

of the *p*-bromophenacyl esters, *viz.*, those of adipic and suberic acids, were analyzed for bromine by means of the Parr peroxide bomb and the results checked with the calculated percentages.

Summary

A number of dibasic organic acids have been converted to the phenacyl and *p*-bromophenacyl esters and their melting points determined.

WORCESTER, MASSACHUSETTS

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

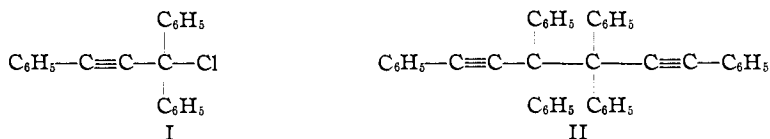
REARRANGEMENTS OF POLYINES. II. TETRAPHENYLDIPHENYLETHINYLETHANE

BY H. E. MUNRO AND C. S. MARVEL

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Several years ago a hydrocarbon, $C_{42}H_{30}$, was prepared by the action of iron on diphenylphenylethynylchloromethane (I) and assigned the formula tetraphenyldiphenylethynylethane¹ (II).



The preparation of this same hydrocarbon has also been reported by Wieland and Kloss,² who used not only the original method of treating diphenylphenylethynylchloromethane with a metal, but two other methods, namely, the reduction of diphenylphenylethynylcarbinol (III) with titanium trichloride and the oxidation of phenylethynyldiphenylmethane (IV) with potassium permanganate solution.



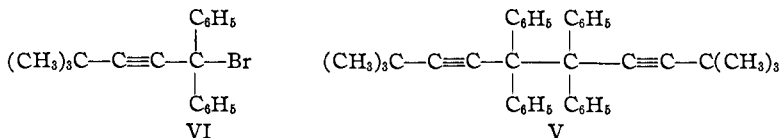
Some recent work³ in this Laboratory on the closely related hydrocarbon tetraphenyl-di-*tert.*-butylethynylethane (V) has demonstrated that it has properties which are altogether unlike those reported for Moureu's hydrocarbon. The *tert.*-butyl derivative is easily cleaved by 40% sodium amalgam, absorbs oxygen rapidly and undergoes rearrangement in solution at room temperature to give an isomeric hydrocarbon, $C_{38}H_{38}$. This re-

¹ Moureu, Dufraisse and Houghton, *Bull. soc. chim.*, [4] 41, 56 (1927).

² Wieland and Kloss, *Ann.*, 470, 217 (1929).

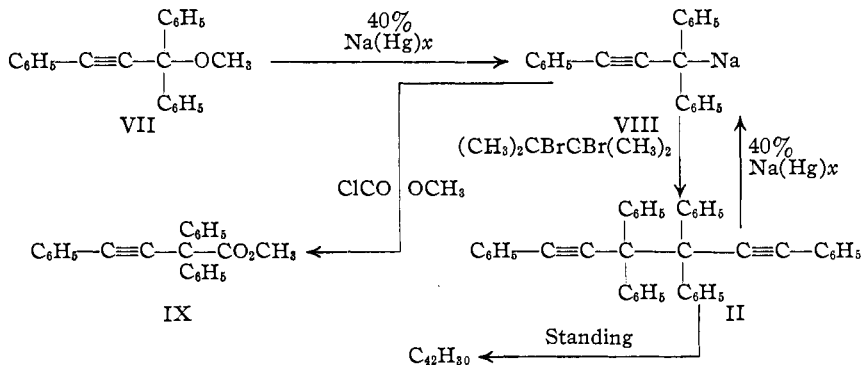
³ Stampfli and Marvel, *THIS JOURNAL*, 53, 4057 (1931).

arranged hydrocarbon, whose structure has been under investigation⁴ in this Laboratory for some time, is more nearly analogous to the hydrocarbon $C_{42}H_{30}$ which Moureu obtained. It has been found^{4a} also that the action of metals on diphenyl-*tert.*-butylethynylbromomethane (VI) leads not to the ethane (V) but to the rearrangement product, $C_{38}H_{28}$. More recently it has been shown⁵ that titanium trichloride reduces di-



phenyl-*tert.*-butylethynylcarbinol to this same rearranged hydrocarbon instead of the ethane. These facts coupled with the wide variation between the properties of Moureu's hydrocarbon and the tetraaryldialkyl-ethynylethane which has been prepared in this Laboratory have led to a further investigation of tetraphenyldiphenylethynylethane.

