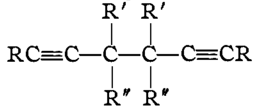
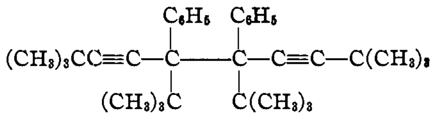
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Rearrangements of Polyynes. VII.[1] Formation of Allenes

BY J. H. FORD, C. D. THOMPSON AND C. S. MARVEL

Previous work has shown that many hexasubstituted ethanes of the type  $RC\equiv C-\overset{R'}{\underset{R''}{C}}-\overset{R'}{\underset{R''}{C}}-C\equiv CR$ undergo rearrangement to produce more stable hydrocarbons of unknown structure and that the ease with which this rearrangement occurs in any given case is largely determined by the nature of R′ and R″. The aim of the present work was to obtain diphenyldi-*t*-butyldi-*t*-butylethynylethane (I)

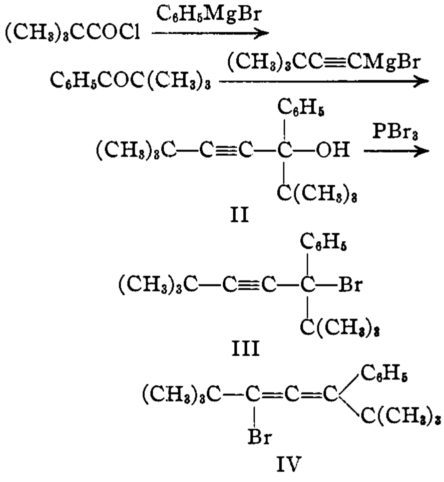


$$(CH_3)_3CC\equiv C-\overset{C_6H_5}{\underset{(CH_3)_3C}{C}}-\overset{C_6H_5}{\underset{C(CH_3)_3}{C}}-C\equiv C-C(CH_3)_3$$

I

in which R′ is a phenyl group and R and R″ are *t*-butyl groups. Some interesting rearrangements were observed in the reactions which were used in the synthesis of the desired ethane and these seem to offer some clues as to the nature of the rearrangements of the polyynes themselves.

Phenyl-*t*-butyl-*t*-butylethynylbromomethane (III) was synthesized by the series of reactions



$$(CH_3)_3CCOCl \xrightarrow{C_6H_5MgBr} C_6H_5COC(CH_3)_3 \xrightarrow{(CH_3)_3CC\equiv CMgBr}$$

$$(CH_3)_3C-C\equiv C-\overset{C_6H_5}{\underset{C(CH_3)_3}{C}}-OH \xrightarrow{PBr_3}$$

II

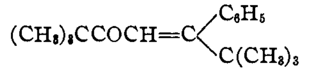
$$(CH_3)_3C-C\equiv C-\overset{C_6H_5}{\underset{C(CH_3)_3}{C}}-Br$$

III

$$(CH_3)_3C-\underset{Br}{C}=C=C\begin{matrix}C_6H_5\\C(CH_3)_3\end{matrix}$$

IV

The carbinol (II) did not react readily with phosphorus trichloride to give an organic chloride but the bromide (III) was formed without difficulty. The bromide had an abnormally high molecular refraction and the bromine was not easily removed by silver, which suggested that possibly the compound did not have the acetylenic structure but was a rearranged allenic bromide of structure IV. However, structure III was established for the bromide by hydrolysis with moist silver oxide to give the carbinol (II). The



$$(CH_3)_3CCOCH=C\begin{matrix}C_6H_5\\C(CH_3)_3\end{matrix}$$

carbinol structure was checked by converting it to the unsaturated ketone by the action of sulfuric acid in acetic acid.[2]

