

ALLENE-ACETYLENE REARRANGEMENTS IN COMPOUNDS
RELATED TO DIPHENYLDI-TERTIARY-BUTYLDI-
TERTIARY-BUTYLETHINYLETHANE

BY

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THESIS

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TABLE OF CONTENTS

I. INTRODUCTION	Page 1
II. HISTORICAL	2
The Preparation of Aliphatic Allenes	2
The Preparation of Aromatic Allenes	7
Allenic Acids and Bases	12
Compounds Having Three adjacent Double Bonds	14
Reactions of Allenes	15
III. THEORETICAL	24
IV. DISCUSSION OF EXPERIMENTAL RESULTS	30
V. EXPERIMENTAL	42
Preparation of Trimethylacetyl Chloride	42
Preparation of Phenyl <u>i</u> -Butyl Ketone	42
Preparation of Phenyl- <u>i</u> -butyl- <u>i</u> -butylethynyl	
Carbinol	43
Attempted Reduction of the Carbinol with Titanium	
Trichloride	44
Preparation of Phenyl- <u>i</u> -butyl- <u>i</u> -butylethynylbromo-	
methane	44
Hydrolysis of Phenyl- <u>i</u> -butyl- <u>i</u> -butylethynylbromo-	
methane	45
Attempt to Couple the Bromide with Copper Bronze	45
Reaction of the Bromide with 40% Sodium Amalgam	45
Attempted Cleavage of the Ethanes with 40% Sodium	
Amalgam	48
Reduction of the Bromide with Zinc and Alcohol	49
Reaction of the Bromide with Lithium	49

TABLE OF CONTENTS
(cont.)

Preparation of 1-Phenyl-1,3-di- <u>t</u> -butylallene	Page 50
Attempt to Add <u>p</u> -Thiocresol to 1-Phenyl-1,3- di- <u>t</u> -butylallene	51
Ozonolysis of 1-Phenyl-1,3-di- <u>t</u> -butylallene	51
Preparation of Phenyl- <u>t</u> -butyl Carbinol	52
Preparation of Phenyl- <u>t</u> -butylbromomethane	53
Preparation of Phenyl- <u>t</u> -butylacetic Acid	53
Isolation of Symmetrical Diphenyl-di- <u>t</u> -butyl- ethane	54
The Action of Ozone on Phenyl- <u>t</u> -butylacetic Acid	54
Preparation of 1-Phenyl-1,3-di- <u>t</u> -butyl-3- carboxyallene	54
Preparation of 1-Phenyl-1,3-di- <u>t</u> -butyl-3- carbonethoxyallene	55
Hydrolysis of the Methyl Ester	56
Ozonolysis of the Methyl Ester	56
Preparation of Trimethylpyruvic Acid	57
Preparation of Methyl Trimethylpyruvate	57
VI. SUMMARY	59
VII. BIBLIOGRAPHY	60
VITA	

INTRODUCTION

The preparation of symmetrical diphenyldi-*t*-butyldi-*t*-butylethynylethane has been undertaken as one of a series of investigations concerning the effect of acetylenic groups on the central carbon-carbon linkages of hexa-substituted ethanes. These studies which have been carried out by Marvel and his students¹ have shown that many of the acetylenic compounds tend to isomerize and undergo various rearrangements.

During the course of this investigation it was found that certain acetylenic compounds underwent allylic rearrangements producing the isomeric allenes. This rearrangement has been used for the synthesis of an allenic acid, a type of compound whose preparation has been undertaken by numerous investigators who wished to test experimentally the prediction made by Van't Hoff² in 1877 that an allene of the type $\begin{array}{c} a \quad \quad b \\ \diagdown \quad \diagup \\ C=C=C \\ \diagup \quad \diagdown \\ b \quad \quad a \end{array}$ would be an asymmetric molecule capable of existing in dextro and laevo forms.

III. THEORETICAL

Allylic Rearrangements in the Acetylene Series

The allylic rearrangement or the so-called α, γ shift is apparently a common type of rearrangement¹⁰. Numerous examples have been cited in which ethylenic compounds undergo this shift, but its significance in the acetylene series has not been as widely recognized.

This rearrangement involves the three carbon systems illustrated below in which the substituent X shifts from carbons 1 to 3 and the double bond changes from the 2,3 to the 1,2 position.

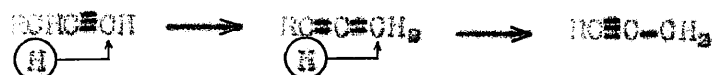


In the case of an acetylenic compound this rearrangement produces an allene although the allene may be unstable and undergo further rearrangement.

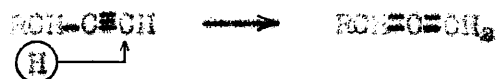


a) Migration of Hydrogen

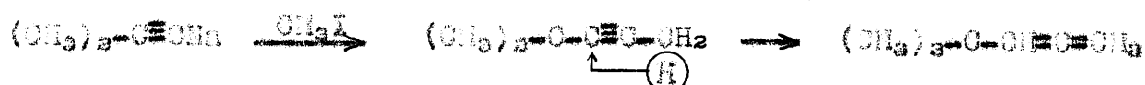
The isomerization of monosubstituted acetylenes by the action of alcoholic alkali has been summarized in a paper by Favorskii.¹⁷ He found that the extent of the rearrangement depended upon R, the substituting group. If R is primary, a disubstituted acetylene is produced, presumably by a second prototropic change.



If R is secondary, the rearrangement stops at the allene stage.



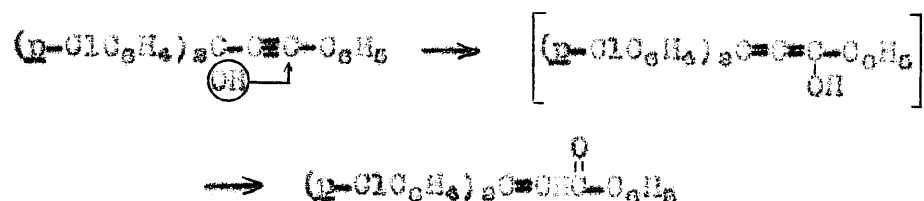
Favorskii did not state whether or not this rearrangement would take place if R were tertiary. However, he did find that methyl-t-butylacetylene is incapable of existing. The reaction of t-butylethynylsodium with methyl iodide yields t-butylallene instead of the expected methyl t-butylacetylene.



b) Migration of an Hydroxyl Group

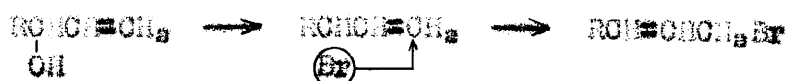
This rearrangement is commonly known as the Meyer-Schuster shift and occurs with many acetylenic carbinols^{78, 79, 80, 81} in the presence of acid reagents.

Meyer and Schuster⁷⁸ proved that this reaction involves a migration of the hydroxyl rather than one of the substituting groups by studying the rearrangement of di-p-chlorophenylphenylethynyl carbinol. An allenic enol of the type indicated below may be an intermediate in this reaction.

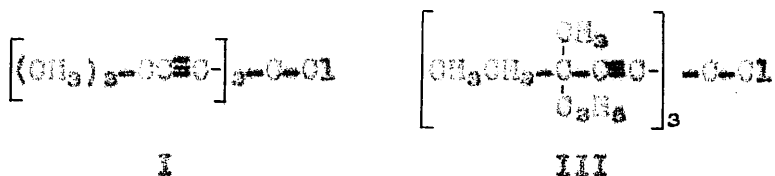


c) Migration of a Halogen

In the ethylenic series, the 1,3 shift of a halogen transformation has been well established. For example, Bouis¹⁶ obtained rearranged bromides when treated substituted allyl alcohols with phosphorus tribromide. Small amounts of the normal bromides were also isolated¹⁶.



This transformation is not yet well established in the acetylenic series but results obtained recently in this laboratory⁸³ seem to indicate that transformations of this sort may take place. The following acetylenic halides dimerize when heated: (I) tri-*t*-butylethynylmethyl chloride, (II) tri-*t*-butylethynylmethyl bromide and (III) tri-(3-methyl-3-ethylpentynyl-1)-methyl chloride.



