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

Rearrangements of Polyynes. VIII.[1] Formation of Diallenes

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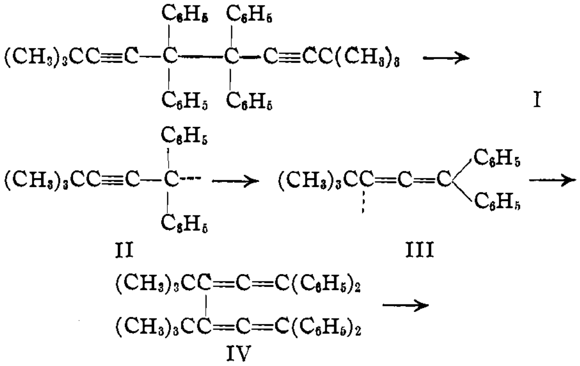
Previous communications from this Laboratory have recorded the rearrangements of hexasubstituted ethanes of the type R—C≡C—CR$_2$—CR$_2$—C≡C—R to more stable hydrocarbons. In the case of tetraphenyldi-*t*-butylethynylethane (I) the stable hydrocarbon has been represented[2] as in the diindenyl (V) which might be expected to form by the steps indicated in the following diagram.



I

II

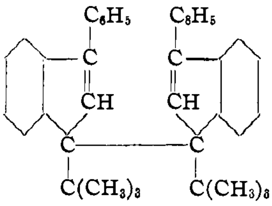
III

IV

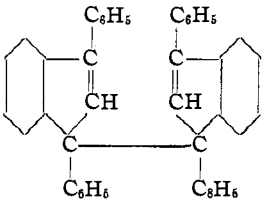
$$(CH_3)_3CC{\equiv}C{-}C(C_6H_5)_2{-}C(C_6H_5)_2{-}C{\equiv}CC(CH_3)_3 \longrightarrow$$

$$(CH_3)_3CC{\equiv}C{-}\dot{C}(C_6H_5)_2 \longrightarrow (CH_3)_3C\dot{C}{=}C{=}C(C_6H_5)_2 \longrightarrow$$

$$\begin{matrix}(CH_3)_3CC{=}C{=}C(C_6H_5)_2\\ |\\ (CH_3)_3CC{=}C{=}C(C_6H_5)_2\end{matrix} \longrightarrow$$



V



VI

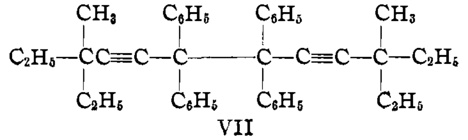
Subsequent evidence has indicated that the formula of the rearranged hydrocarbon is the diallene (IV), and that the diindenyl (V) is only formed by the action of certain reagents on the diallene (IV).

The chief points of evidence which favor the diallene formula for the rearranged hydrocarbon are the following:

(a) The diindenyl (VI) has been synthesized[3] and has been found to differ[4] entirely in its behavior from the rearranged acetylenic ethanes. The diindenyl is very sensitive to oxidizing agents, since even molecular oxygen at elevated temperatures converts it into *o*-dibenzoylbenzene. It also cleaves readily with alkali metals. Neither of these reactions are characteristic of the rearranged hydrocarbons.

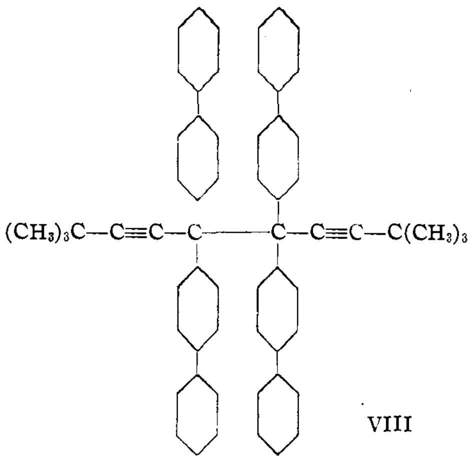
(b) It has been possible to oxidize slowly the rearrangement product of I with oxygen at 140°, and to isolate benzophenone in yields exceeding 50%. This fact appears definitely to exclude the diindenyl formula (V) as a possible structure for the rearranged hydrocarbon. The chief evidence which previously had led to the tentative selection of the diindenyl formula was the production of *o*-benzoylbenzoic acid by chromic acid oxidation and phthalic acid by ozonization. However, we have now observed that acids (which are present in chromic acid oxidation and which may form in ozonization in carbon tetrachloride) cause a rearrangement of the diallene (IV) which involves cyclization to indene derivatives.