The bromide (III) did not couple to yield a hydrocarbon when it was treated with silver or copper. The carbinol (II) did not reduce to give a coupled hydrocarbon when it was treated with titanous chloride solution. The bromide did react with magnesium in dry ether to give about an 80% yield of the Grignard reagent and 10–15% of a mixture of hydrocarbons which had the molecular formula $C_{34}H_{46}$ corresponding to the desired ethane (I). When this Grignard reagent was treated with water, carbon dioxide or methyl chlorocarbonate the resulting product in each case was an allene derivative. The structures of the products were established by ozonization. The product of the action of water on the Grignard reagent was 2,2,6,6-tetramethyl-3-phenyl-3,4-heptadiene (V) as was shown by the fact that on ozonization and oxidative hydrolysis of the ozonide, it yielded trimethylacetic acid and phenyl *t*-butyl ketone. That the phenyl *t*-butyl ketone was not a secondary oxidation product of phenyl-*t*-butylacetic acid was established by synthesizing this acid and showing that it did not oxidize to phenyl *t*-butyl ketone under the conditions used in oxidizing the allene (V). The structure of the 2,2,6,6-tetramethyl-3-phenyl-5-carbomethoxy-3,4-heptadiene (VII) was established by the fact that it yielded methyl trimethylpyruvate $(CH_3)_3CCOCO_2CH_3$ on ozonization. The structure of the acid (VI) follows from the fact that it has been obtained by hydrolysis of the ester (VII).

The formation of an allenic hydrocarbon (IX) by the action of water on diphenyl-*t*-butylethynylmethyl sodium[3] (VIII) has been observed before. It is of some interest to note that 4,4-dimethyl-1,1-diphenyl-1,2-pentadiene (IX) readily dimerizes

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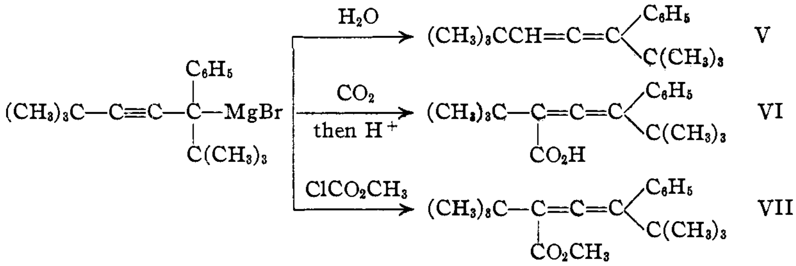
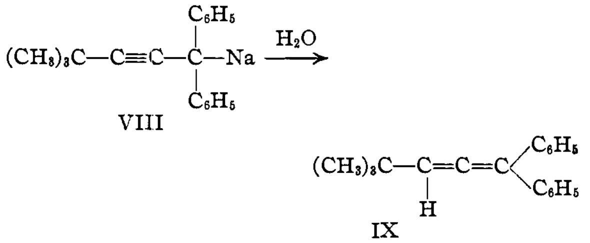
[1] For the sixth paper see Tsao and Marvel, THIS JOURNAL, **55**, 4709 (1933).

[2] Meyer and Schuster, *Ber.*, **55**, 819 (1922).

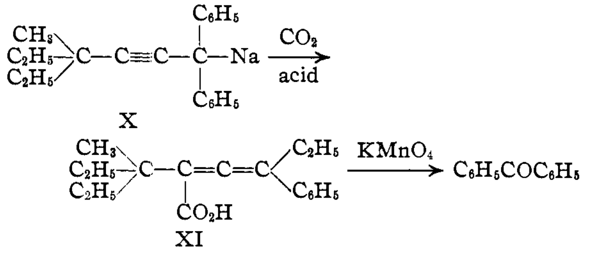
[3] Stampfli and Marvel, THIS JOURNAL, **53**, 4057 (1931).



whereas 2,2,6,6-tetramethyl-3-phenyl-3,4-heptadiene (V) does not. Apparently the addition reactions of the allene group are blocked by the two *t*-butyl groups in this latter molecule.

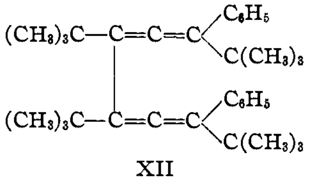


Many acids and esters[4] have been prepared in this Laboratory by the action of carbon dioxide or methylchlorocarbonate on metallic derivatives of the type $R—C{\equiv}C—\overset{R'}{\underset{R'}{C}}—\text{metal}$ and these have been assumed to be the acetylenic acids $R—C{\equiv}C—\overset{R'}{\underset{R'}{C}}—COOH$. The present work leads us to believe that all of these compounds may also be allene derivatives of the type $R—\underset{COOH}{C}{=}C{=}\overset{R'}{\underset{R'}{C}}$. In fact Harmon and Marvel[4g] did observe that the acid (XI) obtained by the action of carbon dioxide on diphenyl-(3-methyl-3-ethylpentynyl-1)-methyl sodium (X) yielded benzophenone



on oxidation with neutral permanganate. Benzophenone would be expected from an acid of structure XI, whereas an acid of acetylenic structure would be expected to give diphenylmalonic acid or, by loss of carbon dioxide, diphenylacetic acid.