It is assumed that the first step is an allylic rearrangement and that the resulting halogen substituted allenes dimerize at the temperature under which the reaction is carried out.



c) Migrations Involved in the Reactions of Organo-Metallic Compounds

Grignard reagents prepared from allyl halides in some cases give products whose formation involves rearrangements. Since in most cases some of the normal products are also isolated it will be assumed in the following discussion that the rearrangements occur, not in the preparation of the organo-metallic compounds, but in the formation of the products that result from their reactions.

Gilman and Harris⁸⁴ found that cinnamylmagnesium chloride gives phenylvinylacetic acid when carbonated.

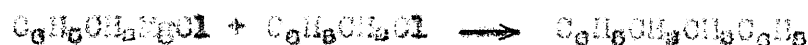


Austin and Johnson⁸⁴ made a thorough investigation of the reactions of benzylmagnesium chloride and found that some of them

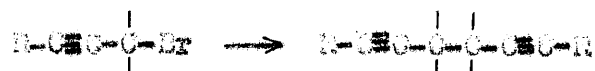
gave the normal products but others gave products which resulted from an allylic rearrangement.



The results with alkyl halides indicate that the Wurtz or coupling reaction is normal.

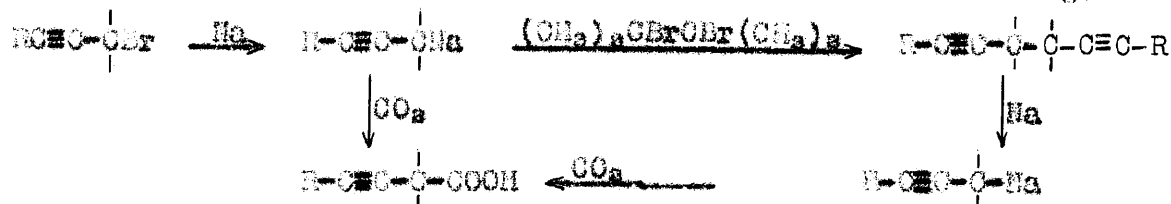


This would tend to support the belief that in preparing various acetylenic ethanes from the bromides by coupling them with a metal M, the first product obtained is the normal one.



The metal M may be silver, magnesium, sodium or lithium. This conclusion has been reached by Farley²⁵ in his study of symmetrical tetraphenyldi-*t*-butylethynylethane and its rearrangement products.

In establishing the structures of several acetylenic ethanes¹, the cleavage with sodium or potassium has yielded metal alkyls which can be carbonated to give acids. These acids were also prepared from the original bromides which had been coupled to give the ethanes. In a few cases, the bromide was converted into the Grignard reagent instead of the sodium alkyl before carbonating.

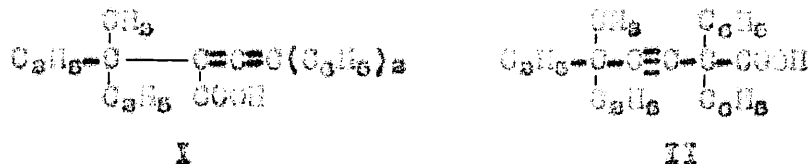


The possibility of allenic rearrangements during the formation of these acids was not taken into account. In that case these

acids would have structures of the type indicated below.



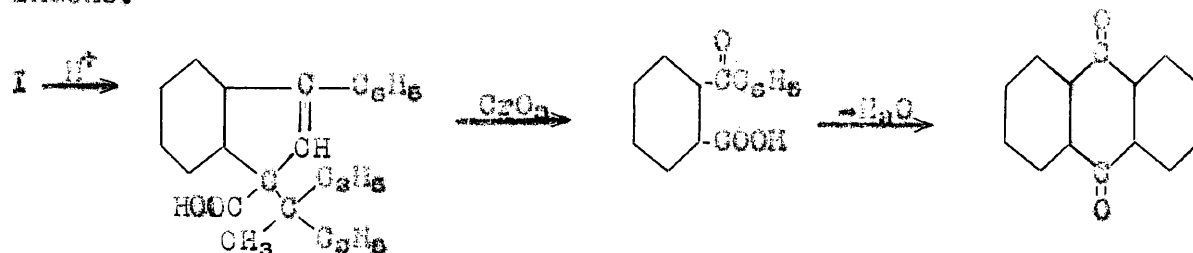
In most cases the only data given on the acids were their analyses and neutral equivalents. Harmon¹ and Stampfli¹ determined the molecular weights of their acids and found them to be monomeric. Harmon oxidized the acid prepared from diphenyl-(3-ethyl-3-methyl-pentynyl-1)-bromomethane and the products obtained can be explained more easily on the basis of the allene structure (I) than by the acetylene structure that was given (II).



Potassium permanganate oxidation gave benzophenone and benzoic acid.



Chromium trioxide in acetic acid also gave the benzophenone and benzoic acid but the acidity of this reagent caused an allene-indene rearrangement too, and the o-benzoylbenzoic acid and anthraquinone which were produced can be explained as oxidation products of the indene.

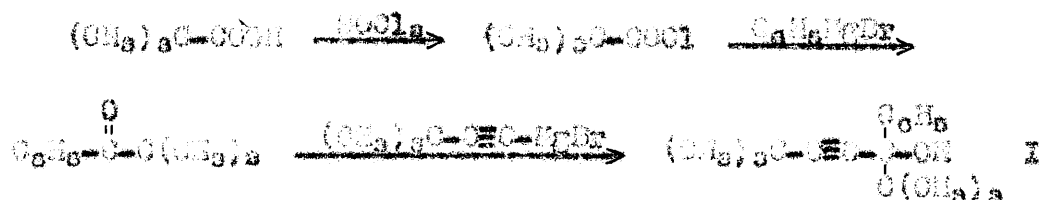


In order to determine with any degree of certainty whether these acids are allenes or acetylenes they should be ozonized as other types of oxidation must be carried out under conditions which are likely to cause rearrangements.

IV. DISCUSSION OF THE EXPERIMENTAL RESULTS

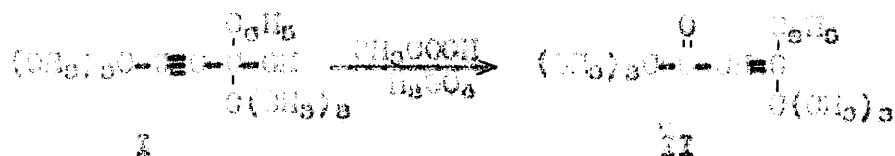
The purpose of this investigation was originally to study the properties and reactions of symmetrical diphenyldi-*t*-butyldi-*t*-butylethynylethane but some of the reactions of the intermediate phenyl-*t*-butyl-*t*-butylethynylbromomethane seemed to merit a more detailed study and consequently the major portion of the investigation deals with the reactions of this compound rather than those of the ethane.

Phenyl-*t*-butyl-*t*-butylethynyl carbinol (I) was prepared by the following series of reactions:



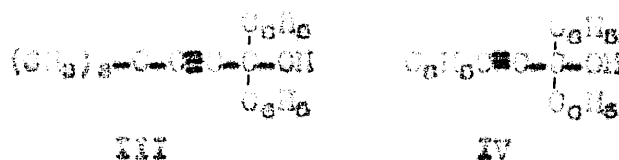
The trimethylacetic acid⁸⁶ was converted into trimethylacetyl chloride⁸⁷ by means of freshly purified thionyl chloride. Purification of the commercial thionyl chloride raised the yield of acid chloride from approximately 50% to 80%. The trimethylacetyl chloride was treated with phenylmagnesium bromide to give phenyl *t*-butyl ketone which has previously been described by Ref⁸⁸. The ketone was added to an ether suspension of *t*-butylethynylmagnesium chloride which had been prepared by the method of Salsberg and Marvel¹. The physical constants of the resulting carbinol (I) checked quite closely with those given by Thompson⁸¹ who originated this method of preparation, but they differed rather widely from those given by Holst for the same compound.⁸⁹ It will be shown later that Holst's sample contained quite an appreciable amount of phenyl-*t*-butyl carbinol.

Thompson²¹ found that the carbinol underwent the usual Meyer-Johuster shift forming phenyl-1-butylpivaloyethylene (II) when heated with glacial acetic acid containing a little sulfuric acid²⁰.



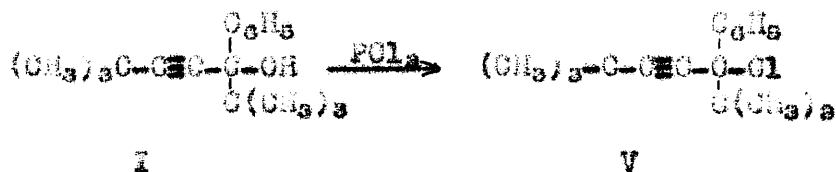
The carbinol (I) was found to be less reactive than those with two phenyl groups on the carbon carrying the hydroxyl group.