Further support of the view that other hexasubstituted ethanes of type I on rearrangement yield diallenes related in structure to IV has been obtained by oxidation experiments. The hydrocarbon $C_{42}H_{46}$[5] which forms when VII rearranges, gives benzophenone on oxidation. Tsao and

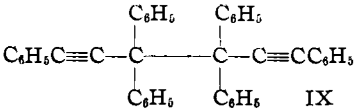


VII

$$C_2H_5{-}C(CH_3)(C_2H_5){-}C{\equiv}C{-}C(C_6H_5)_2{-}C(C_6H_5)_2{-}C{\equiv}C{-}C(CH_3)(C_2H_5){-}C_2H_5$$



VIII



IX

$$C_6H_5C{\equiv}C{-}C(C_6H_5)_2{-}C(C_6H_5)_2{-}C{\equiv}CC_6H_5$$

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[1] For the seventh paper, see Ford and Marvel, THIS JOURNAL, **57**, 2619 (1935).

[2] Althausen and Marvel, *ibid.*, **54**, 1174 (1932).

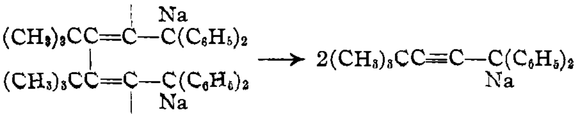
[3] Halley and Marvel, *ibid.*, **54**, 4450 (1932).

[4] Goebel and Marvel, *ibid.*, **55**, 3712 (1933).

[5] Harmon and Marvel, *ibid.*, **55**, 1716 (1933).

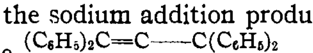
Marvel[6] obtained dibiphenylketone as an oxidation product of the hydrocarbon which formed when VIII isomerized. Willemart[7] has obtained benzophenone as an oxidation product of Moureu's hydrocarbon[8] which is the rearrangement product of IX.[9]

Since very little is known concerning the general behavior of diallenes of the type represented by formula IV, we have reinvestigated the reactions of this compound with a number of reagents. With 40% sodium amalgam the diallene gives a mixture of sodium derivatives which shows that both cleavage by sodium and addition of sodium take place. Evidence for cleavage by sodium was obtained by treating the mixture of sodium derivatives with carbon dioxide. A mixture of acids was produced from which it was possible to isolate a very small amount of the acid which had previously been prepared by the action of carbon dioxide on diphenyl-*t*-butylethynylmethyl sodium (X).[10] This cleavage of the diallene with sodium to give diphenyl-*t*-butylethynylmethyl sodium would be expected if sodium adds first to the carbons carrying the phenyl groups to give a 1,4-diradical (XI).[11]



$$\begin{array}{l}(CH_3)_3C\overset{|}{C}{=}\overset{Na}{C}{-}C(C_6H_5)_2\\ (CH_3)_3C\overset{|}{C}{=}\underset{Na}{C}{-}C(C_6H_5)_2\end{array} \longrightarrow 2(CH_3)_3CC{\equiv}C{-}\underset{Na}{C}(C_6H_5)_2$$

