hydrate upon phenylbromofluorene. With sodium in liquid ammonia solution, the hydrazo compound reacted to form a product, which, when hydrolyzed, yielded phenylfluorene. With various oxidizing agents, hydrazophenylfluorene yielded mainly phenylfluoryl peroxide.

3. In experiments with palladium black, evidence was obtained for the possible momentary existence of azophenylfluorene; the compound, if formed, decomposed under the experimental conditions yielding nitrogen, phenylfluorene and dibiphenylenediphenylethane. The action of oxygen upon hydrazophenylfluorene in the presence of palladium black led to the formation of phenylfluoryl peroxide and phenylfluorenol.

4. The action of hydrogen upon dibiphenylenediphenylethane and upon phenylfluoryl peroxide in the presence of palladium black yielded phenylfluorene.

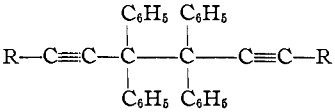
WASHINGTON, D. C. RECEIVED NOVEMBER 16, 1932
PUBLISHED APRIL 6, 1933

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

Rearrangements of Polyines. IV. Tetraphenyl-di-(3-methyl-3-ethylpentinyl-1)-ethane

BY J. HARMON AND C. S. MARVEL

Acetylenic hydrocarbons of the type represented in formula I have been found to be quite unstable and to undergo a characteristic rearrangement to produce more stable isomeric hydrocarbons.[1] The nature of this rearrangement is still unknown and as yet it is impossible to assign definite structures to the stable hydrocarbons. The present communication describes another unstable hydrocarbon of type I and its rearrangement products.



$$R-C\equiv C-\overset{C_6H_5}{\underset{C_6H_5}{C}}-\overset{C_6H_5}{\underset{C_6H_5}{C}}-C\equiv C-R$$

