous experiment was repeated, but at reflux temperature and for 25 hours total. Progress of the reaction was monitored by withdrawing aliquots of 50 μl, quenching in water, and extracting with hexane. The extracts were then examined by analytical vpc under the conditions mentioned previously. A gradual increase in 17b relative to 17a was observed, until after 15 hours the ratio was 41:69, and after 25 hours 52:48. There was an increasing loss of material with increasing length of reflux time and amount of base added. The refluxing mixtures were generally yellow due to an unknown impurity which was extracted into the aqueous layer during workup. Compound 17b was purified for analysis using the same conditions described for 17a. Due to the small difference in retention times, it was necessary to pass 17b through the

column a second time after it was collected. The spectral data on 17b are as follows: Ir(neat) 1698, 1610 cm^{-1}; uv (cyclohexane) 369 nm (ε=60), 350 (94), 336 (100), 298 (8100), 285 (12,800), 276 (11,550); nmr (CCl_4) δ1.05 (6H, s, gem dimethyls at C5), 1.88 (3H, d, J=1.5, allylic methyl at C2), 1.87 (3H, d, J=7.0, ethylidene methyl group), 5.48 (1H, q, J=7.0, ethylidene vinyl proton), 7.63 (1H, m, vinyl proton at C3); mass spectrum (70 eV) m/e 150 (M^+), 107 (base).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.32. Found: C, 80.08; H, 9.50.

Characterization of 3,3,6-Trimethylbicyclo[3.2.0]hept-6-en-2-one (15b). The product was isolated as a colorless liquid. Ir (CCl_4) 1722, 1635 cm^{-1} ; nmr (CCl_4) δ1.00 [3.07], 1.15 [3.0] (3H each, s, gem dimethyl at C3), 1.75 ([1.0], 3H, m, C7 methyl), 1.78 ([2.23], 2H, d, J=5.0, C4 protons, which appear to be equivalent), 3.13 ([1.54], 1H, ≈q, J=5, each peak split into a doublet, J=2, C5 proton), 3.15 ([4.77], 1H, m, C1 proton), 5.80 ([1.85], 1H, m, C6 proton). A spin decoupling experiment was performed to demonstrate that the C5 proton was coupled to the geminal C4 protons and that the two C4 protons were indeed equivalent and therefore not coupled to each other. Thus, irradiation at the absorption frequency of the C5 proton in a $Eu(fod)_3$ shifted spectrum (100 or 60 MHz), in which the C4 proton resonance was shifted clear of the methyl resonances, resulted in the collapse of the sharp C5 proton doublet into a broad singlet. Mass spectrum (70 eV) m/e 150 (M^+), 107 (base). Anal. Calcd. for $C_{10}H_{14}O$: C, 79.95; H, 9.32. Found: C, 79.88; H, 9.33.

Interconversion of 15a and 15b. A solution of .002 g of 15a in .4 ml of TFE (3.3×10^{-2} M) in a 5 x 50 mm Pyrex tube was degassed and

irradiated using a 450 watt lamp with a Pyrex filter. Reaction progress was monitored by vpc (5' x 1/8" 10% FFAP on Chromosorb W DMCS 80/100 at 110°). A gradual reduction in the area of the peak corresponding to 15a, and a simultaneous increase in the peak corresponding to the sole photoproduct 15b was observed. Photoequilibrium was apparently established after about 2 hr, giving a mixture of 47% 15a and 53% 15b. The solvent was removed under reduced pressure yielding a clear liquid residue. An nmr spectrum confirmed the presence of the two compounds in the indicated ratio. Photolysis of a solution of .05 g of 15a in 2 ml of cyclohexane using a Rayonet Photochemical Reactor with 3000 Å lamps gave a mixture of 68% 15a and 32% 15b after 7 hours. The isomers were easily separated using a 5' x 3/8" column of 20% FFAP on 30/60 Chromosorb W at 160°. With the helium carrier gas flow rate at 60 ml/min the retention times were 5.5 and 10.7 min respectively.