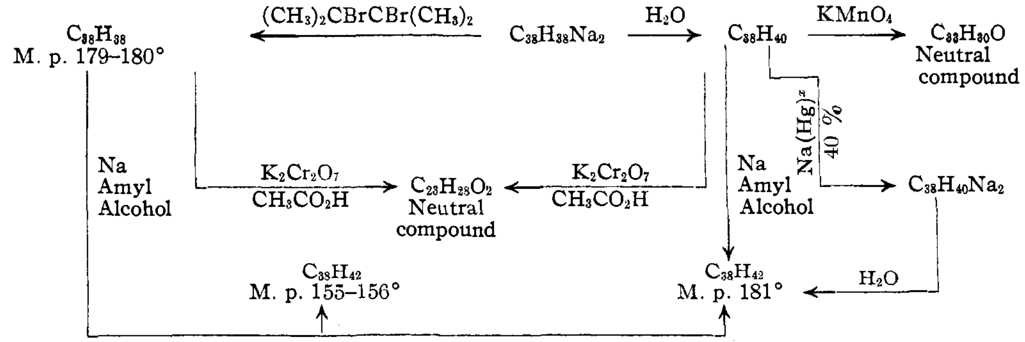
XI X

Sodium also adds to one of the double unions of the diallene to give a disodium compound of the composition $C_{38}H_{38}Na_2$, since previous work[10] has shown that the action of water on the reaction product of 40% sodium amalgam and the diallene gives a hydrocarbon $C_{38}H_{40}$. It has also been found that methyl chlorocarbonate reacts with the mixture of sodium derivatives to give a diester $C_{38}H_{38}(COOCH_3)_2$. One ester group in this product is readily hydrolyzed, and the acid ester which results loses carbon dioxide easily to give a monoester which resists hydrolysis. Schlenk and Bergmann[12] have noted similar reactions in the case of the sodium addition product of tetraphenylallene  $(C_6H_5)_2C{=}\underset{Na}{C}{-}\underset{Na}{C}(C_6H_5)_2$.

Hydrogen iodide in glacial acetic acid converts the diallene to a hydrocarbon $C_{30}H_{24}$. The two *t*-butyl groups must be lost from the molecule in this reduction. It is significant that this product has the same melting point as that recorded by Blum-Bergmann[13] for the dimer of 3-phenylindene. This same $C_{30}H_{24}$ has been obtained by the action of hydrogen iodide on the hydrocarbon $C_{33}H_{38}$ which is formed when the diallene is heated with a glacial acetic acid solution of hydrogen chloride.[2]

In the earlier investigation[2] of the reduction of the diallene a product $C_{19}H_{22}$ was reported. This product is really a C_{38} derivative, and is now believed to be a geometric isomer of the reduction product previously reported as $C_{38}H_{42}$. Both compounds correspond more closely to the composition $C_{38}H_{44}$, but definite structural formulas cannot yet be assigned to these products.

A large number of additional compounds have been prepared directly or indirectly from the sodium addition product of the diallene (IV). It is not possible to assign structural formulas to these compounds, but the relationships indicated in the chart have been established.



As another part of this investigation some reactions of 1,1-diphenyl-4,4-dimethyl-1,2-pentadiene (XII) and its dimer[10] have been studied in order

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(6) Tsao and Marvel, THIS JOURNAL, **55**, 4709 (1933).

(7) Willemart, *Compt. rend.*, **197**, 1659 (1933).

(8) Moureu, Dufraisse and Houghton, *Bull. soc. chim.*, [4] **41**, 56 (1927).

(9) Munro and Marvel, THIS JOURNAL, **54**, 4445 (1932).

(10) Stampfli and Marvel, *ibid.*, **53**, 4057 (1931).

(11) Criegee, *Ber.*, **68**, 665 (1935); a similar cleavage of one of the rearranged hydrocarbons was observed before[5] but the significance of the reaction was not apparent at that time.

(12) Schlenk and Bergmann, *Ann.*, **463**, 1 (1928).

(13) Blum-Bergmann, *ibid.*, **484**, 26 (1930).

to see if any products could be obtained which agreed in properties with those isolated from the reactions of the diallene. No compound obtained from the simple allene (XII) or its dimer was identical with one obtained from the diallene (IV). Since the exact structures of these derivatives from XII and its dimer have not been determined, no discussion of their probable formulas will be given here.

$$(CH_3)_3CCH{=}C{=}C(C_6H_5)_2$$

XII

Experimental

1,1,6,6 - Tetraphenyl - 3,4 - di - *t* - butyl - 1,2,4,5 - hexatetraene (IV).—The hydrocarbon was prepared by treating diphenyl-*t*-butylethynylbromomethane[14] with copper bronze in place of silver which had been used previously. The hydrocarbon was crystallized first from boiling xylene and then by solution in ether and allowing most of the ether to evaporate at room temperature. This procedure gave large crystals of the hydrocarbon, m. p. 152°. Attempts to prepare the same hydrocarbon by reduction of the carbinol with titanous chloride as described by Sweet and Marvel[15] did not give satisfactory results. Some of the desired product was obtained, but it was contaminated with a less soluble, chlorine-containing compound which seemed to be a hydrogen chloride addition product of $C_{38}H_{38}$. This chlorine compound melted at 201°.

Anal. Calcd. for $C_{38}H_{39}Cl$: Cl, 6.64. Found: Cl, 6.59.