Diphenyl-1-butylethynyl carbinol²² (III) and diphenylphenylethynyl carbinol²³ both react with titanous chloride at room temperature to



give the corresponding ethines or their rearrangement products while the carbinol (I) did not react with titanous chloride even when warmed to 50°.

Other acetylenic carbinols¹ have been converted into the corresponding chlorides or bromides by treating them with phosphorus trichloride or tribromide at 0° in petroleum ether solution. When the carbinol (I) was treated with phosphorus trichloride for two hours at 0°, no reaction occurred. Thompson²¹ reported that he obtained a 79% yield of phenyl-1-butyl-1-butylethynylmethyl chloride (V) by this procedure but the density and refractive index of his product were approximately the same as those of the carbinol.

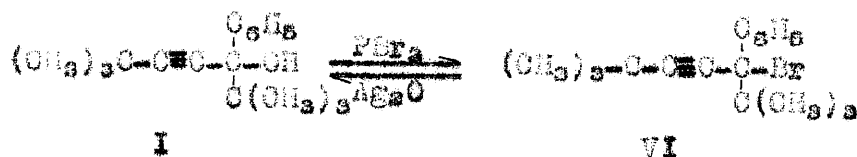


In the present work, the reaction was carried out under various conditions and the results are summarized below.

Temperature	Time (hours)	n_D^{20}	% Chlorine
0°	2	1.5035	trace
25°	30	1.5074	3.5
30°	24	1.5200	11.5
65°	6	1.5204	no analysis

The refractive index of the carbinol (I) was 1.5035 and the theoretical chlorine content of the chloride (V) is 13.5%. These results indicate that the conditions necessary to obtain a reaction with phosphorus trichloride cause part of the carbinol to rearrange, probably by the Meyer-Schuster shift, into a compound which no longer reacts with phosphorus trichloride.

Further attempts at preparing a pure chloride were abandoned when it was found that the corresponding bromide (VI) was very easily prepared. The bromide was converted back to the carbinol by means of moist silver oxide in order to prove that no rearrangement had taken place during its preparation.



The molecular refraction of this bromide was found to be 4.04 higher than the calculated value. The reason for this abnormally high value is not understood as the carbinol from which it was prepared showed an exaltation of only 0.63.

The bromide (VI) gave an immediate precipitate with alcoholic silver nitrate but its reactions indicate that it is less

active than the previously prepared acetylenic bromides¹. It did not react with copper bronze at room temperature⁸⁸ and its reaction with 40% sodium amalgam was not like that of any previously observed bromide of this type.

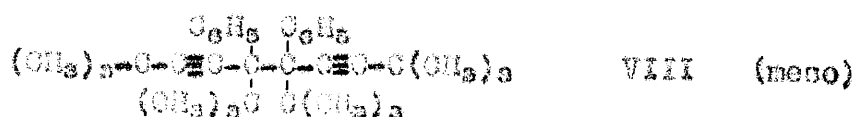
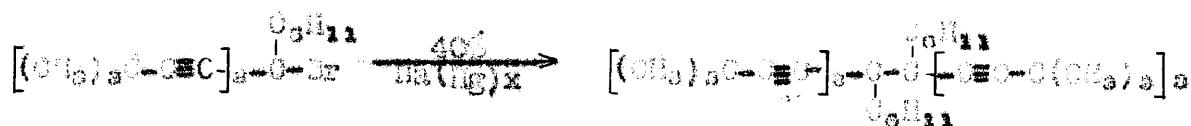
This reaction apparently did not give the expected sodium alkyl except perhaps in very small amounts (VII) although the two previous investigators^{81,89} reported that it did.



Organo-sodium compounds usually have a dark red color^{1,88}, but an ether solution of the bromide (VI) gave a yellowish-green solution when shaken with 40% sodium amalgam. Stampfli¹ observed that diphenyl-1-butylethynylbromomethane also developed this yellowish-green color when shaken with the amalgam but it soon turned to the usual dark red. An organo-sodium compound of some sort must have been formed though, for it required more than a trace of the decomposition reagent to remove the green color from the solution. The exact amounts required to remove this color could not be determined as the end-points were very indefinite and were masked by a finely divided gray precipitate.

As nearly as it could be determined the products obtained by decomposing the green solution were the same regardless of the material added. Tetramethylethylenedibromide and water gave the same mixture of products. About 35% of the bromide was converted into a mixture of solids, 15% into a liquid boiling at 83°/1 mm. and 30% into another liquid boiling at 195°/1 mm. The solids were probably a mixture of the two stereoisomeric ethanes (VIII and IX).

Gillesspie and Marvel¹ observed a similar coupling with 40% sodium amalgam in the case of cyclohexyldi-*t*-butylethynylbromomethane.

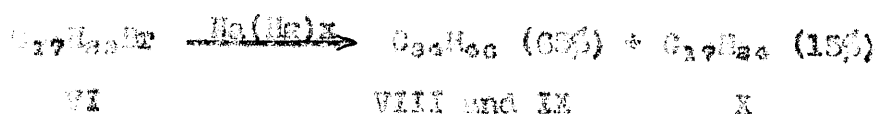


By fractional crystallization the more insoluble ethane was obtained pure, but numerous attempts at purifying the more soluble isomer were unsuccessful. The more soluble fractions yielded a white crystalline material which gave the same elementary analysis and molecular weight that pure ethane did, but it melted over a ten degree range, indicating that it was probably a mixture of the two stereoisomeric forms. The previous workers^{21,22} reported that this product melted over a two degree range.

The physical constants of the lower boiling liquid indicated that it was probably 1-phenyl-1,3-di-*t*-butylallene (X). The structure of this compound will be discussed later.

The higher boiling liquid was extremely viscous at room temperature. A few crystals of the ethanes (VIII and IX) separated on long standing but the major portion did not crystallize. It was probably an impure mixture of the ethanes.

The reaction of the bromide with sodium amalgam can be summarized in the following equation:



The mechanical losses in working with small amounts of liquids are large enough to account for the remaining 30%.

The presence of the reduced compound $\text{C}_{17}\text{H}_{34}$ in the cases where the green solution was decomposed by water would indicate that the sodium alkyl (VII) was present but the facts that decomposition with tetramethylethylenedibromide gave the same reduced product (X) and that the pure ethanes (VIII and IX) do not react with 40% sodium amalgam tend to disprove its existence.

A similar case of reduction without any apparent cause has been recorded by Schlenk and Bergmann⁸⁵. They treated an ether solution of the di-sodium derivative of tetraphenylallene with methyl iodide and obtained a monomethyl derivative (see page 16). The sodium atom on the central carbon of the allene has been replaced by hydrogen.



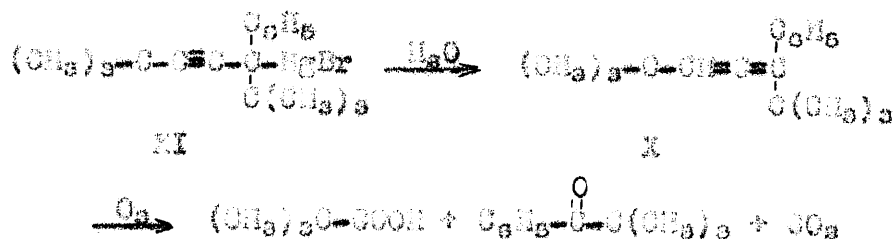
The most probable explanation of these anomalous reductions is that the sodium alkyl is sufficiently active to cleave the ether.



The bromide yielded the same mixture of hydrocarbons when refluxed with zinc dust in 80% alcohol or when an attempt was made to prepare the lithium alkyl using Gilman's⁸¹ method. In both cases the Wurtz or coupling reaction predominated.

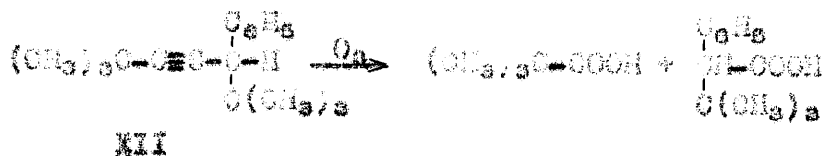


However, the bromide did give an 85% yield of the corresponding Grignard reagent (XI) along with a small amount of coupled product which proved to be the same mixture of ethanes. When decomposed with water, this reagent gave a hydrocarbon $C_{17}H_{24}$ which was proven by ozonolysis to be 1-phenyl-1,3-di-t-butylallene (X).