Photolysis of 14-H^+. Under a nitrogen atmosphere, 5 ml of spectroscopic grade HSO_3F was placed in a 10 ml round-bottomed flask, cooled to -78°. With vigorous magnetic stirring, .4 g (2.6×10^{-3} mol) of 19 was then added through a septum top via a 100 µl syringe. The bright yellow solution was quickly transferred to five smooth-walled nmr tubes which had been previously flushed with nitrogen and cooled to -78°. About .2 g of $(CH_3)_4N^+BF_4^-$ was placed in one of the tubes as an internal standard and the photolysis was monitored by nmr. Spectra at -46° were taken at 2 hr intervals using a Varian A56/60 spectrometer. Cation 14-H^+ displayed signals at δ1.43 (6H, s, gem dimethyl) 2.28 (3H, s, C2 methyl), 2.82 (2H, d, J=5.5, C6 protons), 6.92 (2H, m, C4 and C5 protons), 7.90 (1H, d, J=7.0, C3 proton). The tubes were fastened to a quartz immersion photolysis well which was then immersed in a

Dewar jar containing a dry ice-isopropyl alcohol mixture. Absolute ethanol at -78° was circulated as a coolant. The irradiation was carried out using a 450 watt lamp with a Corning #3718 uranium glass filter. The signals corresponding to $\underset{\sim}{14}\text{-}H^+$ gradually decreased in intensity during the photolysis, to be replaced by those of $\underset{\sim}{16}\text{-}H^+$, δ1.28 and 1.45 (3H each, s, gem dimethyl), 2.13 (3H, s, C2 methyl), 3.67 (1H, broad, C4 proton), 5.52 (3H, broad s, ethylidene group protons), 8.84 (1H, broad s, C3 proton). Conversion of $\underset{\sim}{14}\text{-}H^+$ was complete in 6 hours. The products were recovered by transferring the acid solution to a jacketed dropping funnel, previously cooled to -78° and under a nitrogen atmosphere. The solution was then added dropwise to a vigorously stirred suspension of 10 g of powdered K_2CO_3 in 75 ml of methanol at -78°. The mixture was then brought to room temperature, 25 ml of hexane was added and the organic layer was extracted with saturated NaCl solution until the washings were neutral. The organic layer was dried over $MgSO_4$ and concentrated to a colorless oil under reduced pressure. The crude product was examined by nmr which indicated a 75% yield of $\underset{\sim}{16}$. The remaining 25% of the product mixture consisted of $\underset{\sim}{17a}$, $\underset{\sim}{17b}$ and $\underset{\sim}{18}$. Since each of the products displays a vinyl proton resonance in the region between δ6.98 and δ7.63, the yield of the major product $\underset{\sim}{16}$ was readily determined relative to the minor products. However, the relative yields of each of the three minor products are not yet precisely known and further investigation of this matter is in progress.

The Protonation of $\underset{\sim}{14}$ and $\underset{\sim}{16}$ in FSO_3H. A .1 g sample of each of the compounds $\underset{\sim}{14}$ and $\underset{\sim}{16}$ was dissolved in 1 ml of spectral grade FSO_3H using the method described above, then transferred to nmr tubes (-78°)

containing a small amount of $(CH_3)_4N^+BF_4^-$ as internal nmr standard. The sample of 14 in FSO_3H displayed an nmr spectrum (-46°) identical to the spectrum given above for 14-H^+. This spectrum was unchanged after 48 hr, during which time the sample was kept at -78°. Subsequent quenching of the cation by the procedure given above gave approximately 75 mg of recovered 14. The sample of 16 in FSO_3H displayed an nmr spectrum identical to the spectrum observed for 16-H^+ formed in the photolysis of 14 in FSO_3H. The sample of 16 in FSO_3H was kept at -78° for 7 hr, after which time it was quenched according to the procedure given above. Nmr and vpc analysis of the recovered material showed a 70% conversion of 16 to 55.5% 15b, 25% 15a and 19.3% 18.