Oxidation of 1,1,6,6-Tetraphenyl-3,4-di-*t*-butyl-1,2,4,5-hexatetraene. (a) With Oxygen in Boiling Xylene.—A solution of 1 g. of the hydrocarbon in 20 cc. of technical xylene was heated to 140° in an oil-bath and dry oxygen was slowly bubbled through the solution. The escaping gases were passed through limewater. The oxidation mixture was light yellow in color at the beginning of the experiment, but changed to an orange-red in about two days and deep red in five days. More xylene was added from time to time to keep the volume of the solution constant. After about ten days, the reaction mixture was distilled to remove the xylene and five 10-cc. portions of xylene were added and distilled in order to ensure removal of the volatile products. The volatile portion was extracted with aqueous sodium hydroxide and the aqueous solution was acidified. A phenolic odor developed, and the mixture gave a lavender color with ferric chloride. This was due to small amounts of mixed xylenols formed by oxidation of the xylene.

The residue left after removal of the xylene was taken up in ether, and was extracted with aqueous sodium hydroxide solution. The alkaline solution was acidified and extracted with ether. A non-crystalline acidic mixture was obtained. By sublimation a mixture of acids melting at 86–88° and having a neutral equivalent of 138 was obtained. This was shown to be a mixture of toluic acids derived from the xylene. Pure *o*-xylene under the same conditions yielded pure *o*-toluic acid.

After the acidic substances had been removed from the residue, the remainder was dissolved in 20 cc. of alcohol and heated with 1 g. of hydroxylamine hydrochloride and 6 cc. of 10% sodium hydroxide solution for about twelve hours. From this reaction mixture 0.37 g. (52% of the theoretical amount) of benzophenoneoxime, m. p. 142–143°, was obtained. This did not depress the melting point of an authentic specimen of benzophenoneoxime.

During the oxidation experiment, the lime water in the second tube turned milky showing the formation of carbon dioxide in the oxidation. Attempts were made to find trimethylacetic acid in the alkaline wash water, but the quantities were too small to obtain more than a faint odor of a fatty acid. Larger quantities of the hydrocarbon could not be satisfactorily oxidized.

Control oxidation experiments with xylene alone showed that xylenols and mixed toluic acids were formed; but neither benzophenone, carbon dioxide, nor a volatile fatty acid was present in the oxidation products of xylene.

(b) With Ozone.—The diallene in carbon tetrachloride was treated with ozone as described by Althausen and Marvel.[2] Benzoic acid (m. p. 121°) was isolated from the mixture in addition to the products reported earlier.

(c) With Lead Dioxide.—An attempt was made to oxidize 1 g. of the diallene by refluxing its solution in 8 cc. of xylene with 6 g. of lead dioxide for about six hours, using the procedure which Dufraisse[16] has used for the conversion of Moureu's hydrocarbon to rubrene. No evidence of oxidation was observed, and 0.6 g. of the hydrocarbon was recovered from the experiment.

Oxidation of Sweet's Hydrocarbon.—One gram of the hydrocarbon $C_{42}H_{46}$ obtained by the action of silver on 1,1-diphenyl-4-methyl-4-ethyl-1-bromo-2-hexine[15] was dissolved in hot xylene and oxidized by passing oxygen through the solution for five days. The yield of benzophenoneoxime, isolated as described above, was 0.27 g. (38%).

Attempts to Oxidize Moureu's Hydrocarbon.[8]—One and one-half grams of Moureu's hydrocarbon in 20 cc. of *o*-xylene was treated as described above. No definite products could be isolated.

Reduction of the Diallene. (a) With Sodium and Amyl Alcohol.[17]—The reduction was carried out as described before[2] except larger quantities of material were used. To a solution of 4.5 g. of the diallene in 200 cc. of amyl alcohol was added 25 g. of sodium. The mixture was refluxed about two hours until the sodium had dissolved. The mixture was poured into water, and the alcohol layer was evaporated under reduced pressure until the solution became very concentrated and yellow in color. On cooling, 2.5 g. of a hydrocarbon, m. p. 182°, crystallized. This product was identical with the hydrocarbon, m. p. 182°, which had previously been obtained[2] both by catalytic reduction and sodium–amyl alcohol reduction of $C_{38}H_{38}$. The hydrocarbon was then erroneously described as $C_{19}H_{22}$. It has been found to be $C_{38}H_{44}$, since molecular weight determination by Rast method[18] gave values of 465 and 468, whereas $C_{38}H_{44}$ has a molecular weight of 500 and $C_{19}H_{22}$ only 250.