The trimethylacetic acid and the phenyl t-butyl ketone were both identified by means of derivatives.

The alternative acetylenic structure (XII) of the hydrocarbon $C_{17}H_{24}$ would also give trimethylacetic acid on ozonolysis but the other product should be phenyl-t-butylacetic acid.

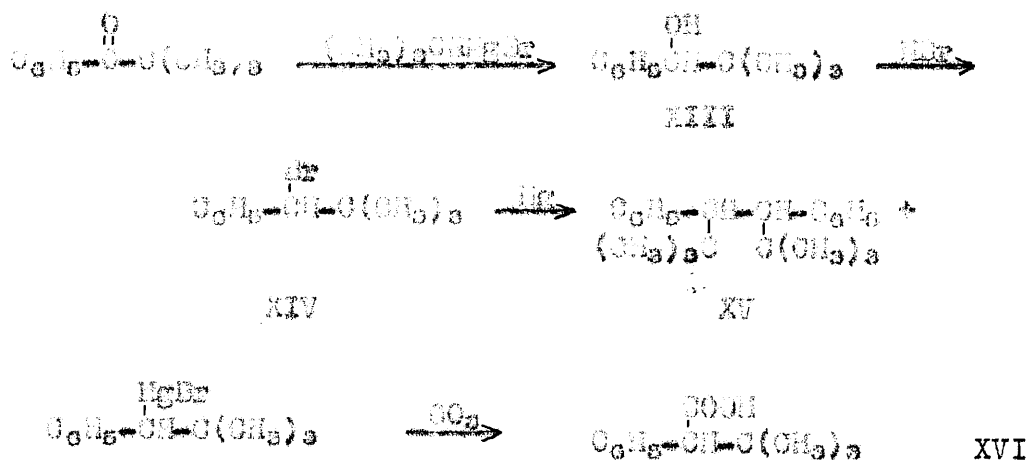


The possibility that the ozone might oxidize the phenyl-t-butylacetic acid to phenyl t-butyl ketone was thought to be worth considering.



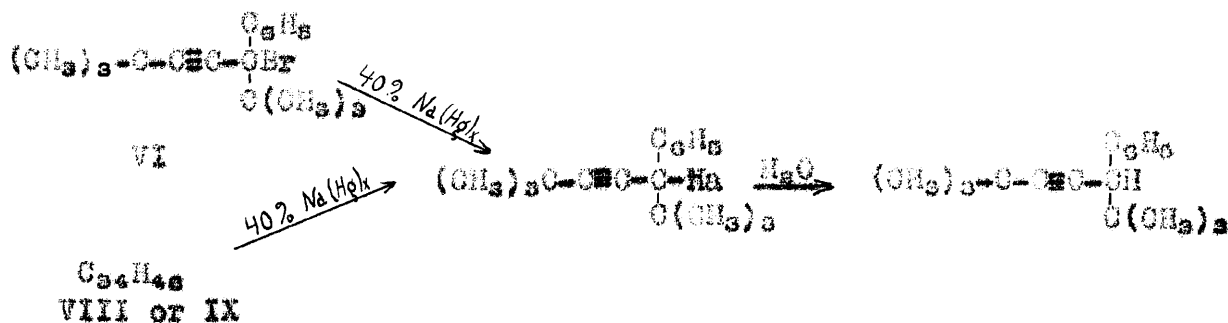
If this were true then obviously the ozonolysis would be useless in deciding between structures X and XII. However, the phenyl-t-butylacetic acid was synthesized and it was found that it did not give phenyl t-butyl ketone when ozonized.

The phenyl-t-butylacetic acid was prepared from phenyl t-butyl ketone by means of the following series of reactions:



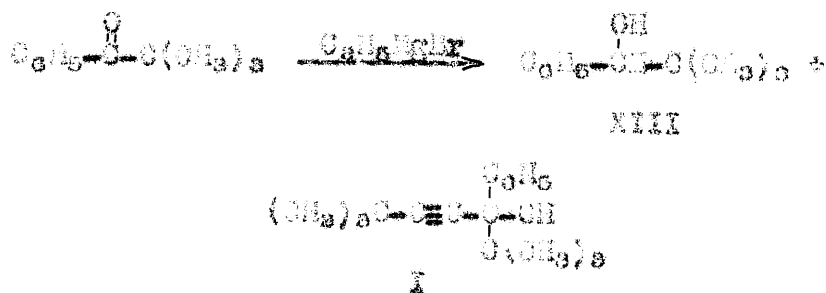
Phenyl t-butyl ketone was reduced to phenyl-t-butyl carbinol by the method of Ramart-Lucas²² using isopropylmagnesium bromide. The carbinol (XIII) was converted into phenyl-t-butylbromomethane (XIV) by means of dry hydrogen bromide. This method was used by Lepin²³. The bromide was then converted into the Grignard reagent and carbonated to give phenyl-t-butylacetic acid.

In preparing the above Grignard reagent, a large amount of the coupled product, diphenyldi-t-butylethane (XV), was formed as a by-product. This compound has been previously described by Conant and Blatt²⁴. It proved to be identical with Holst's "phenyl-t-butyl-t-butylethynylmethane" (XVI) the preparation of which he has reported by two different methods²⁵; first by hydrolyzing the "sodium alkyl" prepared from the bromide (VI); second by hydrolyzing the "sodium alkyls" prepared from either of the stereoisomeric ethenes (VIII and IX).

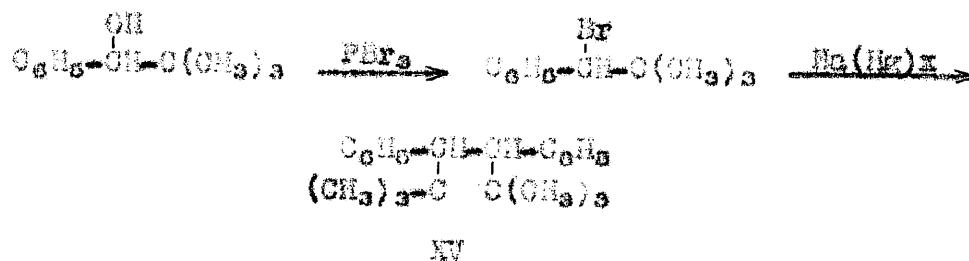


The formation of this compound (XV) from the bromide (VI) can be readily understood but its formation from the two stereoisomeric ethanes is rather difficult to explain.

It has been shown by Conant and Blatt²⁸ that in some cases Grignard reagents may reduce highly branched carbonyl compounds instead of adding to them. It was found during this investigation that a 95% yield of phenyl-*t*-butyl carbinol could be obtained by reducing phenyl *t*-butyl ketone with isopropylmagnesium bromide²⁸. In preparing the carbinol (I) some of the phenyl *t*-butyl ketone was probably reduced by excess ethylmagnesium bromide and in that case the resulting carbinol was contaminated with phenyl-*t*-butyl carbinol.



The physical constants of Holst's carbinol indicate that it was impure, probably containing phenyl-*t*-butylcarbinol. In this case his bromide (VI) would have been contaminated with phenyl-*t*-butylbromomethane which would have coupled to give diphenyldi-*t*-butylethane when treated with sodium amalgam.



Posner²⁹ has shown that vinyl compounds add thiophenols. With styrene the reaction proceeds according to the following

equation:

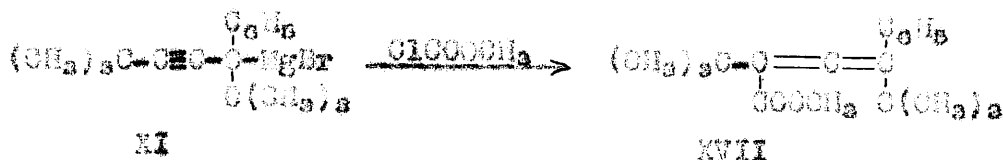


Carothers⁵⁷ found that divinylacetylene would add two molecules of *p*-thiocresol when the mixture of these compounds was allowed to stand at room temperature. He also found that the reaction was powerfully accelerated by light.