The preparation of this compound has now been accomplished by using the general method of Ziegler and Schnell.⁶ Diphenylphenylethynylcarbinol (III) has been converted to the methyl ether (VII) by the procedure described by Moureu, Dufraisse and Blatt.⁷ By treating this ether with 40% sodium amalgam the alkali metal alkyl (VIII) is obtained. The ethane (II) is obtained from this sodium derivative by the action of tetramethylethylene bromide. The ethane is very unstable and has not been isolated in a pure condition. In solution, it is readily cleaved by 40% sodium amalgam to give the metal alkyl (VIII), which has been identified by conversion to the methyl ester of diphenylphenylethynylacetic acid (IX); it absorbs oxygen very rapidly, but does not form a



⁴ (a) Salzberg and Marvel, *THIS JOURNAL*, **50**, 2840 (1928); (b) Althausen and Marvel, *ibid.*, **54**, 1174 (1932).

⁵ Sweet and Marvel, *ibid.*, **54**, 1184 (1932).

⁶ Ziegler and Schnell, *Ann.*, **437**, 244 (1924).

⁷ Moureu, Dufraisse and Blatt, *Bull. soc. chim.*, [4] **35**, 1412 (1924).

stable peroxide; and it rearranges to give Moureu's hydrocarbon, $C_{42}H_{30}$. In spite of the fact that the ethane has not been isolated in a crystalline condition, these reactions show that it is strictly analogous to the corresponding *tert.*-butyl derivative (V) in its behavior.

The reactions of Moureu's hydrocarbon have been investigated to some extent. That it does not absorb oxygen has been demonstrated by the earlier work.^{1,2} It is not cleaved by 40% sodium amalgam but it does add sodium, apparently producing a disodium derivative, $C_{42}H_{20}Na_2$, which on treatment with water gives a solid hydrocarbon $C_{42}H_{32}$ and with methyl chlorocarbonate gives an impure solid ester.

The evidence is thus rather conclusive that the hydrocarbon reported by Moureu does not have the structure which was assumed for it but is analogous to the hydrocarbon, $C_{38}H_{38}$, which is formed by the rearrangement of tetraphenyl-di-*tert.*-butylethynylethane. A diindene formula has been suggested for the isomeric $C_{38}H_{38}$ hydrocarbon but the evidence now available makes this formula seem very unlikely.⁸

Experimental

Diphenylphenylethynylmethyl-sodium.—This sodium alkyl was first obtained from diphenylphenylethynylchloromethane which was prepared by the procedure described by Moureu, Dufraisse and Mackall.⁹ However, better yields of the sodium derivative based on the carbinol were obtained by treating the methyl ether⁷ with 40% sodium amalgam. The procedure using either starting material was that described previously for diphenyl-*tert.*-butylethynylmethyl-sodium.³ The sodium alkyl was not isolated but was used in the succeeding experiments.

Methyl Diphenylphenylethynylacetate.—In order to identify the sodium alkyl an attempt was made to convert it to diphenylphenylethynylacetic acid by treatment with carbon dioxide. The acid thus obtained was apparently unstable and did not crystallize well. However, the methyl ester was obtained by treating the sodium alkyl with methyl chlorocarbonate.

The calculated amount of methyl chlorocarbonate (6 g.) was added to an ether solution of the sodium alkyl prepared from 9.0 g. of the methyl ether. Considerable heat was evolved by the reaction mixture. The red color of the solution disappeared and sodium chloride precipitated. The solution was filtered to remove the salt and the ether was evaporated. A thick reddish oil remained. After two distillations under reduced pressure a product boiling at 98–105° (2–3 mm.) and weighing 3.5 g. (35% of the theoretical amount) was obtained.

This product decolorized bromine in carbon tetrachloride solution, reduced an aqueous solution of potassium permanganate and gave a distinct red color to concentrated sulfuric acid; d_4^{20} 1.0621; n_D^{20} 1.5790; M_D , calcd. for methyl diphenylphenylethynylacetate, 102.26; found, 102.06.

Anal. Calcd. for $C_{29}H_{18}O_2$: C, 84.66; H, 5.52. Found: C, 84.85; H, 5.66.

It may be of interest to report here that treatment of a solution of this sodium alkyl and also the sodium addition product of Moureu's hydrocarbon with phenyl isocyanate in the hope of obtaining crystalline anilides of the corresponding acids gave instead

⁸ Halley and Marvel, *THIS JOURNAL*, **54**, 4450 (1932).

⁹ Moureu, Dufraisse and Mackall, *Bull. soc. chim.*, [4] **33**, 934 (1923).

triphenylisocyanurate, m. p. 281–282°, which has previously been obtained by heating phenyl isocyanate with sodium acetate.¹⁰

Tetraphenyldiphenylethynylethane.—To an ether solution of the sodium alkyl prepared from 10 g. of the methyl ether was added enough of a 10% ether solution of tetramethylethylene bromide to discharge the deep red color of the mixture. The ether was removed under reduced pressure while the temperature was held at about 0°. The residue was treated with about 200 cc. of water to wash out the sodium bromide, the remaining oily material was dissolved in petroleum ether (b. p. 25–40°) and the solution was dried over anhydrous magnesium sulfate. These operations were carried out at room temperature and as rapidly as possible (about ten minutes). The petroleum ether solution was cooled in an acetone–solid carbon dioxide cooling bath and a heavy liquid separated. The petroleum ether was decanted. The oil was then redissolved in fresh petroleum ether at room temperature and again cooled to cause the hydrocarbon to separate. After two such treatments the hydrocarbon separated in white flocculent crystals which melted and turned red when an attempt was made to isolate them by filtration.

