

APPROACHES TO NON-BENZENOID AROMATICS FROM 1, 5-DIACETYLENES

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ABSTRACT

APPROACHES TO NON-BENZENOID AROMATICS FROM 1,5-DIACETYLENES

by Robert E. Krause

Theoretical calculations have suggested three examples of non-benzenoid aromatic compounds which lend themselves to preparation via 1,5-diacetylenic compounds.

The first of these examples studied was that of the 1,4-dehydrobenzene.



1,4-dehydrobenzene

Because of the similarities between 1,4-dehydrobenzenes and cyclobutadienes, methods which have been successful in the preparation of cyclobutadiene derivatives were applied.

After initially failing to produce the necessary intermediates to a 1,4-dehydrobenzene from meso-1,6-diphenyl-3,4-dimethyl-1,5-hexadiyne-3,4-diol (VII)) o-bis(phenylethynyl)benzene (XVI) was synthesized, and attempts were made to form a metal complex of a 1,4-dehydrobenzene from this compound. Regrettably, only polymeric products could be isolated from reactions with this intermediate, and the synthesis of a stable 1,4-dehydrobenzene by these routes could not be successfully completed.



A second non-benzenoid aromatic species of interest was <u>o</u>-phenylene-bis(phenylcyclopropenone) (IV) which was considered interesting because of the close proximity of the two aromatic cyclopropenone groups to each other.



(IV)

Also, isolation of this compound would facilitate the formation of a cyclobutene dication derivative (VI) by photolytic rearrangement to obtain a third non-benzenoid aromatic compound.



Attempts to form the <u>o</u>-phenylene-bis(phenylcyclopropenone) (IV) by reaction with dichlorocarbene on <u>o</u>-bis(phenylethynyl)benzene (XVI) failed, however, to insert two dichlorocarbene units, and only the mono insertion product (<u>o</u>-phenylethynylphenyl)phenylcyclopropenone (XXI) was isolable.



APPROACHES TO NON-BENZENOID AROMATICS

FROM 1, 5-DIACETYLENES

Ву

Robert E. Krause

A THESIS

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TABLE OF CONTENTS

Page

INTRO	DUC		1
RESU	LTS A	AND DISCUSSION	7
EXPE	RIMEI	NTAL	23
	Gene	eral Procedures and Apparatus	23
	A.	1,6-diphenyl-3,4-dimethyl-1,5-hexadiyne- 3,4-diol	23
	в.	Dibenzoate of 2,3-diphenylethynyl-2,3- butanediol	24
	c.	1,3-dioxa-2-ethoxy-4,5-dimethyl-4,5- diphenylethynylcyclopentane, Attempted	25
	D.	2,5-dioxa-3,4-dimethyl-3,4-diphenylethynyl- cyclopentanone	26
	Е.	1,3-dioxa-2-phenyl-4,5-dimethyl-4,5- diphenylethynylcyclopentane	26
	F.	Reaction of 1,6-diphenyl-3,4-dimethyl-1,5- hexadiyne-3,4-diol with triphenylphosphine dibromide	27
	G.	<u>o</u> -bis(phenylethynyl)benzene	28
	н.	o-bis(2-phenylethyl)benzene	29
	J.	. Bis(benzonitrile)palladium II chloride	29
	к.	Bis(acetonitrile)palladium II chloride	30
	L .	Reaction of <u>o</u> -bis(phenylethynyl)benzene with dichlorocarbene; Method I	31
	Μ.	Reaction of <u>o</u> -bis(phenylethynyl)benzene with dichlorocarbene; Method II	32
SPECTRA			
	Infi	rared Spectrum of <u>o</u> -bis(phenylethynyl)benzene	35
	Ult: benz	raviolet Spectrum of <u>o</u> -bis(phenylethynyl)- zene	36

TABLE OF CONTENTS (Cont.)

	Page
Infrared Spectrum of <u>o</u> -bis(2-phenylethyl)benzene	37
Ultraviolet Spectrum of <u>o</u> -bis(2-phenylethyl)- benzene	. 38
Infrared Spectrum of (<u>o</u> -phenylethynylphenyl)- phenylcyclopropenone	, 39
Ultraviolet Sp e ctrum of (<u>o</u> -phenylethynylphenyl)- phenylcyclopropenone	, 40
LITERATURE CITED	. 41

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REACTION SCHEMES

SCHEME		Page
I.	Unsuccessful preparation of 2,3-dimethyl-5,6- diphenyl-1,4-dehydrobenzene from meso-1,6- diphenyl-3,4-dimethyl-1,5-hexadiyne-3,4-diol.	9
II.	Synthesis of o-bis(phenylethynyl)benzene, and unsuccessful conversion to 2,3-diphenyl-1,4- dehydronaphthalene	14
III.	Conversion of <u>o</u> -bis(phenylethynyl)benzene to cyclopropenones	20

INTRODUCTION

A useful precursor for the formation of non-benzenoid aromatic systems is the acetylenic group. Perhaps the best known uses of this functional group for this purpose are in the formation of cyclobutadiene-metal complexes and cyclopropenone aromatic systems. It is also possible, however, that other non-benzenoid aromatic systems can be made via an acetylenic intermediate.

In 1952, Roberts, Streitwieser, and Regan suggested the existence of a stable 1,4-dehydrobenzene by their calculations attributing a resonance energy of 1.66β or about 28 kcal. to the parent bicyclo[2.2.0] hexa-1,3,5-triene, more commonly referred to as 1,4-dehydrobenzene or butalene (1).