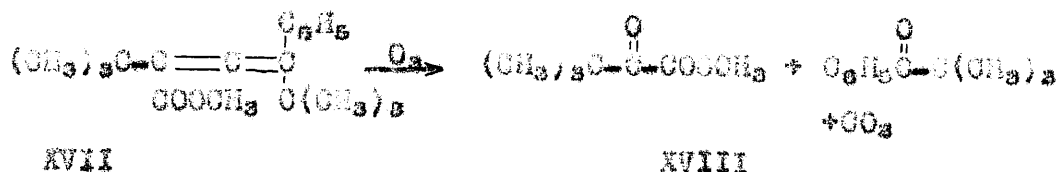


An attempt was made to add *p*-thiocresol to 1-phenyl-1,3-di-*t*-butylallene, but apparently no reaction occurred. This was probably due to the steric effect of the *t*-butyl groups.

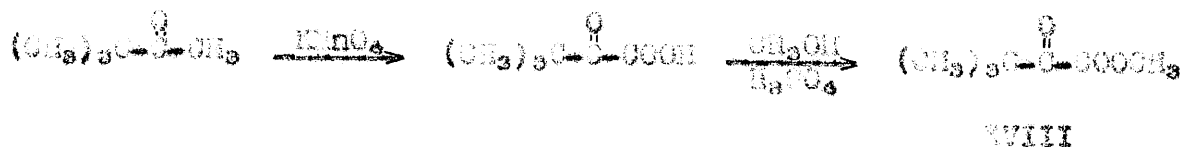
The Grignard reagent (XI) yielded 1-phenyl-1,3-di-*t*-butyl-3-carbomethoxyallene (XVII) when treated with methyl chlorocarbonate.



The structure of this compound was established by ozonolysis.

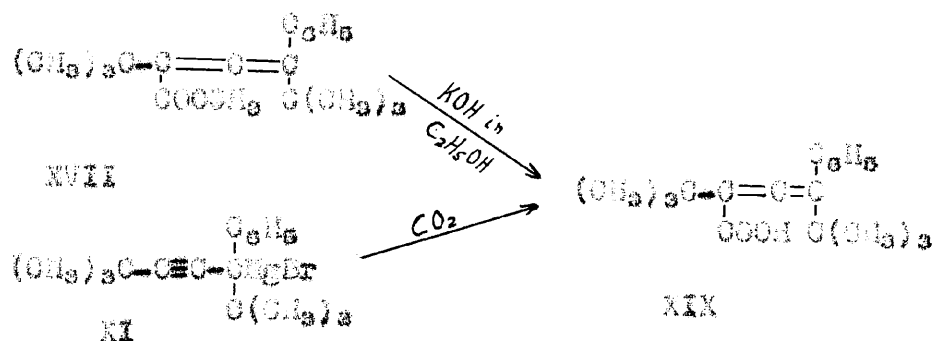


The resulting carbonyl compounds were converted into 2,4-dinitrophenylhydrazones. The methyl trimethylpyruvate (XVIII) was identified by comparing its 2,4-dinitrophenylhydrazone with an authentic sample. The methyl trimethylpyruvate was synthesized by the method of Richard⁵⁸ starting with pinacolone.

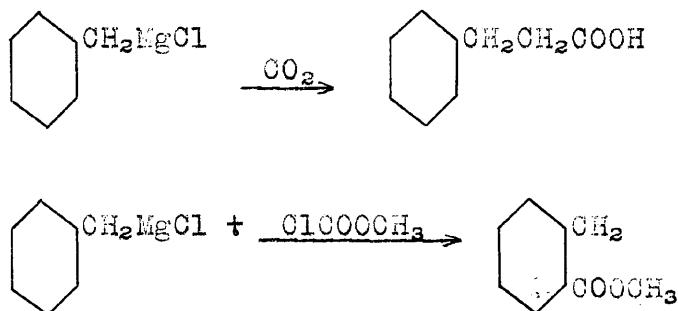


Attempts at isolating the 3,4-dinitrophenylhydrazone of phenyl t-butyl ketone from the mixture were unsuccessful. It is more soluble than the corresponding derivative of methyl trimethylpyruvate and more difficult to purify.

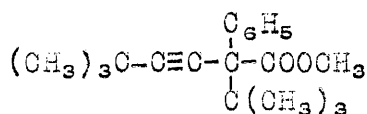
The methyl ester (XVII) was hydrolyzed by prolonged refluxing with alcoholic potassium hydroxide to give 1-phenyl-1,3-di-t-butyl-5-carboxyallene (XIX). It was also found that the same allenic acid could be prepared more easily by carbonating the Grignard reagent (XI) directly.



Had the Grignard reagent (XI) given different acids when treated with carbon dioxide and with methyl chlorocarbonate, it would not have been surprising for Austin and Johnson⁶⁴ found that benzylmagnesium chloride gave the normal product, phenylacetic acid, when treated with carbon dioxide, but with methyl chlorocarbonate it gave the abnormal product, the methyl ester of p-toluic acid.

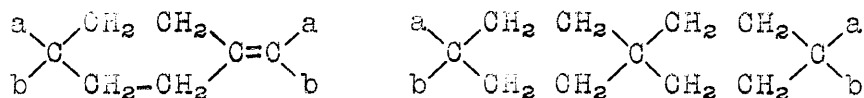


The alternative acetylene structure (XX) for the methyl ester is definitely eliminated as it could not possibly give methyl trimethylpyruvate on ozonolysis.



XX

According to Van't Hoff's prediction² that an allene of the type $\begin{smallmatrix} a & & a \\ & \text{C}=\text{C}=\text{C} & \\ b & & b \end{smallmatrix}$ would be an asymmetric molecule, the allenic acid (XIX) should be resolvable. The fact that spiranes⁹⁹ of the type indicated below have been found to be optically active makes it seem very probable that this will be true also in the case of allenes, for they may be considered as spiranes having two membered rings.



V. EXPERIMENTAL

Preparation of Trimethylacetyl Chloride

A mixture of 400 g. of trimethylacetic acid and 650 g. of thionyl chloride that had previously been purified by distillation from linseed oil was placed in a 3-l. flask equipped with a reflux condenser and a gas trap. After being refluxed gently for three hours, the mixture was fractionally distilled using a two-foot carborundum-packed column. The yield was 380 g. (80%) of a product boiling at $100-4^{\circ}$ at atmospheric pressure.

Preparation of Phenyl t-Butyl Ketone

A solution of 130 g. of trimethylacetyl chloride in 400 cc. of dry ether was placed in a 2-l. three-necked flask and cooled by means of an ice-salt mixture. A slow stream of dry nitrogen was passed through the flask and 1650 cc. of 1.6 N. phenylmagnesium bromide was added during a period of 5 hours. The reaction mixture was decomposed with ice and hydrochloric acid. The ether layer was washed with sodium bicarbonate solution, then water, and dried over anhydrous sodium sulfate. The ether was distilled off at atmospheric pressure and the remaining liquid fractionated under reduced pressure. The yield was 116 g. (67%) of a liquid which boiled at $80-4^{\circ}/3 \text{ mm.}/110^{\circ}$; n_D^{20} 1.5103. When first distilled it was colorless but it became slightly yellow on standing. This product probably contained a small amount of phenyl-t-butyl carbinol but it was sufficiently pure for subsequent preparations.

Preparation of the 2,4-Dinitrophenylhydrazones of

Phenyl t-Butyl Ketone

In the following work all 2,4-dinitrophenylhydrazones were

prepared according to the method of Allen¹⁰⁰. When the carbonyl compound could be obtained in a relatively pure form it was found advantageous to weigh out the materials and use the calculated quantities as the resulting products were much more easily purified.

One gram of 2,4-dinitrophenylhydrazine and 0.83 g. of phenyl *t*-butyl ketone were dissolved in 100 cc. of absolute alcohol and the solution was refluxed for 3 minutes. After 3 cc. of concentrated hydrochloric acid had been added, the refluxing was continued for another three minutes. Hot water was added until it produced a slight turbidity and the solution was allowed to cool slowly. The resulting yellow needles melted at 194-5° (cor.) after two recrystallizations from 95% alcohol.

Anal. Calcd. for $C_{17}H_{15}O_6N_4$: N, 16.37. Found: N, 16.14.

Preparation of Phenyl-*t*-butyl-*t*-butylethynyl Carbinol

The method of preparation was essentially the same as that used by Thompson⁸¹ but the physical constants differ somewhat from those reported by him.