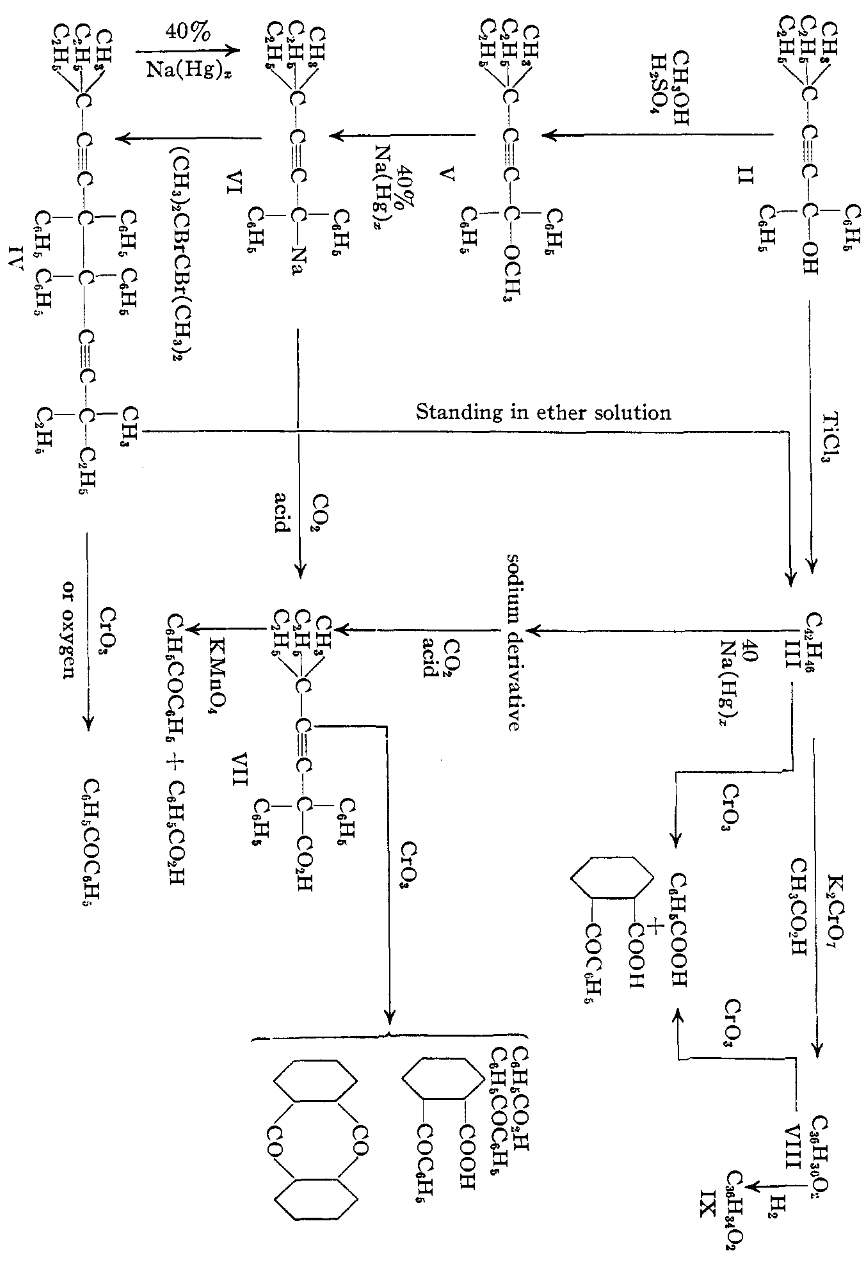
I

The reduction of diphenyl-(3-methyl-3-ethylpentinyl-1)-carbinol (II) with titanium trichloride to give the hydrocarbon $C_{42}H_{46}$ (III) has already been described.[2] The evidence indicated that this hydrocarbon was not the ethane (IV) but its stable rearrangement product. This fact has now been definitely established by the synthesis of the ethane derivative. The following chart indicates the method used in this synthesis and summarizes the reactions of the two isomeric hydrocarbons which have been studied in the hope of furnishing evidence which will eventually make it possible to understand the rearrangement of this class of polyines.

---

[1] For references to earlier work, see Halley and Marvel, THIS JOURNAL, **54**, 4450 (1932).

[2] Sweet and Marvel, *ibid.*, **54**, 1184 (1932).



The new ethane (IV) was easily oxidized in the air and readily rearranged to the isomeric hydrocarbon, $C_{42}H_{46}$ (III). Chromium trioxide oxidized the ethane to benzophenone and the yield was 62%, which indicated that the two halves of this molecule really had the structure indicated. The ethane was readily cleaved with 40% sodium amalgam and yielded a sodium alkyl which could be converted to the acid (VII). The structure of this acid was established by oxidation with alkaline potassium permanganate to give principally benzophenone and a little benzoic acid. Chromium trioxide in acetic acid oxidized this acid to give primarily benzophenone (57%) but ring closures also occurred during the reaction because some *o*-benzoylbenzoic acid and traces of anthraquinone were isolated from the oxidation mixture.

The rearranged hydrocarbon, $C_{42}H_{46}$ (III), was not oxidized by oxygen. With potassium dichromate in acetic acid it was oxidized to a neutral compound $C_{36}H_{30}O_2$ (VIII). This product apparently resulted by the removal of two methyl and two ethyl groups and the addition of two atoms of oxygen. The neutral oxidation product absorbed four atoms of hydrogen when reduced catalytically with hydrogen in the presence of a platinum oxide catalyst.[3] These facts have been interpreted as meaning that the neutral compound is some type of diketone but no derivatives of the carbonyl group could be prepared. Oxidation of either the hydrocarbon, $C_{42}H_{46}$, or of the neutral oxygen compound $C_{36}H_{30}O_2$ by means of chromium trioxide in hot acetic acid gave benzoic acid and *o*-benzoylbenzoic acid. No benzophenone could be obtained from this oxidation reaction.

An unexpected reaction of the hydrocarbon $C_{42}H_{46}$ was its cleavage by 40% sodium amalgam to give a sodium alkyl which upon treatment with carbon dioxide yielded the same acid (VII) which had been obtained from the sodium alkyl prepared from either the methyl ether (V) or the true ethane (IV). However, the yields of acid from the rearranged hydrocarbon were never above 36%. This fact has been interpreted to mean that at least half of the molecule in the rearranged hydrocarbon must retain the carbon chain which was present in the original carbinol.