Irradiation of 2,6,6,7-Tetramethyl-2,4-cycloheptadienone (19) Using >330 nm Light. A solution of .1 g of the dienone in 10 ml of cyclohexane (6×10^{-2} M) in a 4" Pyrex test tube was degassed and irradiated using a 450 watt lamp with a Corning #3718 "uranium glass" filter. Reaction progress was monitored by vpc (5' x 1/8" 3% FFAP on Chromosorb W 80/100 at 120°). The nitrogen carrier gas flow rate was 30 ml/min. Vpc chromatograms at regular intervals revealed a gradual decrease of the peak corresponding to the starting material (3.4 min) and a simultaneous increase in a single photoproduct 21 (7.6 min). Conversion of the starting material was about 90% after 48 hours and the yield of 21 was 100% and no secondary photoproducts. The product was purified for analysis using a 10' x 1/4" 20% FFAP on 30/60 Chromosorb W column at 180°. Ir (neat) 1725 cm^{-1}; nmr (CCl_4) δ.73 [1.7], 1.07 [1.1] (3H each, s, gem dimethyl at C4), .85 ([2.8], 3H d, J=7.5, C3 methyl), 1.23 ([2.4], 3H, s, C1 methyl), 2.63 ([1.6], 1H, s, C5 proton), 2.90 ([4.6], 1H, q, J=7.5 Hz, C3 proton), 6.23

[1.1] (1H, d, J=3 Hz, C6 proton), 6.40 [1.0] (1H, d, J=3 Hz, C7 proton); mass spectrum (70 eV) m/e 164 (M^+), 122 (base), 66 (99%).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.43; H, 9.82. Found: C, 80.52; H, 9.88.

Reaction of 21 with Alkoxide Base. A mixture of .1 g of 21 (6×10^{-4} mol) and 5 equivalents of sodium methoxide in 5 ml of methanol was stirred at room temperature for 5 hours. The reaction was then quenched by adding 5 ml of water and 5 ml of ether. The ether layer was washed with water until the washings were neutral, dried over $MgSO_4$, and evaporated to an oil which was found to be pure 21 unchanged. An identical result was obtained when the reaction was carried out in refluxing methanol or refluxing ethanol-sodium ethoxide.

Reaction of 21 with LiHMDS in THF. One ml of 1.6 M n-butyllithium was added to .5 ml of HMDS at 0°, under a nitrogen atmosphere. Five ml of THF was then added and the solution was allowed to come to room temperature. Compound 21 (.2 g, 1.2×10^{-3} mol) was then added through a septum top dropwise with stirring. After 3 hours, the reaction was worked up by adding 10 ml of cold, dilute HCl and 5 ml of ether. The ether layer was washed three times with water, once with $NaHCO_3$ solution, then dried over $MgSO_4$. Evaporation of the ether yielded pure 21 unchanged.

Reaction of 21 with CH_3ONa in CH_3OD. A mixture of .1 g of 21 and 5 equivalents of sodium methoxide in 5 ml of methanol-d was stirred at room temperature for 2 hours. The reaction was worked up by adding

2 ml of D_2O and 5 ml of hexane, then shaking vigorously. The aqueous layer was discarded and the organic layer was washed with ice water until the washings were neutral. The hexane layer was dried over $MgSO_4$ and evaporated to give pure 21-d. The product had an identical vpc retention time and carbonyl ir absorption frequency as 21. The nmr spectrum of 21-d showed a 3H singlet at δ.85 instead of a doublet, and the absence of the quartet at δ2.90. In all other respects, it was identical to the spectrum of 21. Mass spectrum (70 eV) m/e 165 (M^+), 66 (base), 122 (99.4% of base).

Synthesis of 21. The LiHMDS base was prepared as outlined above using 1.2 ml of n-butyllithium, and 1 ml of HMDS in 5 ml of THF. To this solution, .19 g (1.3×10^{-3} mol) of 1,4,4-trimethylbicyclo[3.2.0] hept-6-en-2-one (5a) was added through a septum cap dropwise with stirring. This solution was allowed to stir at room temperature under a nitrogen atmosphere for 15 minutes, after which 1 ml of methyl iodide was added. The mixture was then refluxed for 30 minutes, cooled and worked up by the procedure outlined above. The product was a colorless oil which was examined by vpc (5' x 1/8" 3% FFAP on Chromosorb W 80/100 at 112°. The nitrogen carrier gas flow rate was 30 ml/min. The chromatogram revealed a 95% conversion of the starting material to compounds 21 (87.5%) and 33 (12.5%) at retention times of 4.8 min and 6.8 min respectively. The formation of 21 was verified by comparison of spectra with the sample obtained previously from the photolysis of 19. Separation of the products for analysis was accomplished easily using a 10' x 1/4" 20% Carbowax 20M on 30/60 Chromosorb W column at 150°. Compound 33 was isolated as a colorless oil which solidified on standing (mp 37-39°). Ir (CCl_4) 1723 cm^{-1}; nmr (CCl_4) δ.83 ([3.0],