Since the bromide (III) was inert toward silver and copper, an attempt was made to convert it to the sodium derivative in order to obtain the ethane (I) by the method of Ziegler and Schnell.[5] It was found that 40% sodium amalgam in ether converted the bromide into a mixture of hydrocarbons and that no sodium derivative could be demonstrated to be present. One hydrocarbon which was isolated from the reaction mixture was the allene (V) which had been obtained by the action of water on the Grignard reagent prepared from the bromide. This allene must have been produced by the formation of some of the desired sodium derivative which then reacted with the ether present to give the allene.[6] In addition to the simple allene, the same mixture of coupled hydrocarbons of the formula $C_{34}H_{46}$ which was formed as a side reaction in the formation of the Grignard reagent, was isolated from the reaction of the bromide and sodium amalgam. Apparently there were two isomeric hydrocarbons in this mixture. One, the less soluble, was isolated in a pure condition but the other, more soluble one, was never completely freed from the less soluble isomer. We believe these two hydrocarbons are stereoisomers of each other but whether they represent the meso and racemic forms of the acetylenic ethane (I) or of a rearrangement product which by analogy to the other derivative obtained from the Grignard reagent would be the diallene (XII) cannot as yet be said. The fact that this mixture of hydrocarbons is formed by the action of sodium amalgam on the bromide and that the hydrocarbons are therefore not cleaved by this reagent seems to be evidence in favor of the diallenic structure.



XII

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[4] (a) Salzberg and Marvel, This Journal, **50**, 1737 (1928); (b) Rossander and Marvel, *ibid.*, **51**, 932 (1929); (c) Gillespie and Marvel, *ibid.*, **52**, 3368 (1930); (d) Davis and Marvel, *ibid.*, **53**, 3840 (1931); (e) Stampfli and Marvel, *ibid.*, **53**, 4057 (1931); (f) Munro and Marvel, *ibid.*, **54**, 4445 (1932); (g) Harmon and Marvel, *ibid.*, **55**, 1716 (1933).

[5] Ziegler and Schnell, *Ann.*, **437**, 227 (1924).

[6] Sodium alkyls have been shown to cleave ethyl ether to give the hydrocarbon which corresponds to the alkyl group. Schorigin, *Ber.*, **43**, 1931 (1910).

Experimental Part

Phenyl *t*-Butyl Ketone.—In a 2-liter three-necked flask fitted with a stirrer, separatory funnel and reflux condenser was placed a solution of 129 g. of trimethylacetyl chloride in 400 cc. of dry ether. The mixture was cooled in an ice-salt bath. A slow stream of dry nitrogen was passed over the surface of the solution to avoid oxidization and 1050 cc. of a 1.6 *N* ether solution of phenylmagnesium bromide was added from the separatory funnel during five hours. The reaction mixture was hydrolyzed with dilute acid and the ether solution was washed with sodium bicarbonate solution to remove trimethylacetic acid. On distillation the ketone boiled at 80–84° at 3 mm. The yield was 116 g. (67%), n^{20}_D 1.5102. The physical properties check those previously reported for the ketone as prepared by other methods.[7]

The 2,4-dinitrophenylhydrazone was prepared by the method of Allen[8] and after two crystallizations from 95% alcohol the yellow needles melted at 194–195°.

Anal. Calcd. for $C_{17}H_{18}O_4N_4$: N, 16.37. Found: N, 16.14.

Phenyl-*t*-butyl-*t*-butylethynylcarbinol.—A solution of 162 g. of phenyl *t*-butyl ketone in 250 cc. of dry ether was added over a period of three hours to the Grignard reagent prepared from 82 g. of *t*-butylacetylene[9] in about 700 cc. of ether. After ten hours the reaction mixture was worked up in the usual manner and the carbinol was very carefully fractionated. The yield was 200 g. (68%) of a viscous liquid, b. p. 125–128° (4 mm.); n^{20}_D 1.5025; d^{20}_4 0.9334. *M*D calcd., 76.65; found, 77.27.