A solution of 162 g. of phenyl-*t*-butyl ketone in 250 cc. of dry ether was added to the *t*-butylethynylmagnesium bromide prepared from 700 cc. of 1.41 N. ethylmagnesium bromide and 82 g. of *t*-butylacetylene¹ during a period of three hours. The mixture was allowed to stand over night and was decomposed with ice and ammonium chloride solution. The ether layer was washed with water and dried over anhydrous magnesium sulfate. After removing the ether, the product was carefully fractionated under reduced pressure using a Widmer column. It is rather difficult to remove the last traces of the unreacted phenyl *t*-butyl ketone and the phenyl *t*-butyl carbinol. The yield was 200 g. (68%) of a colorless viscous liquid boiling at

135-8°/4 mm./160°; n_D^{20} 1.8625; d_4^{20} 0.9334; M_b , found, 77.37; calcd., 76.65.

Anal. Calcd. for $C_{17}H_{24}O$: C, 83.54; H, 9.91. Found: C, 83.43; H, 10.09.

Attempted Reduction of the Carbinol with Titanium Trichloride

Five grams of the carbinol was dissolved in 25 cc. of absolute alcohol and treated with 3 cc. of approximately 50% titanium trichloride solution according to the method used by Goebel⁴⁶ in the preparation of Moureu's hydrocarbon from diphenylphenylethynyl carbinol. The mixture was shaken for several minutes and then heated on the steam cone. The violet color of the solution was not discharged and the starting material was recovered.

Preparation of Phenyl-t-butyl-t-butylethynylbromomethane

A solution of 30 g. of phenyl-t-butyl-t-butylethynyl carbinol in 150 cc. of low boiling petroleum ether was placed in a 200 cc. glass stoppered bottle and 5.4 cc. of phosphorus tribromide was added. After standing about 10 minutes at 25° the solution became slightly turbid. On standing over night a yellowish layer of phosphorous acid settled out and the remaining solution was clear. The upper layer was washed thoroughly with sodium bicarbonate solution and dried over anhydrous magnesium sulfate. The ether was removed and the remaining liquid was vacuum distilled. The yield was 34.4 g. (91%) of a clear slightly yellow liquid; b.p., 115-7°/1 mm./155°; n_D^{20} 1.5400; d_4^{20} 1.1081; M_b , found: 86.93; calcd., 82.89.

Anal. Calcd. for $C_{17}H_{23}Br$: C, 66.43; H, 7.55; Br, 26.02. Found: C, 66.54; H, 7.47; Br, 25.75, 25.82.

Mol. Wt.: Calcd., 307.1; Found: 282 (cryoscopic in camphor).

Hydrolysis of Phenyl-*i*-butyl-*i*-butylethynylbromomethane

The method used was that described by Conant, Small and Sloan¹⁰¹ for the hydrolysis of dicyclohexylphenylchloromethane.

Seventeen grams of silver nitrate was dissolved in water and treated with a slight excess of 10% sodium hydroxide solution. The resulting silver oxide was filtered, washed thoroughly with distilled water, and added to a solution of 4.4 g. of phenyl-*i*-butyl-*i*-butylethynylbromomethane in 100 cc. of acetone that had previously been refluxed over potassium permanganate. The mixture was refluxed 4 hours and then filtered. The acetone was removed and remaining liquid dissolved in petroleum ether and dried over anhydrous magnesium sulfate. The solvent was removed and the product vacuum distilled; b.p., 105-10⁰/1 mm./145⁰; n_D^{20} 1.5020; d_4^{20} 0.9332.

Attempt to Couple the Bromide with Copper Bronze

This method has been used by Farley⁸⁸ for the coupling of diphenyl-*i*-butylethynylbromomethane.

A solution of 3 g. of phenyl-*i*-butyl-*i*-butylethynylbromomethane in 75 cc. of dry ether was shaken with 5 g. of copper bronze powder for 4 days. At the end of this time, the solution was filtered and washed with water. On evaporation of the ether the starting material was recovered and the washings contained only a trace of bromide ions.

The Reaction of the Bromide with 40% Sodium Amalgam

In each case about 200 cc. of dry ether and the 40% sodium amalgam were placed in a 500 cc. round bottom flask having a stop-cock sealed into the side. The air was flushed out with a stream of dry oxygen-free nitrogen¹⁰² and the phenyl-*i*-butyl-*i*-butylethynylbromomethane added. The flask was securely stoppered and placed on

mechanical shaker. A lubricant for stopcocks that has been described by Meloche and Frederick¹⁰³ was found very useful as ordinary lubricants were dissolved out by the ether. A yellowish green color appeared after 10 or 25 minutes but it did not become much more intense on further shaking.

The flask was placed in an ice bath for a few minutes to freeze the amalgam and the solution was decanted through the stopcock into another flask of similar construction, treated with the appropriate reagent until the yellowish-green color disappeared, and then a slight excess of the reagent was added. All of the above operations were carried out under nitrogen. In all cases there remained a finely divided gray suspension which settled out slowly. The ether solution was washed with water and dried over anhydrous sodium sulfate. On evaporating the ether a mixture of a white solid and a yellow oil was obtained. These were separated by dissolving in absolute alcohol and slowly concentrating the solution by drawing a stream of dry air through it. The concentration was continued until nothing more crystallized out and the solid material was filtered, washed with a little cold alcohol, and weighed.

Run No.	Weight of Bromide	Decomposition Reagent (a)	Time of Shaking	Weight of Solids (b)	% Yields
1	5.5 g.	$C_6H_5Br_2$	24 hrs.	0.6 g.	15
2	8.3	$C_6H_5Br_2$	24	0.9	23
3	11.5	H_2O	30	2.0	33.5
4	6.0	H_2O	72	1.0	22.5
5	5.0	H_2O	34	0.9	24
6	5.0	H_2O	70	1.2	32
7	20.0	H_2O	34	5.12	34.5
8	20.0	$C_6H_5Br_2$	34	4.26	29

(a) $C_6H_5Br_2 = (CH_3)_2C-Br-Br-C(CH_3)_2$
Br Br

(b) stopcock leaked

When tetramethylethylenedibromide was used as the decomposition reagent, the excess was removed by exposing the material to the air or allowing it to stand in a vacuum desiccator over concentrated sulfuric acid as tetramethylethylenedibromide sublimes easily.

The crude material melted over a wide range. It was fractionally crystallized using absolute alcohol or a mixture of absolute alcohol and petroleum ether, the mixture giving a more rapid separation. About one-fourth of the solid material could be separated as a white crystalline compound melting at $148-9^\circ$ (cor.).

Anal. Calcd. for $C_{24}H_{48}$: C, 89.80; H, 10.20. Found: C, 89.99; H, 10.38.

Mol. Wt.: Calcd., 454.4. Found: 435 (Oryoscopic in camphor).

The remainder of the material was white and crystalline

in appearance but it did not melt sharply (approximately 118-35°) although many attempts were made to purify it.

Anal. Calcd. for $C_{24}H_{40}$: C, 89.80; H, 10.20. Found: C, 89.84; H, 10.44.

Mol. Wt.: Calcd. for 484.4. Found: 433 (cryoscopic in camphor).

In run No. 7 the alcohol solution which remained after crystallization of the solid hydrocarbons was evaporated. This left a yellow sticky oil which was vacuum distilled.

First fraction: A colorless liquid; b.p., 83-5°/1 mm./135° n_D²⁰ 1.5090; yield 3.1 g. (14%).

Anal. Calcd. for $C_{17}H_{24}$: C, 89.40; H, 10.60. Found: C, 89.70; H, 10.44.

Second fraction: A light yellow viscous liquid which became a glass when cooled; b.p., 100-3°/1 mm./210-30°; yield 4.4 g. (30%).

Anal. Calcd. for $C_{24}H_{40}$: C, 89.80; H, 10.20. Found: C, 89.80; H, 10.20.

On long standing it deposited a few crystals which proved to be a mixture of the solid ethanes.

Residues from other runs were combined and vacuum distilled. The fractions were approximately the same as those described above. The refractive indices of the first fractions varied because they contained small amounts of unreacted bromide.

The Attempted Cleavage of the Ethanes with 40% Sodium Amalgam

A solution of 0.261 g. of the ethane (m.p., 143°) in 85 cc. of dry ether was placed in a 200 cc. flask. The air was flushed out with dry oxygen-free nitrogen and 5 cc. of 40% sodium amalgam was

added. The flask was placed on a mechanical shaker for 24 hours, but at the end of that time the solution was still colorless. The amalgam was frozen and ether solution was poured into another flask and treated with water. These operations were also carried out in dry nitrogen. The starting material was recovered unchanged.