3H, s, C3 endo methyl), .88 ([1.7], 3H, s, C4 endo methyl), 1.00 ([1.3], 3H, s, C4 exo methyl), 1.18 [2.4] and 1.27 [2.9] (3H each, s, C1 and C3 exo methyls), 2.62 ([1.7], 1H, s, C5 proton), 6.17 ([1.7], 1H, d, J=3 Hz, C7 proton), 6.45 ([1.0], 1H, d, J=3 Hz, C6 proton); mass spectrum (70 eV) m/e 178 (M^+), 66 (base).

Photolysis of 19 in Cyclohexane Using 3000 Å Light. A solution of .2 g of 19 in 40 ml of cyclohexane (.028 M) in a 13 mm x 600 mm Pyrex tube was purged with nitrogen and irradiated in a Rayonet Type RS preparative photochemical reactor fitted with 3000 Å lamps. Reaction progress was monitored by vpc (5' x 1/8" 15% FFAP on 80/100 Chromosorb W DMCS at 110°). The N_2 carrier gas flow rate was 30 ml/min. Three peaks were observed, corresponding to 21 (8.2 min), 22 (24.2 min), and 23 (31.8 min) in addition to the starting material peak (19.8 min). Relative yields after 10 hours of photolysis were 54.8%, 12.1% and 33.0% respectively. After 15 hours the yields were 51%, 10.2% and 38.8% respectively. A 60% conversion of the starting material was observed after 20 hours, at which time the yields were 50%, 9.4% and 40.6% respectively. The products were separated for analysis using a preparative vpc column (10' x 3/8" 20% FFAP on 30/60 Chromosorb W at 170°). With the helium carrier gas flow rate at 90 ml/min the retention times were 9.1 min for 21, 22 min for 22 and 26.8 min for 23. The starting material had a retention time of 19.8 min. Compound 21 was identified by comparison with samples obtained previously.

Photolysis of 19 in Cyclohexane Using a 450 Watt Lamp. A solution of .026 g of 19 in 7 ml of cyclohexane (.02 M) in a 12 mm x 200 mm Pyrex tube was purged with nitrogen and irradiated using a 450

watt lamp fitted with a Pyrex filter. A 50% conversion of the starting material was observed after 3 hours, at which time the relative yields of the photoproducts were 91% 21, 3% 22 and 6% 23. The products and remaining starting material were collected by preparative vpc. Examination of the starting material fraction by nmr showed that it contained only 19.

Characterization of 22. The product was isolated as a colorless liquid. Ir (neat) 1700, 1665 (w), 1640 (w) cm^{-1}; uv (cyclohexane) 356 nm (ε=16) 342 (40), 328 (52), 316 (48), 219 (9800); nmr (CCl_4) δ1.18 ([5.9], 3H, d, J=7.5, C5 methyl), 1.72 ([1.0], 3H, d, J=1.5, butylidene methyl), 1.72 ([1.5], 3H, d, J=1.5, butylidene methyl), 1.77 ([6.2], 3H, t, J=2, C2 allylic methyl), 1.90 ([10.7], 1H, q, J= 7.5, each peak split into a doublet, J'=3.0, C5 proton), 3.12 ([5.1], 1H, d, J=9.5 each peak split into a broad multiplet, C4 proton), 4.93 ([2.9], 1H, d, J=9.5, each peak split into a broad multiplet, butylidene proton), 6.98 ([3.9], 1H, m, C3 proton); mass spectrum (70 eV) m/e 164 (M^+), 122 (base).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.43; H, 9.82. Found: C, 80.22; H, 9.89.