Further speculation on the structure of the rearranged hydrocarbon is useless until more evidence bearing on this rearrangement has been accumulated.

Experimental

Diphenyl-(3-methyl-3-ethylpentinyl-1)-carbinol [1,1-Diphenyl-4-methyl-4-ethylhexin-2-ol-4] and the hydrocarbon $C_{42}H_{46}$ were prepared by the methods previously described.[2]

Methyl Diphenyl-(3-methyl-3-ethylpentinyl-1)-methyl Ether.—The carbinol was converted to the methyl ether by the general method which Moureu, Dufraisse and Blatt[4] used for diphenylphenylethinylcarbinol. To a solution of 14 g. of concentrated sulfuric acid in 140 cc. of absolute methyl alcohol cooled to 0° was added 14 g. of the carbinol over a period of about one minute. The mixture was stirred mechanically. A cloudiness developed in about three minutes and oily drops began to separate. Stirring was continued for about thirty minutes. The product was isolated by flooding with water and extracting with ether. The ether extract was washed with sodium bi-

---

(3) Adams, Voorhees and Shriner, "Organic Syntheses," Collective Volume I, 1932, p. 452.

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

carbonate solution, dried over anhydrous magnesium sulfate and distilled. The residual oil was purified by three distillations under reduced pressure. The yield was 12.5 g. (85% of the theoretical amount); b. p. 143–147° (0.32 mm.); n^{20}_{D} 1.5410; sp. gr.$^{20}_{20}$ 0.9892.

Anal. Calcd. for $C_{22}H_{26}O$: C, 86.21; H, 8.56. Found: C, 86.21, 86.15; H, 8.61, 8.58.

Diphenyl-(3-methyl-3-ethylpentinyl-1)-methyl-sodium.—To a solution of 9 g. of the above methyl ether in 250 cc. of anhydrous ether was added 15–20 cc. of 40% sodium amalgam. Air was excluded by flushing out the flask with dry nitrogen. The flask was tightly stoppered and shaken vigorously. A dark green color appeared at once and this changed to a deep red in about five minutes. Shaking was continued for about five hours. The sodium alkyl was not isolated but used in this solution.

Diphenyl-(3-methyl-3-ethylpentinyl-1)-acetic Acid.—The sodium alkyl prepared from 1 g. of the methyl ether was treated with dry carbon dioxide and the organic acid was isolated in the usual fashion. After four recrystallizations from petroleum ether (b. p. 90–100°), 0.616 g. (59% of the theoretical amount) of the acid melting at 141–142° (Maquenne block) was obtained. In a capillary tube the acid softened at 140° and melted at 153–154°. The solution of the acid in carbon tetrachloride did not decolorize an appreciable amount of a solution of bromine in carbon tetrachloride. The acid did not decompose on heating to 170°.

Anal. Calcd. for $C_{22}H_{24}O_2$: C, 82.45; H, 7.54; neutral equivalent, 320; mol. wt., 320. Found: C, 82.46; H, 7.60; neutral equivalent, 316, 319; mol. wt. (Rast), 282, 310.

Oxidation of Diphenyl-(3-methyl-3-ethylpentinyl-1)-acetic Acid. (a) **With Chromium Trioxide.**—One gram of the acid was oxidized by adding it to a solution of 4 g. of chromium trioxide in 50 cc. of glacial acetic acid. The oxidation mixture warmed up to about 45° from the heat of the spontaneous reaction. The mixture was then boiled under a reflux condenser for about three hours. After cooling the mixture, it was poured into water and the water solution was extracted with ether. By extracting the ether with dilute sodium hydroxide and then acidifying the alkaline solution, a mixture of water-insoluble acids was obtained. This mixture was dried and then warmed on a boiling water-bath under a pressure of 25 mm. About 0.02 g. of benzoic acid, m. p. 118–120°, sublimed from the mixture. The material which did not sublime was recrystallized from carbon tetrachloride two or three times and then melted at 126–127°. The yield was about 0.02 g. This material was identified as *o*-benzoylbenzoic acid by a mixed melting point determination.