Anal. Calcd. for $C_{17}H_{24}O$: C, 83.54; H, 9.91. Found: C, 83.46; H, 10.09.

2,2,6,6-Tetramethyl-3-phenyl-3-heptene-5-one.—The carbinol was converted to the unsaturated ketone by heating a few grams of it in a glacial acetic acid solution containing a few drops of sulfuric acid. The ketone boiled at 96–97° (1 mm.); n^{20}_D 1.5063; d^{20}_4 0.9309; *M*D, calcd., 76.67; found, 77.98. On cooling the liquid to about −40° it crystallized to a solid which melted at 30.5°.

Anal. Calcd. for $C_{17}H_{24}O$: C, 83.54; H, 9.91. Found: C, 83.70; H, 10.16.

The 2,4-dinitrophenylhydrazone was a bright orange-red solid melting at 150–151°.

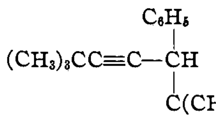
Anal. Calcd. for $C_{23}H_{24}O_4N_4$: N, 13.39. Found: N, 13.40.

Phenyl-*t*-butyl-*t*-butylethynylbromomethane.—To a solution of 30 g. of the carbinol in 150 cc. of low boiling petroleum ether was added 5.4 cc. of phosphorus tribromide. After standing overnight, a layer of phosphorous acid had separated. The upper layer was separated, washed throughly with sodium bicarbonate, dried over magnesium sulfate and distilled. The yield was 34.4 g. (91%) of a slightly yellow liquid, b. p. 115–117° (1 mm.); n^{20}_D 1.5400; d^{20}_4 1.1081; *M*D calcd., 82.89; found, 86.93.

Anal. Calcd. for $C_{17}H_{23}Br$: C, 66.43; H, 7.55; Br, 26.02; mol. wt., 307.1. Found: C, 66.54; H, 7.47; Br, 25.75; 25.82; mol. wt. (Rast.), 282.

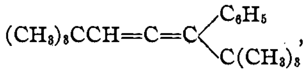
A small amount of the bromide was hydrolyzed by boiling a solution in acetone with a suspension of moist silver oxide.[10] The product was separated by distillation; b. p. 105–110° (1 mm.); n^{20}_D 1.5028; d^{20}_4 0.9332, and was identical with the carbinol from which the bromide had been prepared.

2,2,6,6-Tetramethyl-3-phenyl-3,4-heptadiene.—The Grignard reagent was prepared from 58 g. of the bromide and 5 g. of magnesium turnings in 500 cc. of ether. Iodine was used to start the reaction. The Grignard reagent was then decomposed by adding water and finally a little hydrochloric acid and ice. The ether layer was separated and distilled. After removal of the solvent, the main portion boiled at 78–80° (1 mm.). The yield of the hydrocarbon was 35 g. (82%); n^{20}_D 1.5039; d^{20}_4 0.8808; *M*D calcd. for



$(CH_3)_3CC{\equiv}C{-}\underset{C(CH_3)_3}{\overset{C_6H_5}{CH}}$

75.13; calcd. for



$(CH_3)_3CCH{=}C{=}C{<}^{C_6H_5}_{C(CH_3)_3}$

, 76.19; found, 76.67.

Anal. Calcd. for $C_{17}H_{24}$: C, 89.40; H, 10.60; mol. wt. 228.2. Found: C, 89.26; H, 10.71; mol. wt. (Rast.), 222.

This hydrocarbon was heated to 145° in a sealed tube for about ninety hours and then vacuum distilled.[11] About 85% of the hydrocarbon was recovered unchanged and no definite products could be obtained from the residue.

The original high boiling residue which remained after distilling the allene, slowly solidified. Crystallization gave two products, one melting at 148° and one melting at 115–125°, which were identified as coupled products and will be described in more detail later.