Characterization of 23. The product was isolated as a colorless liquid. Ir (CCl_4) 1700, 1665 (w), 1640 (w) cm^{-1}; uv (cyclohexane) 358 (ε=16), 342 (42), 327 (68), 315 (116), 281 (200), 219 (9000); nmr (CCl_4) δ.93 ([5.8], 3H, d, J=7.5, C5 methyl), 1.73 ([1.2], 3H, d, J=1.5, butylidene methyl), 1.73 ([1.0], 3H, d, J=1.5, butylidene methyl), 1.78 ([5.6], 3H, 5, J=1.5, C2 allylic methyl), 2.43 ([10.0], 1H, quintet, J=7.5, C5 proton), 3.68 ([4.3], 1H, broad triplet, J=7-10, C4 proton), 5.23 ([3.29], 1H, d, J=10.0, each peak split into a septet, J'=1.5,

butylidene proton), 6.92 ([3.94], 1H, m, J=1.5, C3 proton). Spin decoupling of a 100 MHz spectrum (irradiation at the frequency of the three allylic methyls) confirmed the following interactions: 1. The C3 proton signal appeared as a doublet, J=3.0. Therefore, the C3 proton is coupled to the C4 proton, J=3.0 and to the C2 methyl, J=1.5. 2. The butylidene proton signal appeared as a sharp doublet, J=10.0. Therefore the butylidene proton is coupled to the C4 proton, J=10.0 and to the allylic gem methyls, J=1.5. 3. The C4 proton signal appeared as a pair of quartets (pair of doublets of doublets) showing the C4 proton to be coupled to the butylidene proton, J=10.0, to the C5 proton, J'=7.5 and to the C3 proton, J''=3.0. In the absence of decoupling, the C4 proton is also coupled to the allylic gem methyls which gives rise to its broad triplet appearance mentioned above. Mass spectrum (70 eV) 164 (M^+), 122 (base).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.43; H, 9.82. Found: C, 80.38; H, 9.93.

Reaction of 23 with CH_3ONa in CH_3OH. Compound 23 (.05 g) was added to a solution of five equivalents of sodium methoxide in 5 ml of methanol under a nitrogen atmosphere at 0°. After stirring at 0° for 15 min the reaction was quenched by addition of 5 ml of water and 5 ml of hexane. The organic layer was washed with water until the washings were neutral, then dried over $MgSO_4$ and concentrated to a colorless oil. Examination of the mixture by vpc revealed a 90% conversion of 23 to a single product having the same retention time as 22. The product was isolated for analysis using a preparative 5' x 3/8" FFAP column at 150°. Nmr and ir analysis of the product showed it to be identical to 22 obtained from the photolysis of 19.

Photolysis of 21 in Cyclohexane. A solution of .1 g of 21 in 6 ml of cyclohexane (.1M) in a 6 mm x 40 mm Pyrex tube was purged with nitrogen and irradiated in a Rayonet Type RS preparative photochemical reactor fitted with 3000 Å lamps. Reaction progress was monitored by analytical vpc under conditions identical to those used in the photolysis of 19 except for an injector temperature of 140°. The chromatograms revealed the complete conversion of 21 to a single photoproduct (36) after about 4 hours. The retention time of 36 was then compared to that of 19 and found to be identical. Removal of the solvent under reduced pressure yielded the clear oily photoproduct which required no purification. Ir (CCl_4) 1705 cm^{-1}; nmr (CCl_4) δ.73 [2.3] and 1.05 [1.7] (3H each, s, gem dimethyl), .80 ([4.4], 3H, d, J=7.3, C4 methyl), 1.68 ([1.0], 3H, s, C1 methyl), 1.82 ([2.3], 1H, doublet of doublets, J=2.7, J'=2.0, C7 proton), 1.85 ([5.7], 1H, q, J=7.3, C4 proton), 2.13 ([1.9], 1H, doublet of doublets, J=4.3, J'=2.7, C6 proton), 2.47 ([6.3], 1H, doublet of doublets, J=4.3, J'=2.0). The coupling constants were obtained by careful analysis of a 100 MHz spectrum. The compound rearranged rapidly in the presence of $Eu(fod)_3$ shift reagent with a half life of approximately four minutes. However, reasonably good results were obtained by working quickly. Mass spectrum (70 eV) m/e 164 (M^+), 65 (base), 122 (76% of base), 123 (54% of base).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.43; H, 9.82. Found: C, 80.37; H, 9.92.