1,4-dehydrobenzene

Further calculations were done by Dewar and Gleicher who calculated a resonance energy of 0.984 e.v. or 22.7 kcal. by Hückel molecular orbital calculations; 0.191 e.v. or 4.40 kcal. by Pople, Pariser, and Parr methods; and 0.391 e.v. or 9.02 kcal. by a modified split <u>p</u>-orbital approach (2).

Computer calculations done by Lee also duplicate the results obtained by Roberts, Streitwieser and Regan (3).

One possible observation of the formation of stable 1,4-dehydrobenzene was reported by Berry, Clardy, and Schafer in 1965 (4). Analysis of spectroscopic and mass spectral data gathered from the flash initiated decomposition of benzenediazonium-4-carboxylate indicated the formation of a species of mass 76, attributed to 1,4-dehydrobenzene, having a lifetime of two minutes. However, no conclusive evidence was presented to rule out other isomers of this compound.

This empirical evidence, together with the theoretical calculations, lends encouragement to a possible successful synthesis of a stable 1,4-dehydrobenzene.

Because of structural similarities between 1,4-dehydrobenzenes and cyclobutadienes, stabilizing factors for the cyclobutadiene system may be applied to the 1,4-dehydrobenzene system as well.

Roberts, Streitwieser, and Regan have completed Hückel molecular orbital calculations for a number of the cyclobutadiene systems (1). While their calculations have shown cyclobutadiene to exist in a triplet ground state with no delocalization energy, vinyl cyclobutadiene was shown to have a delocalization energy of 0.60β and 1,2divinyl cyclobutadiene to have a delocalization energy of 1.21β . Most significant was phenyl cyclobutadiene which was shown to have a delocalization energy of 2.53β .

The applicability of this data to the 1,4-dehydrobenzene system is indicated by the fact that the delocalization energy of 1.66 β for the parent 1,4-dehydrobenzene is increased to a delocalization energy of 2.47 β when a vinyl group is added across the 2,3 positions of the 1,4dehydrobenzene nucleus. It would thus seem that the best chances for synthesizing a stable 1,4-dehydrobenzene would exist when the 1,4-dehydrobenzene being synthesized was highly substituted, preferably with phenyl groups. Such substitution would also serve to prevent complicating rearrangements due to hydrogen migrations.

In attempting a synthesis of such a compound, it was considered advantageous, because of structural similarities with the cyclobutadiene system, to use reactions and techniques which have led to the successful preparation of metal complexes of cyclobutadiene derivatives. Decomposition of this complex, then, should be expected to produce the free 1,4-dehydrobenzene derivative. Although this last step has failed for cyclobutadienes, it was felt that the increased delocalization energy of the 1,4-dehydrobenzene system, plus the existence in a singlet ground state as against a triplet ground state for cyclobutadienes, should greatly increase the chances for its isolation.

Utilization of this approach necessitates the isolation of an intermediate with either of the following groups, where X indicates a good leaving group which will allow for the <u>in situ</u> formation of intermediate I.



The initial attempt involved converting meso-1,6-diphenyl-3,4-dimethyl-1,5-hexadiyne-3,4-diol (VII) to a suitable intermediate from which a compound of the following type could be synthesized.



A second route involved forming the intermediate <u>o</u>-bis(phenylethynyl)benzene (XVI), which could be converted to the following metal complex.



This intermediate was synthesized as a new compound by the method of Stevens and Castro (5), but it has since been reported in the literature (6).

A second non-benzenoid aromatic species derivable from an acetylene is cyclopropenone. A number of workers have synthesized diphenylcyclopropenone and have shown that it exists in the form of species III (7). This is consistent with theory, as such a species, according to the Hückel 4n + 2 rule, would exhibit aromatic character and thus gain stability.

By analogy with diphenylcyclopropenone (III), it should be possible to convert <u>o</u>-bis(phenylethynyl)benzene (XVI) to species IV.



Formation of such a species would be interesting for two reasons. First, it would be interesting to note the properties of such a molecule containing two cyclopropenone groups in close proximity to each other. Secondly, isolation of this intermediate would allow for the formation of

an interesting derivative of the following non-benzenoid aromatic species (V), which should also exhibit aromatic character as predicted by the Hückel 4n + 2 rule.



Rearrangement of the dicyclopropenone compound (IV), either photolytically, or with heat, might be expected to lead to formation of the species VI, which should exhibit most interesting properties.



(VI)

RESULTS AND DISCUSSION

The initial goal of this investigation involved the synthesis of a stable 1,4-dehydrobenzene. The method proposed to accomplish this synthesis was to convert meso-1,6diphenyl-3,4-dimethyl-1,5-hexadiyne-3,4-diol (VII) to its orthoformate derivative (VIII)(Scheme I). Pyrolysis of this intermediate was expected to result in the loss of carbon dioxide and ethanol with the formation of the olefin (IX)(8) which could be reacted with a palladium chloride derivative to form the palladium chloride complex of 2,3dimethyl-4,5-diphenyl-1,4-dehydrobenzene (XI). Careful decomposition of the complex with a phosphine would then produce the expected 1,3-dimethyl-4,5-diphenyl-1,4-dehydrobenzene (XII) (9).

To accomplish this, 1,6-diphenyl-3,4-dimethyl-1,5-hexadiyne-3,4-diol (VII) was synthesized by the method of Wilson and Hyslop (10). The isomers were separated by fractional crystallization and the low melting isomer was shown to be the meso form by its behavior in the nmr.