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(14) Salzberg and Marvel, THIS JOURNAL, **50**, 2840 (1928).

(15) Sweet and Marvel, *ibid.*, **54**, 1184 (1932).

(16) Dufraisse, *Bull. soc. chim.*, **54**, 5761 (1934).

(17) This experiment was carried out by Dr. M. T. Goebel.

(18) Rast, *Ber.*, **55**, 1051, 3727 (1922).

The mother liquors from which this hydrocarbon was isolated were steam-distilled to remove the amyl alcohol and the non-volatile residue was taken up in ether. After removing the ether the residue was crystallized from alcohol and 0.5 g. of a solid, m. p. 132°, was isolated. This compound was identical with the hydrocarbon described as $C_{38}H_{42}$, m. p. 132°, which was previously[2] obtained by the high pressure reduction of the diallene.

Neither of the hydrocarbons could be further reduced by the action of sodium and amyl alcohol. Neither could be oxidized with neutral permanganate or with potassium dichromate in acetic acid. It seems very likely that the hydrocarbon, m. p. 132°, is really an isomer of $C_{38}H_{44}$, as analytical figures fit this composition slightly better than $C_{38}H_{42}$.

(b) **With Hydrogen Iodide in Acetic Acid.**—A solution of 3 g. of the diallene in 30 cc. of glacial acetic acid was refluxed for two hours with 5 g. of red phosphorus and 25 cc. of 47% hydrogen iodide solution. The solution was filtered hot into 400 cc. of water. Sodium bisulfite was added to remove excess iodine, and the white solid which separated was filtered. After recrystallization from a mixture of one volume of ethyl acetate and two volumes of methyl alcohol, 0.2 g. of a product, m. p. 205–207°, was obtained. Further crystallizations from the same solvent gave a product of constant melting point 210–211°.

Anal. Calcd. for $C_{30}H_{24}$: C, 93.6; H, 6.4; mol. wt., 384. Found: C, 93.7; H, 6.44; mol. wt. (Rast). 352.

The properties of this product check closely with those of a dimer of 3-phenylindene which melts at 207–209°.[13] A direct comparison of the two products has not been made.

The Hydrocarbon, $C_{38}H_{38}$, Produced by the Action of Acid on the Diallene

Preparation.—The diallene was rearranged to the isomeric $C_{38}H_{38}$ by the action of acetic acid and hydrogen chloride.[2] In attempting to oxidize this new hydrocarbon with potassium dichromate in acetic acid, a purification was effected, and the rearranged hydrocarbon, $C_{38}H_{38}$, was obtained, melting at 176° instead of at 173–174° as previously recorded. This hydrocarbon was stable toward potassium dichromate in acetic acid, did not form a metal derivative when treated with 40% sodium amalgam, and could not be reduced with sodium and amyl alcohol.

Reduction with Hydrogen Iodide.—A solution of 1 g. of this hydrocarbon in 50 cc. of glacial acetic acid was refluxed for ten hours with 3 g. of red phosphorus and 10 cc. of 47% hydrogen iodide solution. The reaction mixture was worked up as described in the previous hydriodic acid reduction experiment, and 0.25 g. of a product melting at 211–212°, identical with the hydriodic acid reduction product of the diallene, was obtained.

Reactions of the Sodium Derivative of the Diallene

Preparation.—The sodium derivative was prepared by shaking a mixture of 5 g. of the diallene, 100 cc. of anhydrous ether, and 20 cc. of 40% sodium amalgam in an atmosphere of dry nitrogen for about twenty hours. The amalgam was frozen and the solution of the metal alkyl was decanted into another nitrogen filled flask.

Reaction with Carbon Dioxide.—One run of the metal alkyl was treated with carbon dioxide and the organic acids isolated in the usual manner. A rather complex mixture was obtained, but by careful crystallization of the product from a mixture of two parts of methyl alcohol and one part of ethyl acetate, an acid melting at 171° was obtained. This acid was identical with the acid previously prepared by the action of carbon dioxide on diphenyl-*t*-butylethynylmethyl sodium.[10]

Reaction with Methyl Chlorocarbonate.—Methyl chlorocarbonate was added dropwise to a solution of the sodium derivative until the red color of the latter had disappeared. The reaction mixture was washed with water, and the ether layer was evaporated. The residue was dissolved in a mixture of methyl alcohol and ethyl acetate. On slow evaporation of the solvent, 1 g. of white crystals separated. Recrystallization in the same manner gave a product melting sharply at 173°.