Ozonolysis of the Allene.—A solution of 5 g. of the above allene in 100 cc. of carbon tetrachloride was cooled to −20° and ozonized oxygen was passed through the solution for about ten hours at the rate of 0.5 liter per minute. A white sticky solid separated from solution during this treatment. The reaction mixture was decomposed by adding 75 cc. of water and stirring for several hours at 25°. An excess of sodium bicarbonate solution was then added and the mixture stirred for a short time. The carbon tetrachloride solution was evaporated and the residue treated with 2,4-dinitrophenylhydrazine. The product of this reaction melted at 193–194° and proved to be the 2,4-dinitrophenylhydrazone of phenyl *t*-butyl ketone. The water layer was acidified and distilled with steam. The volatile acid was converted to the *p*-bromophenacyl ester which melted at 75–76° and proved to be identical with the *p*-bromophenacyl ester of trimethylacetic acid.[12]

Phenyl-*t*-butylacetic Acid.—Phenyl *t*-butyl ketone was reduced to the carbinol by the method of Ramart-Lucas[13] in yields of 95%, and this carbinol was converted to the bromide by the method of Lepin[14] in yields of 93%.

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[7] Haller and Bauer, *Compt. rend.*, **148**, 70 (1909): Ramart-Lucas, *Ann. chim.*, [8] **30**, 385 (1913).

[8] Allen, THIS JOURNAL, **52**, 2955 (1930).

[9] Salzberg and Marvel, *ibid.*, **50**, 1737 (1928).

[10] Conant, Small and Sloan, *ibid.*, **48**, 1756 (1926).

[11] Lebedev, *J. Russ. Phys.-Chem. Soc.*, **45**, 1357 (1913); *Chem. Zentr.*, **85**, 1, 1402 (1914).

[12] Powell, THIS JOURNAL, **53**, 1172 (1931).

[13] Ramart-Lucas, *Ann. chim.*, **30**, 361 (1913).

[14] Lepin, *J. Russ. Phys.-Chem. Soc.*, **44**, 1178 (1912); *Chem. Zentr.*, **83**, II, 2081 (1912).

The Grignard reagent, prepared from 10 g. of this bromide and 1.2 g. of magnesium in 100 cc. of dry ether, was treated with carbon dioxide and the organic acid isolated in the usual manner. The yield was 1.1 g. (13%) of a product m. p. 105° after two crystallizations from dilute alcohol and one from low-boiling petroleum ether.

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.96; H, 8.38; neut. equiv., 192.1. Found: C, 74.74; H, 8.37; neut. equiv., 192.8.

The main portion of the bromide reacted with the magnesium to yield diphenyldi-*t*-butylethane, m. p. 185–186°.[15]

A solution of phenyl-*t*-butylacetic acid in carbon tetrachloride was treated with ozonized oxygen under the conditions used for the ozonolysis of the allene. Only about one-fourth of the acid was recovered from the mixture but no phenyl *t*-butyl ketone could be detected in the mixture.

2,2,6,6-Tetramethyl-3-phenyl-5-carbomethoxy-3,4-heptadiene.—The Grignard reagent prepared from 30.7 g. of phenyl-*t*-butyl-*t*-butylethynylbromomethane and 2.5 g. of magnesium in 250 cc. of ether was added during one hour to a solution of 9.45 g. of methyl chlorocarbonate in 100 cc. of dry ether. The reaction mixture was cooled to 0° and nitrogen was passed through the flask to avoid oxidation. The reaction mixture was worked up in the usual way. The yield was 18.5 g. (64%) of a colorless liquid, b. p. 116–120° (2 mm.); n^{20}_{D} 1.5029; d^{20}_{4} 0.9584; M_D calcd., 87.08; found, 87.84.

Anal. Calcd. for $C_{19}H_{26}O_2$: C, 79.67; H, 9.15. Found: C, 79.62; H, 9.02.

A solution of 2 g. of this ester in 50 cc. of carbon tetrachloride was ozonized in the usual manner. The neutral fraction from the decomposition of the ozonide was treated with 2,4-dinitrophenylhydrazine and a lemon-yellow solid, m. p. 205–206° (after recrystallization from alcohol) was isolated. This product was identical with the 2,4-dinitrophenylhydrazone of the methyl trimethylpyruvate described below. Indications of the presence of the 2,4-dinitrophenylhydrazone of phenyl *t*-butyl ketone were also obtained, but since this hydrazone is more soluble than the one isolated above, it could not be purified sufficiently for positive identification.