In a solvent of low polarity, such as deuterochloroform, the racemic isomer would be expected to assume a configuration where minimal interactions between methyl hydrogens will occur. This may result in a very slight deshielding in the nmr, since this places the methyl hydrogens in the vicinity of the acetylene groups, but it places both methyl

groups in an equally unhindered environment. The high melting isomer behaves in this manner and exhibits a single methyl peak at $\tau 8.19$ in the nmr.

In the same solvent, the meso isomer can only orient one of its methyl groups in the same unhindered orientation as in the racemic isomer. The other methyl group must then assume a position where it interacts with a hydroxyl group rather than with an acetylene group. This might be expected to result in less deshielding in the nmr, and the meso isomer should therefore exhibit methyl peaks of slightly different chemical shifts in the nmr. The low melting isomer behaves in this manner and exhibits two methyl peaks at $\tau 8.17$ and $\tau 8.25$ in the nmr.

Further confirmation of the meso structure comes from the behavior of the low melting (mesd) isomer in a polar solvent. In dimethylsulfoxide, intramolecular hydrogen bonding takes place and the methyl groups are drawn into a slightly hindered but unshielded or deshielded position. In this solvent, the methyl groups exhibit a singlet at $\tau 8.29$ in the nmr and the hydroxyl groups exhibit a doublet at $\tau 4.33$ (J= 6 cps). Introduction of a trace of strong acid increases proton exchange and moves this hydroxyl peak to $\tau 3.8$ as a broad singlet. This behavior is consistent with what should be expected, as the intramolecular hydrogen bonding draws the methyl groups out of their slightly different environments and into a single common environment.





Unfortunately, reaction of meso-1,6-diphenyl-3,4-dimethyl-1,5-hexadiyne-3,4-diol (VII) with ethyl orthoformate to produce the orthoformate derivative (VIII) did not appear to form the expected derivative. While a high yield of a liquid product was obtained, its nmr spectrum was in no way consistent with the expected product.

In an attempt to synthesize the olefin 1,6-diphenyl-3,4-dimethyl-3-hexene-1,5-diyne (IX) directly, two other reactions were tried.

First, numerous sets of conditions were tried by which a modified Chugaev type reaction might be used to convert 1,6-diphenyl-3,4-dimethyl-1,5-hexadiyne-3,4-diol (VII) to 1,6-diphenyl-3,4-dimethyl-3-hexene-1,5-diyne (IX). However, in all cases only decomposition products and carbonyl containing rearrangement products were obtained.

An attempt was also made to form 1,6-diphenyl-3,4-dimethyl-3-hexene-1,5-diyne (IX) from 1,6-diphenyl-3,4-dimethyl-1,5-hexadiyne-3,4-diol (VII) by reduction with stannous chloride in methanolic HCl (11). In this case, analysis indicates that some 1,6-diphenyl-3,4-dimethyl-3-hexene-1,5-diyne (IX) may have been formed. Unfortunately, there appears to be a competing reaction taking place which makes conditions extremely critical. After a number of attempts, the best reaction that could be obtained yielded only a moderate yield of crude red oil product along with some carbonyl containing by-product and much contaminated starting materials. Extending the reaction time to consume all

the starting material only resulted in less olefin fraction and more carbonyl containing fraction.

In Pettit's work on cyclobutadiene (12), the second double bond of the cyclobutadiene was formed by the abstraction by diiron enneacarbonyl of two cis vicinal chlorines to form the cyclobutadiene which was then immediately complexed by more diiron enneacarbonyl.

With the prospect that this same type of double bond formation might be possible in the formation of the 1,4dehydrobenzene, attempts were made to replace the hydroxyl groups on the diol with other groups which could be easily displaced, while not causing decomposition of the reagents in the reaction system.

The dihalo derivatives were considered to be the most desirable, and thus were given the most attention. Attempts were made to obtain the dichloroderivative (X) of 1,6-diphenyl-3,4-dimethyl-1,5-hexadiyne-3,4-diol (VII) by treatment with thionyl chloride, but after numerous sets of reaction conditions had been tried, no dichloride was isolable. The reaction either produced black intractable masses of decomposition products, or formed impure nonchlorine containing products which appeared from their infrared spectra to be sulfite esters, a reasonable reaction product in view of the 1,2 arrangement of the hydroxyl groups.

Replacement of the thionyl chloride by phosphorous trichloride again gave only non-chlorine containing products which again gave an infrared spectrum consistent with ester formation, in this case a phosphite ester.

A near success was observed in the reaction of 1,6-diphenyl-3,4-dimethyl-1,5-diyne-3,4-diol (VII) with triphenylphosphine dibromide in dimethylformamide solution (13). However, even running the reaction without external heating gave only an undesired product which gave analyses and nmr spectra consistent with 1,6-diphenyl-3-methylidene-4-methyl-4-bromo-hexa-1,5-diyne (XIII).



It is believed that the desired dibromo compound may actually have been formed, but because of the sterically hindered conditions resulting from the 1,2-arrangement of the bromines, a more stable product was formed by loss of a molecule of hydrogen bromide to give the isolated product.

An attempt to make the dichloroderivative (X) with triphenylphosphine and carbon tetrachloride under reflux gave only starting material containing a trace of some unidentifiable product. Apparently these reaction conditions were too mild.