The ether solution remaining after the removal of the acidic portion with alkali was evaporated. On standing overnight a few yellow crystals separated from the oily residue. These crystals melted at 280° and were identified as anthraquinone.

The remaining oil was dissolved in about 10 cc. of alcohol and to the solution was added 3 cc. of 10% sodium hydroxide, 0.5 g. of hydroxylamine hydrochloride and just enough water to cause the hydrochloride to dissolve. The resulting solution was refluxed for about twenty minutes and then allowed to stand at room temperature for two to three hours. The reaction mixture was poured into about four volumes of water, exactly neutralized with hydrochloric acid and cooled in an ice-bath. The yield of benzophenone oxime, m. p. 135–136, was 0.35 g. (57% of the theoretical amount). After crystallization from 50% alcohol the m. p. was 140–141° and when mixed with authentic benzophenone oxime the melting point was not changed.

(b) **With Potassium Permanganate.**—A mixture of 1 g. of the acid, 7 g. of potassium permanganate and 100 cc. of 1% potassium hydroxide solution was stirred until the spontaneous reaction ceased and then gently refluxed for about three hours. The mixture was acidified with sulfuric acid and filtered. The precipitated manganese dioxide was thoroughly washed with ether and this ether was used to extract the aqueous filtrate. From this ether solution, 0.055 g. of benzoic acid m. p. 121–121.5° was isolated by extraction with alkali. The neutral material in the ether was treated with hydroxylamine as described above and 0.35 g. (57% of the theoretical amount) of benzophenone oxime, m. p. 139–140° was obtained.

Tetraphenyl-di-(3-methyl-3-ethylpentinyl-1)-ethane [6,6,7,7-Tetraphenyl-3,10-dimethyl-3,10-diethyl-dodecadi-ine-4,8].—The cold solution of the sodium alkyl prepared from 2.5 g. of the methyl ether was decanted from the excess amalgam in an atmosphere of dry nitrogen. To the cold solution was added dropwise (about 20 cc.) a 10% solution of tetramethylethylene bromide in dry ether. The addition was stopped when no further change in the color of the solution was observed. The cold ether solution was filtered and the precipitate was washed thoroughly with ether. The filtrate and washings were evaporated under reduced pressure to about 20 cc. and 20 cc. of cold absolute alcohol (cooled to 0°) was added. The solution was finally cooled in a carbon dioxide–acetone bath for about thirty minutes and quickly filtered. The product was washed with ice-cold alcohol and ether and dried in a vacuum desiccator at 0° for about one hour and a half. The yield was 1.05 g. of white crystalline product, m. p. 140–142° (Maquenne block). By the capillary tube method a sample melted at 125–126° when placed in a bath previously heated to 120°.

The ethane did not keep well and even at 0° began to decompose and rearrange in a short time. Analysis of a product which had stood long enough to be dry, always indicated that some oxidation had occurred. The compound was therefore characterized by its reactions.

Cleavage of the Ethane.—To a solution of 0.4 g. of the ethane in 30 cc. of anhydrous ether was added 5 cc. of 40% sodium amalgam. The flask was flushed out with nitrogen, securely stoppered and placed on a shaking machine. The solution quickly turned brown. The color changed to red in about four minutes. After about two hours, the sodium alkyl was treated with dry carbon dioxide and the reaction mixture was worked up to obtain diphenyl-(3-methyl-3-ethylpentinyl-1)-acetic acid. After one crystallization from petroleum ether (b. p. 60–70°) the yield of acid (m. p. 141–144°), was 0.16 g. (34% of the theoretical amount). Recrystallization gave a product melting at 153–154° (capillary tube method) which was shown by mixed melting point determination to be identical with the acid previously described.

The ethane in ether solution did not give a colored solution when treated with 1% sodium amalgam.