Photolysis of 21 in TFE. A solution of .05 g of 21 in 3 ml of TFE in a 6 mm x 12 mm Pyrex tube was purged with nitrogen and irradiated using a 450 watt lamp with a Pyrex filter. A similar sample with cyclohexane as the solvent was irradiated simultaneously for comparison. Reaction progress was monitored by analytical vpc under the same

conditions used in the preceding experiment. A chromatogram of each reaction mixture showed the formation of a single product in each case. Retention times for the photoproducts were identical to each other and, fortuitously, to the retention time of 19. After three hours the TFE sample contained 78% 21 and 22% 34. Irradiation for an additional hour resulted in a photoequilibrium mixture of 70% 21 to 30% 34. This ratio did not change upon further irradiation. The cyclohexane sample contained a mixture of 28% 21 and 72% 36 after 3 hours of irradiation. Examination of the photolysis mixtures by nmr confirmed the ratios given above. Compound 34 was not isolated by vpc, since it underwent (partial to complete) epimerization to 35 under all conditions that were tried. Instead, it was prepared for spectral (nmr and ir) analysis by thermal rearrangement of 36.

Thermal Rearrangement of 36. A solution of .05 g of 36 in .3 ml of CCl_4 was sealed in an nmr tube and placed in an oil bath maintained at 145°. Reaction progress was monitored by nmr at 15 min intervals. A gradual decrease in the signals corresponding to 36 was accompanied by a simultaneous increase in the signals of 34. A complete conversion of the starting material to 34, was observed after 1 hour. No other products were detected in the spectrum. The spectrum of the product was identical to the spectrum of the photoisomer of 21 obtained from the irradiation in TFE described above. Compound 34 had a carbonyl stretching frequency in the infrared (CCl_4) of 1725,1635 (w) cm^{-1};. Nmr (CCl_4) δ.98 [1.5] and 1.12 [1.2] (3H each, s, gem dimethyl), 1.15 ([3.1], 3H, d, J=8.0, C3 methyl), 1.83 ([1.0], 3H, m, C7 methyl), 1.87 ([4.9], 1H, q, J=8.0, C3 proton), 2.77 ([2.0], 1H, m, C5 proton), 3.12 ([4.8], 1H, m, C1 proton), 5.87 ([2.1], 1H, ≈q, J≈1.3, C6 methyl).

In a decoupling experiment, the doublet at δ1.15 collapsed into a singlet upon irradiation at the frequency of the quartet at δ1.87.

Compound 35. The previous experiment was repeated. Continued heating beyond 1 hour led to the complete conversion of 34 to its epimer 35 after an additional 90 min. Compound 35 was stable to further heating and was purified for analysis using a 5' x 3/8" column of 20% FFAP on 30/60 Chromosorb W at 160°. Ir (CCl_4) 1725, 1635 (w) cm^{-1}; nmr (CCl_4) δ.72 [2.2] and 1.17 [1.5] (3H each, s, gem dimethyl), .82 ([4.4], 3H, d, J=7.5, C3 methyl), 1.87 ([1.0], 3H, m, C7 methyl), 2.77 ([6.2], 1H, q, J=7.5, C3 proton), 2.83 ([2.0], 1H, m, C5 proton), 2.92 ([5.7], 1H, m, C1 proton), 5.97 ([2.2], 1H, ≈q, J≈1.3, C6 proton); mass spectrum (70 eV) m/e 164 (M^+), 121 (base). Mixtures of 34 and 35 were obtained in early attempts to purify 36 by preparative vpc. Relative amounts of 34 and 35 varied with column conditions and type. Injection of 36 resulted in a single peak. Collection and subsequent analysis by nmr revealed the complete conversion of 36 to the two isomers. Compounds 34 and 35 had nearly the same retention time of about 19.5 min (single assymetrical peak) on a 5' x 1/8" analytical column of 15% FFAP on 80/100 DMCS Chromosorb W at 110°. This is similar to the retention time of 19. Anal. Calcd. for $C_{11}H_{16}O$: C, 80.43; H, 9.82. Found: C, 80.33; H, 9.81.