A similar experiment was performed using 0.258 g. of the mixture of ethanes (m.p. $115-25^{\circ}$). The mixture was shaken for four days, but none of the green color which was so characteristic of the solutions obtained by shaking the bromide with 40% sodium amalgam could be discerned. The starting material was recovered but it was contaminated with tarry material which probably resulted from the action of the sodium amalgam on the ether.

Reduction of the Bromide with Zinc and Alcohol

A mixture of 5 g. of phenyl-t-butyl-t-butylethynylbromomethane, 22 g. of zinc dust, and 60 cc. of 80% ethanol was refluxed for 8 hours. The zinc dust was filtered out and washed with hot alcohol. The filtrates were combined and evaporated a white solid contaminated with a yellow liquid. The mixture was recrystallized from absolute alcohol giving a white solid melting at $110-30^{\circ}$. The filtrate gave a yellow liquid upon evaporation; b.p., $80^{\circ}/1\text{ mm.}$; n_D^{20} 1.5026. The physical constants indicate that this liquid was probably 1-phenyl-1,3-di-t-butylallene.

By recrystallizing several times from a mixture of absolute alcohol and petroleum ether, the solid material was separated into a pure compound melting at $148-9^{\circ}$ (cor.) and a mixture melting at $115-25^{\circ}$. Mixed melting points showed these to be identical with the products of the sodium amalgam coupling.

Reaction of the Bromide with Lithium

Five grams of phenyl-t-butyl-t-butylethynylbromomethane,

6.4 g. of freshly cut lithium, and 50 cc. of dry ether were added to a 250 cc. 3-necked flask equipped with a reflux condenser and a mercury seal stirrer. After about 5 minutes the ether began to reflux gently, but the reaction was not at all vigorous. The stirrer was started and an electric light was placed under the flask to keep the ether refluxing. After 10 hours absolute alcohol was added to decompose the excess lithium and dry ice was added to neutralize the lithium ethoxide. The mixture was filtered and the solvent evaporated. The residue was dissolved in ether and the solution washed with dilute hydrochloric acid. On evaporating the ether a sticky solid remained. This yielded 1.1 g. (30%) of the same mixture of hydrocarbons that was obtained by treating the bromide with 40% sodium amalgam or zinc and alcohol. The liquid residue also appeared to be the same but it was not distilled.

Preparation of 1-Phenyl-1,3-di-t-butylallene

Five grams of magnesium turnings was placed in a 1-l. 3-necked flask equipped with a reflux condenser, a mechanical stirrer, and a dropping funnel. A solution of 58 g. of phenyl-t-butyl-t-butylethynylbromomethane in 500 cc. of dry ether was placed in the dropping funnel and about 20 cc. added to the magnesium. A few small crystals of iodine were added and the flask was warmed to start the reaction. The stirrer was started and the remainder of the bromide added during 2 hours. At the end of this time the flask was warmed so that the ether refluxed gently and stirred for three more hours. The Grignard solution was decomposed by adding water through the separatory funnel and the contents of the flask were then poured on to a mixture of ice and hydrochloric acid. The ether layer was washed with water and dried over anhydrous sodium sulfate. The ether

was evaporated slowly but no solid material separated out as it had done in previous cases when the bromide was treated with sodium amalgam, zinc, or lithium. The resulting liquid was fractionated under reduced pressure using a Widmer column. The main fraction boiled at $72-80^{\circ}/1 \text{ mm.}/180^{\circ}$. The yield was 35 g. (80%) of a clear straw colored liquid; n_D^{20} 1.5030; d_4^{20} 0.8000 M_0 , calcd. for an acetylene, 75.13; for an allene 76.19; found: 76.07.

Anal. Calcd. for $C_{17}H_{22}$: C, 89.49; H, 10.60. Found: C, 89.26; H, 10.71.

The high boiling residue formed crystals on standing. On purification these were shown to be the coupled products melting at 140° and $115-25^{\circ}$.

Attempt to Add p-Thiocresol to 1-Phenyl-1,3-di-t-butylallene

A solution of 0.37 g. of p-thiocresol in 0.5 g. of the allene was placed in a small test tube and exposed to the rays of a mercury arc lamp for 24 hours. At the end of this time, the solution had not darkened or become more viscous, indicating that no reaction had occurred.

Ozonolysis of 1-Phenyl-1,3-di-t-butylallene

A solution of 5 g. of the allene in 100 cc. of dry carbon tetrachloride was placed in a gas wash bottle and surrounded with cracked ice. Ozonized oxygen was passed in for 10 hours at the rate of 0.5-1. per minute. The solution became turbid and a small amount of white sticky ozonide precipitated. The bottle was disconnected, 100 cc. of water was added, and the mixture was stirred over night using a mechanical stirrer which gave good contact between the two layers. An excess of sodium bicarbonate was added and the mixture

was stirred another hour. The carbon tetrachloride layer was separated and the solvent removed by distillation. To the remaining yellow liquid was added 5 cc. of 2,4-dinitrophenylhydrazine solution and the derivative was prepared according to the method of Allen¹⁰⁰. When recrystallized from 95% alcohol, the resulting yellow needles melted at 133-4° (cor.) and a mixed melting point with the 2,4-dinitrophenylhydrazone of phenyl *t*-butyl ketone gave no depression.

The water layer was acidified with phosphoric acid and steam distilled. The distillate was titrated with standard alkali using phenolphthalein indicator. This solution was evaporated to dryness on the steam cone and the resulting potassium salt was converted into the *p*-bromophenacyl ester by the method of Reid¹⁰⁶. The product melted at 75-6° and a mixed melting point with the *p*-bromophenacyl ester of trimethylacetic acid showed no depression.

Preparation of Phenyl *t*-Butyl Carbinol

Three hundred cubic centimeters of 1.9 N.¹⁰⁶ isopropylmagnesium bromide was placed in a 1-l. 3-necked flask equipped with reflux condenser, mercury seal stirrer, and dropping funnel. A solution of 65 g. of phenyl *t*-butyl ketone in 50 cc. of dry ether was added to the Grignard reagent during 1 hour. Each drop produced an intense red color which faded rapidly. The mixture was refluxed and stirred for three hours and then hydrolyzed with ice and hydrochloric acid. The ether solution was washed with water, dried over anhydrous sodium sulfate, and the ether removed by distillation. The resulting product was distilled under reduced pressure and 62.5 g. (95%) of phenyl *t*-butyl carbinol boiling at 70-5°/2 mm./95° was obtained. It crystallized to a white solid melting at 42-5° ^{92.93}.

Preparation of Phenyl-*t*-butylbromomethane

A rapid stream of dry hydrogen bromide, prepared by burning hydrogen in bromine, was passed into a gas wash bottle containing 60.5 g. of phenyl *t*-butyl carbinol. The solid melted slowly and became quite hot. The mixture separated into two layers and in about 2 hours it began to cool. The bromide layer was dissolved in petroleum ether, washed with sodium bisulfite solution to remove the small amount of bromine that had been carried over with the hydrogen bromide, washed with sodium bicarbonate solution, and dried over anhydrous sodium sulfate. The product was vacuum distilled and 39.7 g. (63%) of a colorless liquid boiling at $118-20^{\circ}/19$ mm. was obtained; n_D^{20} 1.5401.

Preparation of Phenyl-*t*-butylacetic Acid

The procedure used in the preparation of the following Grignard reagent is essentially the same as that described in the preparation of 1-phenyl-1,3-di-*t*-butylallene.

The Grignard solution was prepared using 1.2 g. of magnesium turnings and 10 g. of phenyl-*t*-butylbromomethane in 100 cc. of dry ether. It was cooled to 0° and carbon dioxide gas was bubbled through for 4 hours. The reaction mixture was decomposed with ice and hydrochloric acid. The ether layer was washed with water and extracted with sodium bicarbonate solution. On acidifying this extract an oil separated which solidified on standing.

The yield of crude product was 1.1 g. (13%). After recrystallizing twice from dilute alcohol and once from low boiling petroleum ether, the melting point was $105-105.5^{\circ}$.

Neutral Equivalent, Calcd.: 192.1; Found: 192.8.

Anal. Calcd. for $C_{20}H_{26}$: C, 74.36; H, 8.55. Found: C, 74.74; H, 8.37.