Anal. Calcd. for $C_{38}H_{38}(COOCH_3)_2$: C, 82.35; H, 7.19; mol. wt., 612. Found: C, 81.2, 83.5; H, 7.18, 7.16; mol. wt. (Rast), 535.

This ester was hydrolyzed by boiling 0.5 g. with a solution of 0.4 g. of potassium hydroxide in 20 cc. of methyl alcohol for one hour. On acidifying, 0.32 g. of crystalline material separated. This material melted over a range, sintering at 136–138°, and completely melting at about 160°. It was heated to 180°, and a vigorous evolution of gas (presumably carbon dioxide) occurred. After cooling the melt and recrystallizing the residue from a mixture of ether and alcohol, a pure product melting at 162° was obtained.

Anal. Calcd. for $C_{38}H_{39}(COOCH_3)$: C, 86.7; H, 7.59. Found: C, 87.13; H, 7.55.

Reaction with Water.—Treating the ether solution of the sodium derivative with water gave the hydrocarbon $C_{38}H_{40}$, m. p. 163°, which has previously been described.[10]

Reaction with Tetramethylethylene Bromide.—The isomeric $C_{38}H_{38}$, m. p. 179–180°, previously described[2] was obtained by treating the sodium derivative of the diallene with tetramethylethylene bromide.

Reactions of the Hydrocarbon $C_{38}H_{40}$ Obtained by the Action of Water on the Sodium Derivative of the Diallene

Oxidation. (a) **With Potassium Permanganate.**—To a solution of 1.5 g. of $C_{38}H_{40}$ in 75 cc. of acetone was added 5 g. of powdered potassium permanganate. This solution was refluxed for about twenty-four hours, then 50 cc. of acetone and 3 g. of potassium permanganate were added and the mixture was again boiled for about twenty-four hours. The mixture was filtered and the excess potassium permanganate in the filtrate was destroyed by adding a little hydrogen peroxide and sulfuric acid. The acetone was removed by evaporation and the residue was taken up in ether. On evaporation of most of the ether, about 0.7 g. of white crystalline material, m. p. 217–218°, was obtained. This product was a neutral compound.

Anal. Calcd. for $C_{33}H_{30}O_2$: C, 86.4; H, 6.54; mol. wt., 496. Found: C, 86.16; H, 6.53; mol. wt. (Rast), 420.

(b) **With Potassium Dichromate in Acetic Acid.**—A solution of 0.1 g. of $C_{38}H_{40}$ and 1 g. of potassium dichromate in 10 cc. of glacial acetic acid was refluxed for five hours. The change in color showed that oxidation began almost at once. The reaction mixture was poured into water and extracted with ether. No acidic substance could be extracted from the ether with aqueous alkali. After drying the ether solution, it was evaporated and the residue was recrystallized to constant melting point (169°) from alcohol. The yield was 20 to 30 mg. of a neutral compound.

Anal. Calcd. for $C_{28}H_{28}O_3$: C, 78.4; H, 7.9. Found: C, 79.1; H, 7.4.

Reduction. (a) With Sodium and Amyl Alcohol.—A solution of 0.25 g. of $C_{38}H_{40}$ in 30 cc. of boiling amyl alcohol was treated with 3 g. of sodium. When the sodium had dissolved the reaction mixture was worked up in the usual manner. About 0.15 g. of hydrocarbon was separated in the first crop of crystals from the amyl alcohol and after recrystallization from ether it melted at 197°.

Anal. Calcd. for $C_{38}H_{42}$: C, 91.56; H, 8.44. Found: C, 91.44; H, 8.52.

On concentrating the amyl alcohol mother liquors, a second crop of crystals, melting at 184–186°, was obtained. This was obviously a mixture of hydrocarbons containing some of the $C_{38}H_{42}$, melting at 197°, and a lower melting isomer. This mixture proved to be identical with the product, m. p. 181–182°, which was previously obtained[2] by the reduction of $C_{38}H_{40}$ with sodium and ethyl alcohol. It seems probable that the low melting isomer in this mixture is identical with the $C_{38}H_{42}$, m. p. 155°, which will be described later as a reduction product of an isomeric $C_{38}H_{38}$, but this point could not be definitely established.