2,4-Dinitrophenylhydrazone of Methyl Trimethylpyruvate.—Trimethylpyruvic acid was obtained from pinacolone in 50% yields by the method of Richard.[16] Its 2,4-dinitrophenylhydrazone was prepared and melted at 169–171° with decomposition.

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

Methyl trimethylpyruvate was formed in 70% yields by direct esterification of the acid with methyl alcohol[16] and its 2,4-dinitrophenylhydrazone was prepared in the usual manner. This product melted at 205–206°. It could be crystallized from alcohol but acetone was a better solvent. This product showed no depression in melting point when mixed with the material obtained from the ozonolysis of the methyl ester of the allenic acid.

Anal. Calcd. for $C_{13}H_{16}O_6N_4$: N, 17.29. Found: N, 17.46.

2,2,6,6-Tetramethyl-3-phenyl-5-carboxy-3,4-heptadiene.—The Grignard reagent prepared from 47 g. of phenyl-*t*-butyl-*t*-butylethynylbromomethane and 4 g. of magnesium in 400 cc. of dry ether was carbonated and the reaction mixture was worked up in the usual way. The yield of crude solid acid was 30 g. (72%). Two crystallizations from benzene gave a product melting at 160–161°. The acid was quite weak and only slightly soluble in sodium bicarbonate solution, although readily soluble in either sodium carbonate or sodium hydroxide solution.

Anal. Calcd. for $C_{18}H_{24}O_2$: C, 79.35; H, 8.88; mol. wt., 272.2. Found: C, 79.21; H, 9.02; mol. wt. (titration) 274, (ebullioscopic in acetone) 275, 220.

This same acid was obtained by boiling a solution of 2 g. of the ester obtained from the Grignard reagent and methyl chlorocarbonate and 2 g. of potassium hydroxide in 30 cc. of methyl alcohol for two hours. From this mixture 1.7 g. of the ester was recovered, but a small amount of acid melting at 159–160° was separated by acidification of the alkaline solution. A sample of this material mixed with some of the acid obtained by direct carbonation of the Grignard melted at 160°.

Action of 40% Sodium Amalgam on Phenyl-*t*-butyl-*t*-butylethynylbromomethane.—A solution of 20 g. of the bromide in 200 cc. of dry ether was shaken for about thirty-five hours with 25 cc. of 40% sodium amalgam in an atmosphere of dry nitrogen. The amalgam was frozen, the green colored ether solution was decanted into another nitrogen-filled flask and water was added. On working up the ether solution in the usual manner, a white solid and a yellow oil were obtained. By crystallization from absolute alcohol about 5.12 g. (34%) of solid material was obtained. By fractional crystallization from a mixture of absolute alcohol and petroleum ether, about one-fourth of this solid material was obtained as a pure hydrocarbon, m. p. 148–149°.

Anal. Calcd. for $C_{34}H_{46}$: C, 89.80; H, 10.20; mol. wt., 454.4. Found: C, 89.88; H, 10.38; mol. wt. (Rast.), 435.

The remaining solid was crystalline but melted over a range of ten degrees (115–125°). It contained some of the compound just described and an isomeric hydrocarbon.

Anal. Calcd. for $C_{34}H_{46}$: C, 89.80; H, 10.20; mol. wt. 454.4. Found: C, 89.84; H, 10.44; mol. wt. (Rast.), 436.

The yellow oil which was obtained from the original alcoholic solution was distilled under reduced pressure. The first fraction (2.1 g.) boiled at 83–85° (1 mm.); n^{20}_{D} 1.5090 and proved to be the allene 2,2,6,6-tetramethyl-3-phenyl-3,4-heptadiene.

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

The second fraction (4.4 g.) boiled at 190–198° (1 mm.) and on long standing a few crystals separated. Analysis showed it to be a mixture of the two hydrocarbons of the composition $C_{34}H_{46}$ which had been obtained from the solid fraction.

In some preliminary experiments the bromide was treated with 40% sodium amalgam and to this mixture tetramethylethylene bromide was added. The same mixture of hydrocarbons was produced as was obtained in the

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[15] Conant and Blatt, This Journal, **50**, 556 (1928).