Isolation of Symmetrical Diphenyl-di-t-butylethane

The ether solution which remained from the bicarbonate extraction in the above preparation deposited white needles when evaporated slowly. After two recrystallizations from absolute alcohol, these melted at $188-6^{\circ}$ (cor.).

Anal. Calcd. for $C_{20}H_{26}$: C, 88.72; H, 10.28. Found: C, 88.64, 88.82; H, 10.37, 10.19.

Mol. Wt.: Calcd: 264.2; Found: 266 (cryoscopic in camphor).

A sample of Holst's²⁰ "tertiary-butylphenyl-tertiary-butylethynylethane" melting at $130-1^{\circ}$ was recrystallized from absolute alcohol. The resulting white needles melted at $185-6^{\circ}$ (cor.) and gave no depression when mixed with sym. diphenyl-di-t-butylethane.

The Action of Ozone on Phenyl-t-butylacetic Acid

A solution of 0.866 g. of phenyl-t-butylacetic acid in 50 cc. of carbon tetrachloride was ozonized under the same conditions that were used in the case of the allene. The bicarbonate extract yielded 0.131 g. of starting material when acidified. The neutral portion gave a few drops of an oily liquid on evaporation of the carbon tetrachloride. The odor of the material was not at all like that of phenyl t-butyl ketone and it solidified on standing. Treatment with 2,4-dinitrophenylhydrazine solution^a failed to yield a crystalline product.

Preparation of the 1-Phenyl-1,3-di-t-butyl-3-carboxyallene

The Grignard reagent was prepared in the manner described under the preparation of 1-phenyl-1,3-di-t-butylallene using 2.5 g.

of the copper-magnesium alloy described by Gilman¹⁷ and 27.1 g. of phenyl-t-butyl-t-butylethynylbromomethane in 100 cc. of dry ether. The solution was cooled to 0° and a slow stream of dry carbon dioxide gas was passed over the surface with rapid stirring for 1.5 hours. The mixture was hydrolyzed with ice and hydrochloric acid and the ether solution was extracted twice with 15 cc. portions of 10% sodium hydroxide. The extract was acidified and the oily material which separated solidified on standing. The crude product melted at 140-53°. Dissolving in 95% alcohol and precipitating with water gave a product which softened at 145° and melted at 157-8°. A final recrystallization from benzene gave a product which melted at 160-1° (cor.).

Anal. Calcd. for $C_{18}H_{24}O_2$: C, 79.35; H, 9.83. Found: C, 79.21; H, 9.02.

Neutral Equivalent: Calcd.: 272.3; Found: 274. The titration was carried out by dissolving the sample in absolute alcohol. The alkali was standardized against benzoic acid using approximately the same volumes of alcohol and alkali that were used in the above titration as the phenolphthalein end-point varies with the concentration of the alcohol.

Preparation of 1-Phenyl-1,3-di-t-butyl-3-carbomethoxyallene

A solution of 9.45 g. of methyl chlorocarbonate in 100 cc. of dry ether was placed in a 500 cc. 3-necked flask equipped with condenser, mercury seal stirrer, and dropping funnel. The flask was cooled to 0° and a slow stream of dry nitrogen was passed over the surface of the solution. The stirrer was started and the Grignard solution prepared from 30.7 g. of phenyl-t-butyl-t-butylethynylbromomethane and 2.5 g. of magnesium turnings in 350 cc. of dry ether

was added during one hour. The resulting mixture was refluxed for 3 hours and then decomposed with ice and ammonium chloride solution. The ether layer was washed with water, dried over anhydrous sodium sulfate, and the ether removed with a current of dry air. The straw colored liquid which remained could not be induced to crystallize and it was distilled under reduced pressure. The yield was 13.5 g. (64%) of a clear liquid boiling at $112-20^{\circ}/2$ mm./ 135° ; n_D^{20} 1.5029; d_4^{20} 0.9584; M., calcd. 87.03; Found: 87.94.

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 79.07; H, 9.15. Found: C, 79.63; H, 9.23.

Hydrolysis of the Methyl Ester

Three grams of the methyl ester and 3 g. of powdered potassium hydroxide were dissolved in 30 cc. of absolute methyl alcohol and the mixture was refluxed 2 hours then diluted with water. The oily layer which rose to the surface was extracted with petroleum ether and 1.7 g. of starting material was recovered by distillation. The water layer was acidified and the light yellow oil which separated solidified on standing over night. After one recrystallization from 95% alcohol, the product melted at $158-60^{\circ}$ (cor.) and a mixed melting point with the allenic acid showed no depression.

Ozonolysis of the Methyl Ester

A solution of 3 cc. of the methyl ester in 50 cc. of dry carbon tetrachloride was treated with ozone using the same procedure that was described for the ozonolysis of 1-phenyl-1,3-di-i-butylallene. The bicarbonate extract did not have the odor of trimethylacetic acid after it was acidified. The neutral material that was obtained by evaporating the carbon tetrachloride solution was treated with 2,4-dinitrophenylhydrazine³. A small amount of a rather

insoluble yellow solid was obtained. After recrystallizing from 95% alcohol, it melted at $200-2^{\circ}$ (cor.) and when mixed with a known sample of the 3,4-dinitrophenylhydrazone of methyl trimethylpyruvate it melted at $200-3^{\circ}$ (cor.).

Preparation of Trimethylpyruvic Acid

This method is essentially the same as that described by Richard¹⁸.

Forty grams of pinacolone was added to a solution of 135 g. of potassium permanganate and 40 g. of sodium hydroxide in 3 l. of water and stirred rapidly for three hours. The mixture was then heated for 30 minutes just below the boiling point to coagulate the manganese dioxide. After cooling it was filtered with suction and the filtrate was evaporated on the steam cone until solid material separated. It was then cooled to 0° and acidified with concentrated hydrochloric acid. The free acid was extracted with ether and the ether solution was dried over anhydrous sodium sulfate. The ether was removed and the product distilled under reduced pressure. The yield was 33.1 g. (50%) of a colorless liquid boiling at $80-2^{\circ}/18$ mm. / 105° .

The 3,4-dinitrophenylhydrazone was prepared according to the usual procedure¹⁰⁰. After two recrystallizations from methyl alcohol, it melted at $168-71^{\circ}$ with decomposition. It could be extracted from an ether solution with sodium bicarbonate.

Anal. Calcd. for $C_{12}H_{14}O_6N_4$: N, 18.01%. Found: N, 18.17%

Preparation of Methyl Trimethylpyruvate

A solution of 10 g. of trimethylpyruvic acid and 3 cc. of concentrated sulfuric acid in 20 cc. of absolute methanol was re-

fluxed for 3 hours and then poured into 25 cc. of cold saturated sodium chloride solution. The ester layer separated and was extracted with ether. The extract was washed with sodium bicarbonate solution, then with water, and dried over anhydrous magnesium sulfate. The ether was removed and the product vacuum distilled. The yield was 7.7 g. (70%) of a colorless pleasant smelling liquid boiling at 58-60°/21 mm./85°.

The 2,4-dinitrophenylhydrazones, prepared according to the usual procedure¹⁰⁰, melted at 204-5° (cor.) after one recrystallization from acetone.

Anal. Calcd. for $C_{13}H_{15}O_6N_2$: H, 17.39. Found: H, 17.40

VI. SUMMARY

1. Symmetrical diphenyldi-t-butyldi-t-butylethynylethane has been prepared and found to be stable toward 40% sodium amalgam.
2. The "phenyl-t-butyl-t-butylethynylethane" of Holst has been identified as symmetrical diphenyldi-t-butylethane.
3. The reactions of phenyl-t-butyl-t-butylethynylmagnesium bromide with water, methyl chloroacetate, and carbon dioxide have been found to involve allylic rearrangements with the production of allenic compounds.
4. An allenic acid which should be suitable for testing Van't Hoff's prediction concerning the optical activity of allenes of the type $\begin{array}{c} a \quad \quad a \\ \diagdown \quad \diagup \\ C=C=C \\ \diagup \quad \diagdown \\ b \quad \quad b \end{array}$ has been prepared.

112A

The writer was born at Oberlin, Ohio, on June 14, 1911. He attended the public schools of Oberlin and graduated from Oberlin High School in June, 1927. He attended Oberlin College from September, 1927, until June, 1931, when he was granted the degree of Bachelor of Arts. Since September, 1931, he has been registered in the Graduate School of the University of Illinois. He was granted the degree of Master of Arts in June, 1932, and was employed as a Graduate Assistant in Chemistry from September, 1932, until January, 1935.

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