(b) By Treatment with 40% Sodium Amalgam and then Water.—A solution of 0.4 g. of $C_{38}H_{40}$ in 50 cc. of dry ether was shaken with 15 cc. of 40% sodium amalgam in an atmosphere of nitrogen for twenty-four hours. A red color developed within ten minutes. The amalgam was frozen and the sodium alkyl was treated with freshly boiled water until the color disappeared from the solution. On removal of the excess solvent and recrystallization of the residue from ether, 0.12 g. of hydrocarbon $C_{38}H_{42}$, m. p. 197–198°, was obtained. This was identical with one of the isomers obtained by the sodium–amyl alcohol reduction of $C_{38}H_{40}$.

Reactions of the Hydrocarbon $C_{38}H_{38}$ Obtained by the Action of Tetramethylethylene Bromide on the Sodium Derivative of the Diallene

Oxidation.—To a solution of 0.2 g. of this hydrocarbon in 10 cc. of glacial acetic acid was added 1 g. of potassium dichromate and the mixture was refluxed for five hours. No acidic substances were found, but 20 mg. of a neutral white solid, m. p. 169°, was obtained. This was identical with the potassium dichromate oxidation product of $C_{38}H_{40}$ described above. Neutral potassium permanganate did not attack this isomer of $C_{38}H_{38}$.

Reduction.—A solution of 0.25 g. of the hydrocarbon in 30 cc. of amyl alcohol was reduced by adding 3 g. of sodium. From this reduction, 0.08 g. of the hydrocarbon $C_{38}H_{42}$, m. p. 197°, identical with one of the reduction products of $C_{38}H_{40}$ was obtained. From the more soluble portion another product, melting at 155–156° after recrystallization from alcohol, was obtained. It was apparently an isomeric $C_{38}H_{42}$ not previously isolated.

Anal. Calcd. for $C_{38}H_{42}$: C, 91.56; H, 8.44. Found: C, 91.27; H, 8.57.

Reaction with 40% Sodium Amalgam.—A solution of 0.5 g. of the hydrocarbon in 50 cc. of ether was shaken with 5 cc. of 40% sodium amalgam solution in a nitrogen atmosphere for about twenty hours. A red color developed quickly. At the end of the shaking period, the excess amalgam was frozen and the metal alkyl solution was decanted and then decomposed with water. From this reaction mixture 0.1 g. of the hydrocarbon $C_{38}H_{40}$, m. p. 163°, was obtained, indicating that this sodium derivative was identical with that prepared from the diallene.

Reactions of 1,1-Diphenyl-4-dimethyl-1,2-pentadiene and its Dimer

The Monomer and 40% Sodium Amalgam.—A solution of 3 g. of 1,1-diphenyl-4,4-dimethyl-1,2-pentadiene[10] in 100 cc. of dry ether was treated with 10 cc. of 40% sodium amalgam under the usual conditions. A red color developed at once. After about twelve hours, the excess amalgam was frozen and the ether solution was divided into two portions.

One portion was treated with a 10% ether solution of tetramethylethylene bromide until the color of the solution had disappeared. On working up the mixture and crystallizing the product from petroleum ether, 0.3 g. of a product melting at 143–144° was obtained.

Anal. Calcd. for $C_{38}H_{40}$: C, 91.93; H, 8.07; mol. wt., 496. Found: C, 91.54; H, 8.51; mol. wt., 435.

The second portion of the solution of the sodium derivative was treated with water. No crystalline products could be isolated from this reaction.

The Dimer and 40% Sodium Amalgam.—A solution of 3 g. of the dimer of 1,1-diphenyl-4,4-dimethyl-1,2-pentadiene[10] in 100 cc. of ether was treated with 10 cc. of 40% sodium amalgam. A red color developed at once. After twelve hours' shaking, the excess amalgam was frozen and the solution of the sodium derivative was decanted and divided into two parts.

One portion of this solution was decolorized by treatment with a 10% ether solution of tetramethylethylene bromide. From this mixture there was obtained 0.3 g. of yellow crystalline material, m. p. 176°, identical with the original dimer.

A second portion of the solution of the sodium derivative was treated with water. On working up this reaction mixture, 0.25 g. of a product melting at 133° after two crystallizations from absolute alcohol was obtained. This product was not identical with the $C_{38}H_{44}$, m. p. 132°, obtained by the sodium–amyl alcohol reduction of the diallene (IV).