[16] Richard, *Ann. chim.*, [8] **21**, 360 (1910).

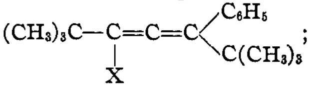
experiment described above. Hence the tetramethylethylene bromide apparently was not concerned in the reaction.

Action of Other Metals on the Bromide.—Silver and copper had no effect on solutions of the bromide. Lithium reacted with an ether solution of the bromide to give the same products that were obtained by the action of sodium amalgam. Reduction of the bromide with zinc dust in alcohol also gave the same mixture of hydrocarbons.

Properties of the Hydrocarbons $C_{34}H_{46}$.—Neither the pure hydrocarbon (m. p. 147–148°) nor the mixture (m. p. 115–125°) showed any sign of cleavage with alkali metals. Neither hydrocarbon could be converted to the other isomer by the action of heat. Neither hydrocarbon showed the property of absorbing oxygen. Both products showed signs of slow oxidation when heated in boiling xylene in the air, but no definite products were isolated. Attempts to ozonize these hydrocarbons gave only tarry products similar to the products previously obtained by the ozonization of other rearranged polyynes.

Summary

1. The Grignard reagent prepared from phenyl - *t* - butyl - *t* - butylethynylbromomethane reacts with water, methyl chlorocarbonate and carbon dioxide to give allene derivatives of the type



$$(CH_3)_3C-\underset{\underset{X}{|}}{C}=C=C\begin{matrix}\diagup C_6H_5\\ \diagdown C(CH_3)_3\end{matrix};$$

where X represents the group introduced into the organic molecule by the reaction.

2. Phenyl-*t*-butyl-*t*-butylethynylbromo-methane reacts with 40% sodium amalgam but does not give a stable sodium alkyl. Instead some of the bromide is reduced to the allene and some of it is coupled to give two isomeric hydrocarbons of the composition $C_{34}H_{46}$ which are thought to be diallenic hydrocarbons.

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[CONTRIBUTION FROM THE UNIVERSITY OF MARYLAND]

The Action of Sulfuric Acid on Butanol-2[1]

BY NATHAN L. DRAKE AND FLETCHER P. VEITCH, JR.

In continuation of our study of the conversion of alcohols to higher olefins by acid catalysts, we have examined the effect of sulfuric acid on butanol-2.

When treated with 75% sulfuric acid under conditions which were found to be most favorable for converting methylisopropylcarbinol into a mixture of decenes,[2] butanol-2 yielded no octene. It was likewise impossible to obtain appreciable yields of octene by use, at atmospheric pressure, of any concentration of acid from 50 to 100%, although time of heating was varied from twenty minutes to forty-eight hours, and reaction temperature from 25 to 100°. Acid of higher than 90% concentration caused the formation of a quantity of high boiling material, probably a mixture of substances of the composition $(C_4H_8)_x$ where x is greater than 2.

The failure to obtain any octene in the experiments cited is unquestionably due to the fact that at the temperatures investigated the formation of butene takes place more readily than does its polymerization, with the consequence that the butene produced escapes before it has had the opportunity to polymerize.

It seemed logical, therefore, to study the effect of operating in a closed system, and preliminary experiments demonstrated that if the butene formed was not allowed to escape, but held in contact with the acid, slow formation of octene took place. Various conditions for effecting the polymerization under pressure were studied, and it was found that with our particular apparatus (see experimental part) the best yield of octene was obtained by the action of 75% sulfuric acid at 80° for forty-eight hours.

The formation of higher polymers from the dimer takes place very readily; distillation of the octene in the presence of a very small quantity of acid results in the formation of substances of higher molecular weight.

A quantity (2.5 kg.) of product having a boiling range which would include any octenes formed, (110–125°) was prepared and subjected to fractional distillation, from which it became apparent that there were at least two chemical individuals present.

Ozonolysis of several fractions of nearly constant refractive index yielded acetaldehyde and methyl *s*-butyl ketone. From these facts it became apparent that the octene present in the fractions ozonized was 3,4-dimethylhexene-2.

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[1] From the Ph.D. dissertation of Fletcher P. Veitch, Jr.

[2] Drake, Kline and Rose, THIS JOURNAL, **56**, 2076 (1934).