Photolysis of 19 in TFE. A solution of .1 g of 19 in 10 ml of TFE (.06 M) in a 1.5 cm x 12.5 cm Pyrex tube was purged with nitrogen and irradiated for 1 hour using a 450 watt lamp with Pyrex filter. Reaction progress was monitored by vpc under the same conditions used in the photolysis of 19 in cyclohexane. An 85% conversion of 19 to photoproducts was observed. Compounds 21 (28%), 22 (5.7%) and 23 (7.5%) had the previously observed retention times. Also observed were

compounds 24 (43%) and 25 (15.8%) at retention times of 19.8 and 11.2 min respectively. The chromatogram also showed two other peaks (6.0 and 8.2 min) totalling about 8%. These were shown to be secondary photoproducts arising from 24 and were not investigated further. Compound 24 had the same retention time as 19 and was rapidly converted to secondary photoproducts under the reaction conditions. The peak corresponding to 19 and 24 was therefore collected and analyzed by nmr to determine the relative amounts of each isomer in the photolysis mixture. Preparative vpc conditions were the same as those used in the separation of the cyclohexane photolysis mixture. Pure 24 was obtained by another method (see below) and isolated as a colorless liquid. Ir (neat) 1660 cm^{-1}; uv (cyclohexane) 346 nm (ε=88), 317 (sh 270), 268 (3700), 244 (4660); nmr (CCl_4) δ.80 [2.2] and 1.22 [1.0], (3H each, s, gem dimethyl), 1.15 ([1.7], 3H, d, J=7.5, C2 exo methyl), 1.45 ([2.7], 3H, d, J=1.5, C4 allylic methyl), 2.50 ([7.6], 1H, q, J=7.5, each peak broadened by further coupling, C2 endo proton), 6.72 ([2.4], 1H, d, J=5.5, each peak split into a q, J=1.5, C5 vinyl proton. The C1 and C6 protons appeared as multiplets in the δ.90-1.50 region which could not be satisfactorily shifted away from the methyl signals. Mass spectrum (70 eV) m/e 164 (M^+), 122 (base).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.43; H, 9.82. Found: C, 80.30; H, 9.92.

Compound 25 was identified as the main product of the photolysis of 24 in TFE. Irradiation of a .05 g sample of pure 24 under the conditions of the preceding experiment led to a 75% conversion. In addition to an 80% yield of 25, two minor products (observed above in the TFE photolysis of 19) were formed in about 20% total yield. These were

not investigated further. Compound 25 had a carbonyl stretching frequency of 1730 cm^{-1} in the infrared (neat). Uv (cyclohexane) 319 nm (ε=179), 307 (256), 296 (230), 280 (sh 18), 214 (2410); nmr (CCl_4) δ.92 [1.4] and 1.07 [1.0] (3H each, s, gem dimethyl), .97 ([2.3], 3H, s, C1 methyl), 1.02 ([2.3], 3H, d, J=7.0, C3 endo methyl), 2.25 ([3.9], 1H, q, J=7.0, each peak split into a doublet, J'=3.5, C3 exo proton), 2.50 ([1.4], 1H, broad t, C4 proton), 5.55 ([1.8], 1H, d, J=6.0, C6 vinyl proton), 6.38 ([1.3], 1H, d of d, J=6.0, J'=3.0, C5 vinyl proton); mass spectrum (70 eV) m/e 164 (M^+), 107 (base), 93 (99% of base).

Photolysis of 19-H^+. The procedure for the preparation and irradiation of 19-H^+ and the recovery of its photoproduct was identical to that used for 14-H^+. The cation displayed nmr signals at δ1.23 and 1.32 (3H each, s, gem dimethyl), 1.47 (3H, d, J=7.5, C7 methyl), 2.18 (3H, s, C2 methyl), 2.87 (1H, q, J=7.5, C7 proton), 6.65 (2H, broad s, C4 and C5 protons), 7.85 (1H, broad d, J≈6, C3 proton). These gradually decreased in intensity during the photolysis, and were replaced by the signals corresponding to 24-H^+, δ.87 and 1.53 (3H a-piece, s, gem dimethyl), 1.45 (3H, d, J=7.0, C2 methyl), 2.08 (3H, s, C4 methyl), 3.35 (1H, q, J=7.0, C2 proton), 8.58 (1H, d, J=6.5, C5 proton), C1 and C6 protons appeared as multiplets at about 1.90 and 2.60, partially obscured by the methyl signals. Conversion of 19-H^+ was apparently complete in 6 hours, but irradiation was continued for an additional 3 hours to insure purity of the product. Cation 24-H^+ was stable and unaffected by further irradiation. Upon quenching, the sole product, 24, was obtained as a pure, pale yellow oil.