Anal. Calcd. for $C_{38}H_{42}$: C, 91.56; H, 8.44. Found: C, 91.66; H, 8.13.

Reduction of the Dimer with Sodium and Amyl Alcohol.—A solution of 0.6 g. of the dimer in 100 cc. of amyl alcohol was reduced by adding 3 g. of sodium. From this reaction mixture 0.22 g. of white needles, m. p. 133°, was obtained. This product gave a depression of 30° in melting point when mixed with $C_{38}H_{44}$, m. p. 132°, and a depression of about 5° when mixed with the hydrocarbon $C_{38}H_{42}$, m. p. 133°, obtained by action of sodium amalgam and water on the dimer. It is probably identical with this last compound.

Reduction of the Dimer with Hydrogen Iodide.—A solution of 0.6 g. of the dimer in 40 cc. of glacial acetic acid was refluxed with 2 g. of red phosphorus and 10 cc. of 47% hydrogen iodide solution for ten hours. From this reaction mixture a product, m. p. 134–135°, was obtained. It showed only a slight depression in melting point when mixed with the product obtained by reducing the dimer with sodium and amyl alcohol.

Anal. Calcd. for $C_{38}H_{42}$: C, 91.56; H, 8.44; mol. wt., 498. Found: C, 91.33; H, 8.49; mol. wt. (Rast), 435.

Oxidation of the Dimer.—A solution of 1 g. of the dimer in 20 cc. of glacial acetic acid was refluxed for eight hours with 3 g. of potassium dichromate. No acidic substances were isolated from the oxidation mixture. A small amount of a neutral product, m. p. 227°, after crystallization from ether was isolated.

Anal. Calcd. for $C_{26}H_{26}O_2$: C, 84.3; H, 7.02. Found: C, 84.29; H, 7.05.

No benzophenone could be detected in the products of oxidation.

Summary

The structure of the hydrocarbon $C_{38}H_{38}$, which forms when tetraphenyldi-*t*-butylethynylethane undergoes rearrangement, has been found to be that of a diallene, 1,1,6,6-tetraphenyl-4,5-di-*t*-butyl-1,2,4,5-hexatetraene. Many reactions of this and closely related compounds have been investigated.

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The Spectrum and the Force Constants of the Ethylene Molecule

BY LYMAN G. BONNER

Introduction

The first investigation of the infra-red absorption spectrum of ethylene gas was made by Coblentz[1] in 1905. Using a prism spectrometer he was able to locate a number of absorption maxima but did not resolve any of the fine structure. In 1928, Levin and Meyer[2] reinvestigated the spectrum of this molecule, using higher dispersion instruments and taking greater care to obtain pure gas and to exclude atmospheric effects. In the region 2–15 μ they found a total of ten absorption bands, most of which were at least indicated on Coblentz' prism curve.

The spectrum of ethylene in the photographic region of the infra-red has been investigated by Badger and Binder,[3] who found only one band, at 8720 Å.

The most recent work on the Raman spectrum of this molecule was carried out by Dickinson, Dillon and Rassetti.[4] They used the gas at high pressure and mercury resonance excitation and found a total of six lines.

Any attempt to obtain a complete vibrational analysis of ethylene, for force constant evaluation, showed, however, that there were a good many gaps and inconsistencies in the experimental data. There has been made, then, in the present work, a complete reinvestigation of the photographic, infra-red, and Raman spectra. The results of this work lead to a satisfactory determination of eleven of the twelve fundamental vibration frequencies of the ethylene molecule, and permit an estimate to be made of the twelfth.

Eleven new absorption bands have been found in the photographic infra-red. Experiments using liquid ethylene have shown the presence of three new Raman lines, and have failed to show two of those reported by Dickinson, Dillon and Rassetti.

Experimental

All infra-red absorption experiments were done with the stainless steel absorption tube and twenty-one foot grating spectrograph recently constructed in this Laboratory.[4a] The tube measures approximately seven-eighths inch in diameter and it has a maximum length of seventy feet. The full length was used in investigations of all regions of the spectrum except that beyond 10,000 Å. For this region, due to the low sensitivity of all available plates, it was necessary to reduce the path length to twenty-eight feet. Pressures of gas used in the tube ranged from one to seven atmospheres and the entire spectral region investigated lay between 6000 and 12,000 Å. Eastman spectroscopic plates were used for wave lengths below 10,300 Å., but for longer wave lengths their sensitivity was too low, even with the reduced tube length.

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