Oxidation of the Ethane. (a) With Oxygen.—One gram of the ethane was placed in 100 cc. of purified petroleum ether (b. p. 90–100°) in a flask mounted on a shaker and connected to a gas buret filled with oxygen. The absorption of gas was very rapid and 84 cc. of oxygen (28°, 745 mm.) was absorbed within a minute. The quantity of oxygen for one mole to be absorbed by one mole of hydrocarbon was 43 cc. After permitting the mixture to shake overnight in an atmosphere of oxygen, the solvent was removed under reduced pressure at a temperature below 40°. The brown oil which remained was dissolved in ether. No acid could be isolated in sufficient quantity for identification by extracting this ether solution with aqueous sodium hydroxide. The ether solution was evaporated and the neutral oil which remained was treated with hydroxylamine as described above. White crystalline benzophenone oxime (0.06 g.), m. p. 138.5–139.5°, was obtained.

(b) With Chromium Oxide.—To a mixture of 3 g. of chromium trioxide and 40 cc. of glacial acetic acid at 20°, 0.4 g. of the ethane was added in portions. The oxidation mixture was stirred vigorously during the addition of the ethane, and held at about 20–25° for a day. It was then slowly warmed to 95°. After the reaction seemed complete, the mixture was cooled to about 50° and poured into 100 cc. of water. The water solution was extracted with ether. The ether solution was extracted with dilute sodium hydroxide solution but no water-insoluble acid was obtained by acidifying the alkaline extract. The ether solution was evaporated. The remaining oil was treated with hydroxylamine as already described and 0.18 g. (62% of the theoretical amount) of benzophenone oxime, m. p. 139.5–140.5°, was obtained.

Rearrangement of the Ethane.—A solution of 0.2 g. of the ethane in about 15 cc. of dry ether was slowly concentrated under reduced pressure. The residual material was washed once with absolute alcohol previously cooled to 0°. The crystals which remained weighed 0.1 g. and melted at 106–108.5°. After one recrystallization from absolute alcohol, pure rearranged hydrocarbon, $C_{42}H_{46}$, m. p. 106.5–108°, was obtained. This sample showed no depression in melting point when mixed with a sample of the hydrocarbon prepared by the reduction of the carbinol with titanium trichloride.

Oxidation of the Rearranged Hydrocarbon, $C_{42}H_{46}$. (a) With Potassium Dichromate in Acetic Acid.—The oxidation of the hydrocarbon $C_{42}H_{46}$, reported by Sweet and Marvel[2] was repeated. From 3 g. of the hydrocarbon, 0.94 g. of the neutral oxidation product, m. p. 137–138°, was obtained.

Anal. Calcd. for $C_{36}H_{30}O_2$: C, 87.41; H, 6.12; mol. wt. 494. Found: C, 87.01; H, 6.04; mol. wt. (Rast), 490.

In addition to this neutral oxidation product, about 0.1 g. of *o*-benzoylbenzoic acid, m. p. 126–127°, was obtained.

(b) **With Chromium Trioxide.**—A solution of 2 g. of the hydrocarbon, $C_{42}H_{46}$, in 60 cc. of glacial acetic acid was treated with 4 g. of chromium trioxide and the solution was boiled for ten hours. From this oxidation 0.1 g. of *o*-benzoylbenzoic acid, m. p. 126–127°, and 0.28 g. of the indifferent oxidation product, $C_{36}H_{30}O_2$, m. p. 137–138°, were obtained.

(c) **Other Oxidation Experiments.**—Oxonized oxygen was passed into a solution of the hydrocarbon in carbon tetrachloride. The only compound which could be identified among the oxidation products was benzoic acid. This was isolated in extremely small amounts. Perbenzoic acid apparently did not attack the hydrocarbon.

Cleavage of the Rearranged Hydrocarbon, $C_{42}H_{46}$.—A solution of 1 g. of the hydrocarbon in 40 cc. of dry ether was shaken in an inert atmosphere with 6 cc. of 40% sodium amalgam. The solution appeared red after about six minutes when the temperature was about 35°. After shaking the mixture for fifteen hours, dry carbon dioxide was introduced. From the reaction mixture, 0.42 g. (36% of the theoretical amount) of diphenyl-(3-methyl-3-ethylpentinyl-1-)-acetic acid, m. p. 141° (Maquenne block), was obtained.