The Quenched Photolysis of 21. Into each of five 5 mm x 50 mm Pyrex tubes was placed 2.5 mg of 21. To one of the tubes was added

.3 ml of cyclohexane. Into each of the remaining tubes was placed .3 ml of a cis 1,3-pentadiene solution in cyclohexane. The concentrations of quencher in these four solutions were 1M, 2M, 3M, and 4M. The five tubes were then fastened to a quartz immersion photolysis well and irradiated for 45 min using a 450 watt lamp with a Pyrex filter. A 1µl aliquot of each of the five samples was then injected into an analytical vpc column (5' x 1/8" 10% FFAP on DMCS Chromosorb W at 120°) and the ratio of the areas of the two observed peaks (starting material at shorter retention time and photoproduct at longer retention time) was recorded for each sample. The following ratios of 21 to photoproduct were observed: .09 (no quencher), 2.3 (1M quencher), 3.3 (2M quencher), 4.3 (3M quencher), 3.8 (4M quencher). Since the conversion of 21 was greater than 90% in the absence of quencher and decreased with increasing quencher concentration, 36 was assumed to arise (at least in part) via a triplet excited state of 21. At higher quencher concentrations (above 3M) the photoproduct peak undoubtedly contained 34, the alternative photoproduct of 21. This experiment was complicated by the fact that 36 is rapidly converted to 34 in a vpc column (see above) so that the amount and identity of the photoproduct(s) could not be determined by inspection of a vpc chromatogram. In an attempt to identify the photoproduct(s) formed in the presence of the triplet quencher, a preparative photolysis (.025 g of 21 in 3.5 ml of the 3M quencher solution irradiated for 90 min) was carried out. Evaporation of the solvent gave a colorless oil which was examined by nmr and ir. The nmr spectrum of this crude material was complicated by the presence of polymerized quencher. However, peaks corresponding to 34 (δ5.87, 3.12, 2.77, 1.83) were visible in the spectrum of the crude product.

Also visible was a peak at δ1.68 corresponding to the bicyclobutyl methyl of 36. All other peaks of the photoproducts 36 and 34 were hidden by peaks corresponding to the starting material 21 and to polymerized quencher. The nmr spectrum suggested an approximately 1:1 ratio of 36 to 34. The ir spectrum (CCl_4) of the crude mixture showed strong carbonyl absorption at 1722 cm^{-1} corresponding to 34 and 21. A shoulder (1705 cm^{-1}) of this band was perhaps due to the presence of 36 in the mixture.

A qualitative quenching experiment was then performed using a 3M cis 1,3-pentadiene in TFE solution as the solvent. Irradiation of 2.5 mg of 21 in .3 ml of this quencher solution for 90 min resulted in a starting material to photoproduct ratio of 1.4. An identical ratio was obtained from the photolysis of 2.5 mg of 21 in .3 ml of TFE. This result is perhaps an indication that 34 is formed via an excited singlet state of 21. However, no preparative photolysis was carried out in TFE-quencher solution, and so the identity of the photoproduct formed under these conditions remains unconfirmed. Also unknown is the effect of the change in solvent polarity (TFE-quencher vs pure TFE) on the type of photoproduct formed.

Methylation of 21. To a solution of 1 ml of HMDS, 1 ml of 1.6M n-butyllithium in hexane and 5 ml of THF was added .2 g (.0012 mol) of 21. Addition of 1 ml of methyl iodide was then followed by 30 minutes of refluxing. The mixture was worked up by adding 5 ml of dilute HCl and extracting the mixture with ether. The ether layer was dried and concentrated to an oil. A vpc chromatogram showed a near quantitative transformation of 21 to 33. Compound 33 prepared in this manner was identical (ir, nmr) to the minor product of the methylation of 5a.

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