Two other derivatives were attempted, but neither was

entirely successful. Reaction of 1,6-diphenyl-3,4-dimethyl-1,5-hexadiyne-3,4-diol (VII) with ethyl chloroformate gave a product with only phenyl and methyl peaks in the nmr. No complete structure proof was done, but the spectral evidence is consistent with a carbonate product. Reaction of 1,6diphenyl-3,4-dimethyl-1,5-hexadiyne-3,4-diol (VII) with benzaldehyde to form an acetal was also attempted, but in spite of a moderate yield of product, as identified by nmr, the experimental problems of heavy foaming and poor chromatographic separation resulted in this reaction being set aside from further work.

Because of a lack of success with the diol system, it was decided to try another system which contained a builtin 3,4 double bond. Modeled on the work of Castro and Stevens in synthesizing tolanes (5), it was decided that <u>o-bis(phenylethynyl)benzene (XVI)</u> would be a useful intermediate since it contains three benzene rings to stabilize the 1,4-dehydrobenzene product.

The <u>o</u>-bis(phenylethynyl)benzene (XVI) was synthesized by the method of Castro and Stevens using <u>o</u>-diiodobenzene (XV) which was synthesized by the method of Friedman (14) (Scheme II). The yield of product was 75% of purified crystalline material which analyzed properly. The structure was confirmed by a four mole hydrogen uptake per mole of hydrocarbon during atmospheric pressure hydrogenation over Adam's catalyst. This is consistent with the presence of two acetylene groups. The nmr spectra of both the

SCHEME II



acetylenic and the saturated compounds were also consistent with their assigned structures and thus served as additional proof of structure.

Rearrangement of the <u>o</u>-bis(phenylethynyl)benzene (XVI) to form the 1,4-dehydrobenzene product was attempted using two different palladium reagents. Stirring a benzene solution of the acetylene with the benzonitrile complex of palladium chloride formed no product (15). Changing to the use of an acetonitrile solution with the acetonitrile complex of palladium chloride, because of the weaker bonding in this complex, was more productive. However, again no useful product was obtained. Instead, along with a large recovery of nitrile-palladium complex, only a quantity of brown powder was obtained. Fractional crystallization gave a number of fractions with various melting points. However, all fractions gave essentially the same infrared spectrum, and it was concluded that they were polymers of various molecular weights.

Since molybdenum hexacarbonyl, molybdenum carbonyls complexed with glycol ethers, and cyclopentadienyl cobalt dicarbonyl have all been reported to form tetraphenylcyclobutadiene from tolane (16), reactions were tried between <u>o-bis(phenylethynyl)benzene (XVI)</u> and each of these complexing agents. Again, as in the palladium cases, the only products, other than starting acetylene, were polymers of various molecular weights.

Diiron enneacarbonyl is also well known for its ability to react with certain precursors to form stabilized cyclobutadienes (12). While the use of this compound has been restricted to cases where it was first necessary to abstract two chlorines, thus forming the cyclobutadiene, before complexing with the resultant cyclobutadiene, there was no reason to believe that it should not also function with acetylenes in the manner of other metal carbonyls such as molybdenum. However, even after stirring a reaction mixture of diiron enneacarbonyl and \underline{o} -bis(phenylethynyl)benzene (XVI) in benzene at 40°C. for 72 hours, only contaminated iron carbonyls could be crystallized from the reaction mixture.

Refluxing <u>o</u>-bis(phenylethynyl)benzene (XVI) in benzene with cobalt octacarbonyl for two hours was slightly more successful, but still yielded only a mixture of starting material and polymer.

It has been reported in the literature (17) that tolane reacts with lithium in ether to form the 1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene which slowly rearranges to the 1,4-dilithio-1,2,3-triphenylnaphthalene. Reaction of the dilithiobutadiene with cupric bromide apparently resulted in the formation of tetraphenylbutadiene diradical, but this species immediately dimerized to form the cyclooctatetraene instead of forming the cyclobutadiene.

However, when this lithium reaction was applied to o-bis(phenylethynyl)benzene (XVI), the reaction was found to

proceed extremely slowly. After 90 hours of contact time, hydrolysis of the products yielded much unreacted starting material, and only polymer could be isolated as a product.

Only one fact can be concluded from the consistent formation of polymer from these many attempts to form the 1,4dehydrobenzene. It appears that the benzene ring, of which the 3,4 double bond is a part, is preventing the system from reacting properly. This fact is made clear when the geometry of this system is examined.



First of all, the fact that the 3,4 double bond is part of a benzene ring means that the two cis vicinal bonds will extend at a 60° angle to each other. With this geometry, the two acetylene bonds are placed at such a large distance from each other that they cannot easily achieve the <u>p</u>-orbital overlap necessary for bond isomerization and formation of the cyclobutadiene nucleus. This problem is further complicated by the presence of the 3,4 double bond in a rigid benzene ring, which prevents the bond deformation which is necessary to bring the two acetylene bonds into close proximity with each other.

The result of this is that rather than obtaining intramolecular reactions, intermolecular reactions take place to give polymers which are probably highly cross-linked, since the monomer is bifunctional.

In 1966, Müller, Sauerbier, and Heiss attempted to prepare 1,3-diphenyl-1,4-dehydronaphthalene (XII) by direct photolysis of <u>o</u>-bis(phenylethynyl)benzene (XVI) in methylcyclohexane solution (18). They obtained, instead, a fused azulene derivative. Hoping that sensitization might aid the photochemical reaction, the reaction was repeated using a Hanovia high pressure mercury lamp to photolyze an acetone solution of <u>o</u>-bis(phenylethynyl)benzene (XVI). Instead of obtaining the desired dehydronaphthalene, however, infrared analysis and melting points of the resultant products indicated that a free radical polymerization, probably initiated by an acetoxy radical, had taken place.