Reactions of the Neutral Compound, $C_{36}H_{30}O_2$.—A solution of 0.5 g. of the compound $C_{36}H_{30}O_2$ in 15 cc. of glacial acetic acid was treated with 1 g. of chromium trioxide and refluxed for about six hours. From this oxidation mixture 0.036 g. of hydrated *o*-benzoylbenzoic acid, m. p. 88–92°, was obtained. After drying and recrystallizing this acid from carbon tetrachloride, the melting point was 126–127°.

Ozone oxidation of the neutral compound gave traces of benzoic acid. Perbenzoic acid and sodium hypobromite did not oxidize the neutral compound.

A solution of 1 g. of $C_{36}H_{30}O_2$ in 130 cc. of absolute alcohol was reduced with hydrogen under pressure in the presence of 0.05 g. of platinum oxide catalyst.[3] The absorption of hydrogen was complete in fifteen minutes. The catalyst was removed by filtration and the alcohol solution was concentrated to a small volume. On cooling, crystals separated. After recrystallization from alcohol the yield of product was 0.16 g. The melting point of the pure product was 226.5–228° (corr.).

Anal. Calcd. for $C_{36}H_{34}O_2$: C, 86.70; H, 6.68; mol. wt. 498. Found: C, 86.83, 86.92; H, 6.99, 7.02; mol. wt. 489.

Although the analytical evidence indicated that $C_{36}H_{30}O_2$ was a diketone, no derivatives of the carbonyl group were obtained. Furthermore, the reduction product did not give reactions of the hydroxyl group although four atoms of hydrogen were apparently added to the diketone.

Summary

1. The polyine, tetraphenyl-di-(3-methyl-3-ethylpentinyl-1)-ethane has been prepared. It is oxidized by air, cleaved by 40% sodium amalgam, and rearranges spontaneously to give a more stable isomeric hydrocarbon, $C_{42}H_{46}$.

2. Some reactions of the rearranged hydrocarbon $C_{42}H_{46}$ have been studied in the hope of establishing its structure. Cleavage by sodium amalgam has furnished evidence that at least half of the molecule retains the original carbon skeleton.

3. The question of final structure of the isomeric hydrocarbon $C_{42}H_{46}$ and the exact nature of the rearrangement by which it is formed must be left open until further evidence can be obtained.

URBANA, ILLINOIS

RECEIVED NOVEMBER 21, 1932
PUBLISHED APRIL 6, 1933

[CONTRIBUTION FROM THE BIOCHEMICAL LABORATORIES, STATE UNIVERSITY OF IOWA]

The Oxidation of Citric Acid

BY ADRIAN C. KUYPER

Except for the questionable procedure of Nordbo and Schersten[1] the only method for the quantitative determination of minute amounts of citric acid is that of Thunberg[2] which is based on the speed of decolorization of methylene blue in the presence of citric acid and the specific citric acid dehydrogenase of cucumber seed. With certain modifications,[3] this method, although time-consuming, has proved satisfactory but, as with other biological methods, trustworthy results are obtainable only at the cost of continuous checking of the uniformity of reagents and procedure. For the study of the metabolism of citric acid a precise microchemical method is greatly needed and the oxidation of citric acid by permanganate, with manometric measurement of the carbon dioxide evolved, offered some promise.

By analogy with the permanganate oxidation of lactic acid by Avery and Hastings,[4] in which 1 mole of carbon dioxide is obtained from each mole of lactic acid, the production of 3 moles of carbon dioxide per mole of citric acid should be expected, especially since the commonly used quanti-

---

[1] Nordbo and Schersten, *Skand. Arch. Physiol.*, **63**, 124–132 (1931).

[2] Thunberg, *Biochem. Z.*, **206**, 109 (1929).

[3] Kuyper and Mattill, *Proc. Soc. Expt. Biol. Med.*, **28**, 863 (1931).

[4] Avery and Hastings, *J. Biol. Chem.*, **94**, 273 (1931).