When the petroleum ether solution of this substance was allowed to stand for an hour at room temperature and then chilled, a hydrocarbon melting at 160–165° was obtained. This was identical with Moureu's hydrocarbon as demonstrated by mixed melting point determinations.

In order to establish definitely the presence of the unstable ethane cleavage experiments with forty per cent. amalgam were carried out on the material which separated when the solutions were cooled in carbon dioxide–acetone baths. About 1 g. of this oily material was taken up in 30 cc. of dry ether and treated with 5 cc. of 40% sodium amalgam. The deep red color of the diphenylphenylethynylmethyl-sodium was apparent within three minutes. After three hours the mixture was treated with methyl chlorocarbonate and the reaction mixture was worked up for methyl diphenylphenylethynylacetate. Only a few drops were obtained, but this had a refractive index of 1.5820 whereas the ester prepared from the known alkyl gave the value 1.5790.

To further establish this point, the metal alkyl from 8 g. of the methyl ether was coupled with tetramethylethylene bromide and then the decolorized solution treated with 15 cc. of 40% sodium amalgam. The deep red color reappeared in a few minutes and after treatment with methyl chlorocarbonate 2.5 g. (30% of the theoretical amount) of product was obtained; d_4^{20} 1.058; n_D^{20} 1.5790 boiling at 122–23° (8 mm.).

From the residues left on the distillation of this ester was isolated a product melting at 93–96° which was identical with the one obtained from the sodium addition product of Moureu's hydrocarbon on treatment with methyl chlorocarbonate.

In the early experiments it was found that Moureu's hydrocarbon could be obtained readily by treating a solution of diphenylphenylethynylmethyl-sodium with tetramethylethylene bromide, and then working up the colorless solution without keeping the temperature low. The product thus obtained on recrystallization from alcohol melted at 165–167° and as much as 2 g. at a run was isolated. Samples of Moureu's hydrocarbon were prepared by each of the methods which have been described^{1,2} and were found to melt at 169°. A mixture of this material prepared from the sodium alkyl melted at 165–167°.

On one occasion the impure ethane prepared from 10 g. of the methyl ether was dissolved in 50 cc. of 95% alcohol and heated on the steam cone for fifteen minutes. An orange-red solid separated and was filtered. After recrystallization from alcohol this melted at 233–234°. The yield was 0.56 g. This compound is another isomer in the series.

¹⁰ Hofmann, *Ber.*, 18, 765 (1885).

Anal. Calcd. for $C_{42}H_{30}$; C, 94.34; H, 5.66. Found: C, 94.0, 94.1; H, 5.61, 5.55.

The mother liquors from the above preparation yielded 0.25 g. of Moureu's hydrocarbon which melted at 168–169°.

Treatment of a solution of the ethane with 1% sodium amalgam did not give the desired alkyl but from such solutions Moureu's hydrocarbon was obtained. Apparently rearrangement proceeded more rapidly than combination with the dilute amalgam.

A solution of the crude ethane (from 2 g. of the methyl ether) in 100 cc. of dry ether was connected with a gas buret filled with dry oxygen. The gas was absorbed quite rapidly at first and then the rate of absorption dropped off gradually. By flushing out the flask above the ether solution with fresh oxygen, further rapid absorption of oxygen was resumed. No accurate estimates of oxygen absorption were attempted because the hydrocarbon was so impure. However, this experiment showed that 135 cc. of oxygen was taken up and this is a sufficient quantity to prove that the new ethane will oxidize with gaseous oxygen. From the oxidized reaction mixture, no peroxide could be isolated but some of the rearrangement product, Moureu's hydrocarbon, was obtained. Moureu's hydrocarbon does not oxidize in gaseous oxygen under the conditions of this experiment. A solution of the new ethane decolorizes a carbon tetrachloride solution of bromine very rapidly. An ether solution of Moureu's hydrocarbon under the same conditions did not decolorize a carbon tetrachloride solution of bromine.

Some Reactions of the Sodium Derivative of Moureu's Hydrocarbon, $C_{42}H_{30}$.—In order to be certain that the sodium alkyl obtained from methyl diphenylphenylethynylmethyl ether and from the cleavage of tetraphenyldiphenylethinylolethane was really different from the sodium addition product of Moureu's hydrocarbon, some comparative experiments were performed.