Since it had become quite apparent that the acetylene groups in <u>o</u>-bis(phenylethynyl)benzene (XVI) are too rigidly oriented at too great a distance from each other to readily cyclize to a cyclobutadiene system, it was decided to attempt to form other non-benzenoid aromatic systems from <u>o</u>-bis(phenylethynyl)benzene (XVI) in which this condition would not act as so great a hindrance.

The synthesis of diphenylcyclopropenone (III) from tolane has been reported in the literature (7), and the

similarity between tolane and <u>o</u>-bis(phenylethynyl)benzene
(XVI) made it desirable to synthesize the dicyclopropenone
<u>o</u>-phenylene-bis(phenylcyclopropenone) (IV) from <u>o</u>-bis(phenylethynyl)benzene (XVI), and to examine its properties.



Also, it was hypothesized that such a dicyclopropenone should rearrange under irradiation to form the substituted cyclobutene dication, which fits the theoretical conditions for aromaticity.

The initial attempt at forming the dicyclopropenone <u>o</u>-phenylene-bis(phenylcyclopropenone) (IV) was by the method of Seyferth and Damrauer using dichlorocarbene generated from phenyl(trichloromethyl)mercury (Scheme III) (19). This method of carbene generation had the advantage of requiring no harsh reagents, and it produces easily removed by-products. A cyclopropenone product was isolated, as indicated by the characteristic infrared peaks of 1840 and 1620 cm⁻¹, although the presence of an acetylenic peak at 2200 cm⁻¹ indicated that only the monocyclopropenone had been formed (7). The elemental analysis, however, was inconsistent with a simple



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(XXII)

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(XXI)

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monocyclopropenone. A mass spectrum of the product showed mercury peaks as well as chlorine and chloromethyl peaks. With this data in mind, the elemental analysis confirmed a product composed of two molecules of (<u>o</u>-phenylethynylphenyl)phenylcyclopropenone coordinated to one molecule of phenyl-(trichloromethyl)mercury (XXII).

In an effort to increase the rate of decomposition of the phenyl(trichloromethyl)mercury to dichlorocarbene, and thus, increase the concentration of dichlorocarbene in the reaction mixture at any time, the Seyferth method using phenyl(trichloromethyl)mercury with sodium iodide to generate dichlorocarbene was tried (20). However, only phenylmercuriciodide and starting acetylene were isolated. Apparently, the problem is confined to the lack of reactivity of the acetylene and not to the slowness of formation of the carbene.

As a possible means of overcoming this, the phenyl-(trichloromethyl)mercury was added incrementally over 40 hours. However, only the same complexed (<u>o</u>-phenylethynylphenyl)phenylcyclopropenone (XXII) product was isolable, along with some starting material and other by-products.

A reaction of <u>o</u>-bis(phenylethynyl)benzene (XVI) with dichlorocarbane, generated by reaction of chloroform with potassium tertiary but ϕ xide (21) gave only (<u>o</u>-phenylethynylphenyl)phenylcyclopropenone (XXI), as indicated by its infrared spectrum which contained the characteristic peaks of 2200, 1840, and 1620 cm⁻¹; and by the elemental analysis.

Even when an excess of chloroform and potassium tertiary butoxide were used, only the monocyclopropenone could be isolated.

It is apparent that <u>a</u>-bis(phenylethynyl)benzene (XVI) does not add two moles of dichlorocarbene readily. However, exactly what type of association, or other factor, prevents addition of the second mole of dichlorocarbene is unknown.

Moreover, no insight into the nature of this phenomenon could be gathered from the photochemical reactions of this compound or its hydrochloride. Irradiation of (\underline{o} phenylethynylphenyl)phenylcyclopropenone (XXI) with a Hanovia high pressure mercury lamp succeeded only in splitting out carbon monoxide to reform \underline{o} -bis(phenylethynyl)benzene (XVI). Photolysis of the hydrochloride in methanolic HCl formed a number of uncharacterizable products, none of which gave infrared spectra consistent with the product which might be expected from an intramolecular rearrangement to a benzodehydrotropylium salt.

EXPERIMENTAL

General Procedures and Apparatus

Melting points were determined on a Thomas Hoover Capillary melting point apparatus and are uncorrected.

Infrared spectra were obtained on a Perkin-Elmer 237B Grating Infrared Specrophotometer. The sample holders were sodium chloride cells or plates.

Ultraviolet spectra were obtained on a Unicam SP-800 Ultraviolet Spectrophotometer. The sample holders were one centimeter quartz cells.

Nuclear magnetic resonance spectra were obtained on a Varian A-60 high resolution spectrometer using tetramethylsilane as internal reference.

Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

A. 1,6-diphenyl-3,4-dimethyl-1,5-hexadiyne-3,4-diol (VII)

To 24.4g.(1.0 mole) magnesium turnings in a flame dried apparatus was added 15 ml. of a solution of 108.6g.(1.0 mole) ethyl bromide in 250 ml. anhydrous ether. Once the exothermic reaction had begun, 50 ml. ether was added and the remaining bromide solution was added over one hour. Following one further hour of refluxing on a steam bath, 102.12g(1.0 mole) phenylacetylene was added over 15 minutes. After adding 100 ml. ether to obtain a solution, this solution

was refluxed for four hours. After cooling to $0^{\circ}C$. and adding 300 ml of ether, a solution of 43.0q.(0.5 mole) diacetyl in 200 ml. ether was added over 40 minutes to the vigorously stirred solution. The mixture was stored at $0^{\circ}C$. for three days, after which 200g. ice, followed by a mixture of 75g. concentrated sulfuric acid and 200g. ice, was added and the layers were separated. The aqueous layer was extracted with ether $(3 \times 100 \text{ ml.})$. The ether extracts were combined, dried over sodium sulfate, and evaporated to leave an oily yellow-brown solid. This solid was washed with carbon tetrachloride $(4 \times 100 \text{ ml.})$ and the remaining solid was fractionally crystallized from chloroform-petroleum ether $(30 \text{ to } 60^{\circ})$ to give 4.19g. (3.36%) high melting isomer, m.p. 125°C., nmr (CDCl₃): $\tau 2.48$ (multiplet, 10H), $\tau 6.81$ (singlet, 2H), and $\tau 8.19$ (singlet, 6H); and 55.1g. (37.95%) low melting isomer, m.p. 115-7°C., v^{CHCl}3: 3550 (broad), 3000, 2950, 2180, 1600, 1490, 1445, 1378, 1340, 1110, 1065, 945, 925, and 880 cm⁻¹; nmr (CDCl₃): $\tau 2.48$ (multiplet, 10H), $\tau 6.79$ (singlet, 2H), $\tau 8.17$ (singlet, 3H), and $\tau 8.25$ (singlet, 3H).

B. Dibenzoate of 2,3-diphenylethynyl-2,3-butanediol

To 1.45g.(0.005 mole) 2,3-diphenylethynyl-2,3-butanediol (m.p. 117°C.), partially dissolved in 0.79g.(0.010 mole) pyridine, was added 1.41g.(0.010 mole) benzoyl chloride. After heating the mixture on a steam bath for one hour, it was poured into 25 ml. ice water. The resultant

oil was extracted into 5 ml. chloroform. The chloroform was evaporated and the resultant oil was partially redissolved in ether, leaving behind 0.95g. pale gold crystals (m.p. 70° C.). The ether solution was evaporated and the resultant oil was redissolved in methanol. The addition of water precipitated 0.38g. tan solid. Recrystallization from methanol gave 0.30g. (12.0%), m.p. 163-5°C., nmr (CCl₄): τ 2.4 (multiplet, 20H), and τ 7.65 (singlet, 6H).

C. <u>1,3-dioxa-2-ethoxy-4,5-dimethyl-4,5-diphenylethynyl-</u> cyclopentane, Attempted

One average sized crystal of paratoluenesulfonic acid was added to a mixture of 1.45g.(0.005 mole) 2,3-diphenylethynyl-2,3-butanediol (m.p. 117°C.) and 3.70g.(0.025 mole) ethyl orthoformate. The clear solution was allowed to stand at room temperature for 180 hours, and the volatile products were then aspirated off. The remaining colorless oil was chromatographed on silicic acid with an eluent of chloroform. A yield of 1.5g. (85.9%) colorless oil was obtained. v_{max}^{neat} : 2980, 2930, 2250, 1600, 1485, 1440, 1375, 1325, 1270, 1100 (broad), 985, 760, and 690 cm⁻¹; nmr (CCl₄): $\tau 2.5$ (multiplet,10H), $\tau 3.88$ (doublet, J=2cps.,1H), $\tau 6.17$ (pentuplet, J=7.5cps.,2H), $\tau 8.09$, $\tau 8.15$, $\tau 8.29$, $\tau 8.34$ (complex multiplet,6H), and $\tau 8.72$ (triplet, J=7.5cps.,3H).

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D. 2,5-dioxa-3,4-dimethyl-3,4-diphenylethynylcyclopentanone
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To a solution of 1.45q. (0.005 mole) 2,3-diphenylethynyl-1,3-butanediol (m.p. 117°C.) and 1.11g.(0.011 mole) triethylamine in 10 ml. anhydrous ether, stirred at 0⁰C., was slowly added 1.09g. (0.01 mole) ethyl chloroformate. The resultant mixture was stirred at $0^{\circ}C$. for five minutes, and at room temperature for 24 hours. Filtration removed 0.24q. white solid (m.p. $250-4^{\circ}C.$), and the filtrate was evaporated to dryness. The remaining solid was redissolved in 10 ml. ether and a small amount of remaining solid was filtered off. Another evaporation produced 1.40g. residue, m.p. 101-6°C.. Chromatography on silicic acid with a chloroform eluent gave 0.35g. (22.0%) white solid, m.p. $90^{\circ}C.$, vmax^{CHC1}3: 3000, 2235, 1810, 1485, 1445, 1375, 1250 (broad), 1115, 1075, 1055, and 1000 cm⁻¹; nmr (CCl₄): $\tau 2.42$ (multiplet, 10H), τ 7.99(singlet, 3H), and τ 8.16(singlet, 3H).