An ether solution of the true ethane prepared from 0.15 g. of the methyl ether was treated with 5 cc. of 40% sodium amalgam and a bright reddish-purple color developed within twenty minutes. Under exactly similar conditions 0.075 g. of Moureu's hydrocarbon in 100 cc. of ether gave no color with 40% sodium amalgam in twenty minutes but within forty minutes a reddish-brown color developed. The color of the solution was distinctly different.

The sodium addition product was prepared by shaking an ether solution of 4 g. of Moureu's hydrocarbon with 15 cc. of 40% sodium amalgam. To the reddish-brown solution was carefully added a few cc. of boiled distilled water. When the color of the metal derivative had disappeared, 200 cc. more of water was added, the ether solution was separated and evaporated. The residue was a brown sticky mass which was very insoluble. By purification with petroleum ether a product melting at 239–241° was obtained. It was apparently a dihydro derivative of Moureu's hydrocarbon although a satisfactory molecular weight was not obtained.

Anal. Calcd. for $C_{42}H_{32}$: C, 94.03; H, 5.97. Found: C, 93.33, 93.44; H, 5.98, 5.93. *Mol. wt.* (Rast). Calcd. for $C_{42}H_{32}$: 536. Found: 394.

The sodium addition product prepared from 6 g. of Moureu's hydrocarbon and 15 cc. of 40% sodium amalgam in dry ether was treated with enough methyl chlorocarbonate to discharge the color of the solution. On working up the reaction mixture as described under methyl diphenylphenylethynylacetate, a thick gummy product which did not distil at 275° (2 mm.) was obtained. When this residue was treated with alcohol, a reddish-brown precipitate was formed. Attempts to purify this material by recrystallization from various organic solvents were unsuccessful. A light tan powder was obtained by dissolving the dark material in hot glacial acetic acid, filtering off the insoluble tarry material and adding water. After drying in a desiccator under reduced

pressure, this material melted at 90–93°. The melting point was not changed by further treatment. The material was evidently not a single product but analysis indicated a formula $C_{42}H_{30}(COOCH_3)_2$.

Anal. Calcd. for $C_{42}H_{30}O_4$: C, 84.7; H, 5.52. Found: C, 85.4; H, 5.68.

This product requires further study but it is of interest because it shows that the true ethane and its rearrangement product give distinctly different compounds when treated with sodium amalgam.

Summary

Tetraphenyldiphenylethinyethane has been prepared in solution. This hydrocarbon is oxidized by oxygen, is cleaved by 40% sodium amalgam, and readily rearranges to an isomeric hydrocarbon, $C_{42}H_{30}$, which is identical with the hydrocarbon which has previously been prepared by the action of metals on diphenylphenylethynylchloromethane.

URBANA, ILLINOIS

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

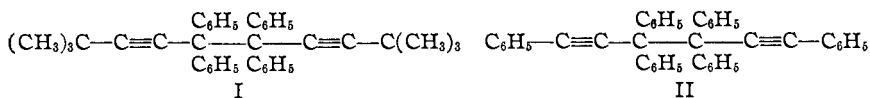
REARRANGEMENTS OF POLYINES. III. THE SYNTHESIS OF BIS-1,1'-(1,3-DIPHENYLINDYL)

BY L. F. HALLEY AND C. S. MARVEL

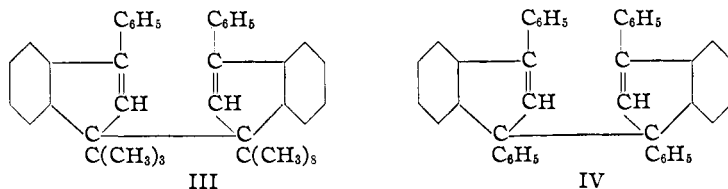
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Recent investigations¹ have shown that certain tetraaryl-diethynylethanes readily undergo rearrangement and yield isomeric hydrocarbons of unknown structures. The two compounds which have been studied thus far are *sym.*-tetraphenyldi-*tert.*-butylethinyethane (I) and *sym.*-tetraphenyldiphenylethinyethane (II). While these ethanes exhibit a reactivity which resembles that of the hexa-arylethanes, the isomeric



hydrocarbons obtained by their rearrangement are much more stable compounds. A study of the reactions of the hydrocarbon, $C_{38}H_{38}$, obtained by the rearrangement of tetraphenyldi-*tert.*-butylethinyethane (I) led to the suggestion that it might have a diindene structure (III).



¹ (a) Stampfli and Marvel, *THIS JOURNAL*, **53**, 4057 (1931); (b) Althausen and Marvel, *ibid.*, **54**, 1174 (1932); (c) Munro and Marvel, *ibid.*, **54**, 4445 (1932).