E. <u>1,3-dioxa-2-phenyl-4,5-dimethyl-4,5-diphenylethynyl-</u> cyclopentane

Two crystals of paratoluenesulfonic acid were added to a solution of 2.90g.(0.01 mole) 2,3-diphenylethynyl-2,3butanediol (m.p. 117°C.) and 1.06g.(0.01 mole) freshly distilled benzaldehyde in 50 ml. dry benzene contained in the flask of a Soxhlet extractor. Calcium hydride was placed in the extractor thimble and the reaction mixture was refluxed through the extractor for three hours. The resultant green solution was treated with solid sodium carbonate to neutralize the acid, and the solvent was evaporated to leave 3.90g. green oil This oil was chromatographed on silicic acid with chloroform eluent to give 1.70g. orange semisolid oil. Crystallization from chloroform-petroleum ether (30-60°) gave 0.65g. (17.2%) light tan crystals, m.p. 111-2°C., $v_{max}^{CHCl_3}$: 3000, 2245, 1600, 1485, 1445, 1375, 1365, 1100 (broad), and 975 cm⁻¹; nmr (CHCl₃): $\tau 2.40$ (multiplet, 15H), $\tau 3.53$ (singlet),1H), and $\tau 7.95$ and $\tau 8.00$ (two singlets, 6H).

F. <u>Reaction of 1,6-diphenyl-3,4-dimethyl-1,5-hexadiyne-</u> 3,4-diol with triphenylphosphine dibromide

To a nitrogen protected refluxing solution of 3.36g. (0.0128 mole) triphenylphosphine in 25 ml. carbon tetrachloride was added 2.05g. (0.0128 mole) bromine in 8.5 ml. carbon tetrachloride over 15 minutes. The resultant cream suspension was refluxed one hour, cooled and filtered, and the collected solid was added unweighted to 15 ml. nitrogen purged dimethylformamide. While stirring the resultant orange suspension, a solution of 1.8520g.(0.0064 mole) 1,6diphenyl-3,4-dimethyl-1,5-hexadiyne-3,4-diol (m.p. $117^{\circ}C$.) in 10 ml. dimethylformamide was added dropwise over 15 minutes. This solution was stirred at room temperature for 48 hours. The solvent was evaporated at reduced pressure and the remaining tan mush was purified by elution from a silicic acid chromatography column with a 10:2 carbon tetrachloride:benzene eluent to yield 1.15g. yellow solid. the solid was recrystallized from ethanol to produce tan crystals of 4-bromo-1,6-diphenyl-3-methylidene-4-methyl-1,5-hexadiyne, m.p. 122-4^oC., Analysis: $C_{20}H_{15}Br$ requires C, 71.05%; H, 4.56%; Found: C, 71,76%; H, 4.46%; $v_{max}^{CS_2}$: 3050, 2200, 1305, 1205, 905, 750, and 680 cm⁻¹; nmr (CCl₄): $\tau 2.69$ (multiplet,10H), $\tau 5.61$ (singlet,2H), and $\tau 7.77$ (singlet,3H).

G. <u>o-bis (phenylethynyl)benzene (XVI)</u>

A mixture of 23.5g. (0.143 mole) cuprous phenylacetylide, 23(52g.(0.072 mole) o-diiodobenzene, and 350 ml. pyridine were refluxed in a nitrogen atmosphere for 18 hours, and the resulting mixture was poured into 1500 ml. water. After extracting with ether $(3 \times 500 \text{ ml.})$, the combined ether extracts were washed successively with 10% hydrochlorid acid $(3 \times 250 \text{ ml.}), 5\%$ sodium bicarbonate $(3 \times 250 \text{ ml.}),$ and water (3 x 250 ml.). The ether solution was dried over magnesium sulfate and was evaporated to leave 20.55g. dark This oil was crystallized from methanol to give 15.5g. oil. brown crystals. The crystals were redissolved in 100 ml. methylene chloride and this solution was decolorized by filtering through a thin pad of Norit. The solution was then evaporated and the product was recrystallized from methanol to give 15.0g. (75.4%) white crystals. $v_{max}^{CHCl_3}$: 3050, 3000, 2200, 1600, 1485, and 1435 cm⁻¹; λ_{max}^{EtOH} (log ϵ): 221.5(4.39), 302(4.30), 312(4.32), and 331(3.95) mµ.;

Analysis: C₂₂H₁₄ requires C, 94.93%; H, 5.07%; Found: C, 94.92%; H, 5.30%.

H. <u>o</u>-bis(2-phenylethyl)benzene (XVII)

Into a 50 ml. round bottom flask assembled in an atomospheric pressure micro hydrogenation apparatus was placed 40mg. Adam's catalyst covered by minimal methanol. After prereducing the catalyst, 0.5576g.(0.002003 mole) o-bis-(phenylethynyl)benzene dissolved in 35 ml. methanol was added and the hydrogenation was allowed to proceed until no further hydrogen uptake was noted. Hydrogen uptake was 188.8 ml. (105% of theoretical at S.T.P.). After removal of the catalyst by filtration, the methanol was evaporated to leave an oil. Vacuum distillation gave 0.4990g. (89.5%) of pale yellow oil, b.p. $144-5^{0}/0.175 \text{ mm.}, v_{\max}^{\text{neat}}: 3055$, 3025, 2925, 2855, 1600, 1495, 1450, 750, and 700 cm⁻¹; $\lambda_{\max}^{\text{EtOH}}$: (log ε): 242.5(2.60)s, 248(2.76)s, 253.5(2.87)s, 259 (2.93), 261 (2.93), 264.5 (2.92), 268 (2.86), and 271.5 (2.69) s m μ .; nmr (CCl₄): τ 2.89 and τ 2.97 (two singlets, 14H), and τ **7.19** (singlet, 8H).

J. Bis (benzonitrile) palladium II chloride

To 30 ml. freshly distilled benzonitrile was added 2.1030g.(0.0118 mole) palladium chloride, and this mixture was stirred at 120°C. for one hour. The resultant redbrown suspension was filtered hot, and the filtrate was then cooled to precipitate an orange-yellow solid which was filtered off. The filtrate was recombined with the previously isolated residue, and this mixture was again heated to 120° C. for one hour. Again, the hot solution was filtered from a trace of undissolved material and was then cooled to precipitate more product. The filtrate was then diluted with petroleum ether $(30-60^{\circ})$, and the solution was chilled to yield a further crop of product. The combined product fractions were dried over phosphorous pentoxide in a vacuum oven at room temperature for 18 hours to yield 3.9050g. (86.1%), $v_{max}^{CHCl_3}$: 3450 (broad), 2990, 2280, 2225, 1600, 1485, 1450, and 1200 (broad) cm⁻¹.

K. Bis (acetonitrile) palladium II chloride

To 30 ml. freshly distilled acetonitrile was added 2.1140q. (0.0119 mole) palladium chloride, and this mixture was refluxed for one hour. The mother liquor was then decanted from the undissolved solid. This liquor was cooled and the resultant precipitate was filtered off. The filtrate was then returned to the reaction flask, and the reaction mixture was refluxed for another hour. Again the mother liquor was decanted, cooled and filtered to yield more product. This process was repeated until no more solid remained undissolved. The isolated yellow-tan solid was then dried over phosphorous pentoxide in a vacuum oven at toom temperature overnight to yield 2.8141g. (91.0%) hexachlorobutadiene: 2960, 2900, and 2300 cm⁻¹; complex. v_{\max}^{Nujol} : 1150, 1020, and 725 cm⁻¹.

L. Reaction of o-bis(phenylethynyl)benzene with dichlorocarbene; Method I.

A solution of 2.78q. (0.010 mole) o-bis (phenylethynyl) benzene and 7.92q. (0.020 mole) phenyl (trichloromethyl)mercury in 50 m. anhydrous nitrogen purged benzene was refluxed under nitrogen for 48 hours. After cooling and filtering off 4.90g. phenyl mercuric chloride, 30 ml. 95% ethanol was added, and the mixture was refluxed for 30 minutes. The resultant solution was evaporated to dryness under reduced pressure to leave 5.80q. red oil. This oil was chromatographed on silicic acid using an eluent of 10:12 benzene:methylenechloride to remove unreacted starting material fractions and by-products. An eluent of chloroform removed the product fraction as 3.39g. golden crystals. Crystallization from methylene chloride-n. hexane gave 1.10 g. $(21.8\% \text{ as } 2(C_{23}H_{140}) \text{ to } 1(C_7H_5HgCl_3) \text{ complex})$, m.p. 146-7°C., $v_{max}^{CHCl_3}$: 3000, 2200, 1840, 1620, 1490, 1470, 1440, 1330, and 1235 cm⁻¹; $\lambda_{\max}^{\text{EtOH}}(\log \epsilon)$: 221(4.43), 234(4.36), 260 (4.37), 273 (4.47), 279.5 (4.42), 302 (4.24), 331 (3.93), and 350 (3.66) mµ.; nmr (CCl₄): τ 2.6 (broad multiplet); Analysis: C₅₃H₃₃HgCl₃O₂ requires C, 63.10%; H, 3.30%; Cl, 10.5%; Found: C, 63.55%; H, 3.58%; Cl, 9.05%.

M. <u>Reaction of o-bis(phenylethynyl)benzene with dichloro-</u> <u>carbene;</u> <u>Method II</u>.

A solution of 1.19g.(0.01 mole) chloroform in 10 ml. benzene was added dropwise during one hour to a rapidly stirred ice cold suspension of 3.36q.(0.03 mole) potassium tertiary butoxide and 1,39g.(0.005 mole) o-bis(phenylethynyl)benzene in 25 ml. benzene protected by a nitrogen atomosphere. When the addition was complete, the ice bath was removed and the mixture was stirred at room temperature for 30 minutes. The reaction mixture was then poured into 50 ml. water and the layers were separated. The aqueous layer was extracted with benzene $(3 \times 10 \text{ ml.})$ and the combined benzene extracts were washed with water $(2 \times 10 \text{ ml.})$. After drying the benzene solution over magnesium sulfate, the solvent was evaporated to leave 1.70g. red oil. After dissolving this oil in 20 ml. anhydrous ether, hydrogen chloride gas was bubbled in to saturate the solution, and the solution was chilled to $0^{\circ}C$. overnight. Filtration isolated 0.35g. off-white solid which was partially dissolved in a mixture of 15 ml. water and 10 ml. ethanol. The mixture was made basic with sodium carbonate, and the mixture was stirred vigorously for 30 minutes to convert the salt form to the free cyclopropenone. The resulting mixture was extracted with ether $(2 \times 10 \text{ ml.})$, the ether extracts were dried over magnesium sulfate, and the ether was evaporated to leave 0.30g. off-white crystals.

Recrystallization from methylene chloride-<u>n</u>. hexane yielded 0.295g. (19.3%) white crystals of phenyl(2-phenylethynylphenyl) qyclopropenone, m.p. 107-8°C., $v_{max}^{CHCl_3}$: 3000, 2200, 1840, 1620, 1485, 1470, 1435, 1330, and 1230 cm⁻¹; λ_{max}^{EtOH} (log ε): 221(4.37), 232.5(4.31), 260(4.40), 273(4.51), 279.5(4.45), 301(4.30), 330(4.04), and 347(3.94) mµ; Analysis: C₂₃H₁₄O requires C, 90.17%; H, 4.60%; Found: C, 89.62%; H, 4.83%. SPECTRA

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