The writer expresses his thanks to Professor W. A. Noyes for advice and help during the progress of this investigation.

Summary

The explanation given by Noyes and Skinner for the formation of the unsaturated acid obtained by the decomposition of iso-aminocamphonanic acid with nitrous acid is shown to be based on an erroneous interpretation of the analytical data.

No member of the trimethylglutaric acid series is formed on oxidation of this unsaturated acid.

The decomposition of α,β,β-trimethyl-α-carboxyglutaric acid proceeds normally, giving α,β,β-trimethylglutaric acid whether decomposition is effected by heat alone or by heating the ester with hydrochloric acid in a sealed tube at 200°.

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

SYMMETRICAL DIPHENYL-TETRA-TERTIARY-BUTYLETHYNYLETHANE

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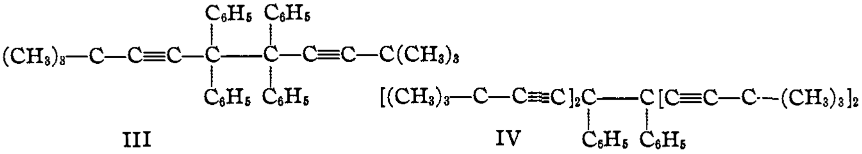
RECEIVED NOVEMBER 16, 1928 PUBLISHED MARCH 6, 1929

As the first step in a study of the effect of acetylenic groups on the stability of the ethane linkage in a hexa-substituted ethane, Salzberg and Marvel[1] have prepared hexa-*tert.*-butylethynylethane (II). This hydrocarbon was found to be stable toward oxygen and in this respect to differ very markedly from the hexa-aryl ethanes. However, it did react with 1% sodium amalgam to give tri-*tert.*-butylethynylmethyl sodium. This reaction indicates that this hexa-substituted ethane has a central linkage that is about as easily ruptured with metals as that in hexaphenylethane (I).

$(C_6H_5)_3C—C—(C_6H_5)_3$
I

$[(CH_3)_3C—C{\equiv}C]_3C—C[C{\equiv}C—C—(CH_3)_3]_3$
II



III

$$(CH_3)_3—C—C{\equiv}C—\underset{C_6H_5}{\overset{C_6H_5}{C}}—\underset{C_6H_5}{\overset{C_6H_5}{C}}—C{\equiv}C—C(CH_3)_3$$

IV

$$[(CH_3)_3—C—C{\equiv}C]_2\underset{C_6H_5}{C}—\underset{C_6H_5}{C}[C{\equiv}C—C—(CH_3)_3]_2$$

For further information concerning these acetylenic derivatives a study of the compounds intermediate between hexaphenylethane and hexa-*tert.*-butylethynylethane has been made. A hydrocarbon $C_{38}H_{38}$, which may be *sym.*-tetraphenyl-di-*tert.*-butylethynylethane (III), was described

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[1] Salzberg and Marvel, THIS JOURNAL, 50, 1737 (1928).

by Salzberg and Marvel.[2] This hydrocarbon was much more stable than was expected for one with the structure represented by Formula III.

In the present paper the preparation and properties of *sym.*-diphenyl-tetra-*tert.*-butylethynylethane (IV) are described. This hydrocarbon was produced by the action of silver on phenyl-di-*tert.*-butylethynylbromomethane. It is stable in oxygen and shows no tendency to form a peroxide. When a solution is heated, color develops and this color does not disappear when the solution is cooled. It is changed by heat but apparently does not rearrange to a solid stable compound as does hexa-*tert.*-butylethynylethane. It reacts with 40% sodium amalgam and with liquid sodium-potassium alloy to give the alkali metal derivative of phenyl-di-*tert.*-butylethynylmethyl. It does not react with 1% sodium amalgam.

There is little doubt concerning the structure of this hydrocarbon, since the alkali metal derivatives obtained by splitting the ethane can be converted into phenyl-di-*tert.*-butylethynylacetic acid. For comparison this acid was prepared from phenyl-di-*tert.*-butylethynylbromomethane by the Grignard reaction.

If the reaction between silver and phenyl-di-*tert.*-butylethynylmethyl bromide is carried out in the presence of oxygen, the ethane is not produced. Instead, oxygen is absorbed and only tarry products are left when the solvent is removed. The amount of oxygen absorbed is greater than would be needed for the formation of a peroxide. This absorption of oxygen is similar to that observed in the case of diphenyl-*tert.*-butylethynylbromomethane. It is especially interesting in this connection to note that in the reaction of tri-*tert.*-butylethynylbromomethane with silver no oxygen is absorbed.

Experimental Part

Phenyl-di-*tert.*-butylethynylcarbinol.—The Grignard reagent was prepared from 20 g. of *tert.*-butylacetylene by adding it from a separatory funnel to 75 cc. of a 4.116 *N* ether solution of ethylmagnesium bromide. The heat of the reaction caused the ether to reflux and an efficient condenser filled with water at about 5° was needed to avoid loss of the acetylene. To the ether solution of the Grignard reagent was added 23.8 g. of ethyl benzoate. The best results were obtained by adding half of the ester, stirring for three or four hours and then adding the second half of the ester over a period of two hours. The mixture was stirred for two hours longer and then it was decomposed by pouring into an ice-cold solution of saturated ammonium chloride. The ether layer was separated, dried over anhydrous sodium sulfate, filtered and the solvent evaporated. The residue was distilled under reduced pressure. The product boiled at 135–139° (1.5 mm.). This product solidified after standing at 0° for about ten days. The material was recrystallized by dissolving in petroleum ether and cooling the solution in carbon dioxide snow. The yield of recrystallized carbinol was 10–12 g. (55–64% of the theoretical amount); m. p. 46–47°.

Anal. Subs., 0.2182: CO_2, 0.6788; H_2O, 0.1745. Calcd. for $C_{19}H_{24}O$: C, 85.02; H, 9.03. Found: C, 84.84; H, 8.96.

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[2] Salzberg and Marvel, THIS JOURNAL, **50,** 2840 (1928).

This carbinol was rearranged to the α,β-unsaturated ketone by dissolving 1 g. in 6 cc. of glacial acetic acid and adding to the solution 1 cc. of concentrated sulfuric acid. The mixture was poured into cracked ice and the ketone was extracted with ether. The ether was concentrated to about 10 cc. and cooled in carbon dioxide snow. The ketone was separated as yellow crystals. After four recrystallizations a product was obtained which melted at 108–110°. An ether solution of this product did not react with sodium. The yield was only 0.5 g.

Anal. Subs., 0.1074: CO_2, 0.3346; H_2O, 0.0865. Calcd. for $C_{19}H_{24}O$: C, 85.02; H, 9.03. Found: C, 84.96; H, 9.00.

Phenyl-di-*tert*.-butylethynylbromomethane.—Three g. of the carbinol was dissolved in 20 cc. of dry ether and the solution was cooled to 0°. Then 1 g. of phosphorus tribromide was added and the solution was stirred at 0° for one-half hour. To the mixture was added 100 cc. of 10% sodium bicarbonate solution and stirring was continued for ten minutes. The ether layer was separated, dried over sodium sulfate and evaporated under reduced pressure. The residue was dissolved in the least possible amount of absolute ether and 8 cc. of absolute alcohol was added. This solution was again evaporated under reduced pressure until crystals appeared and was then allowed to stand at about 0° overnight until the bromo compound had crystallized. It was collected on a filter and then again crystallized from ether and alcohol. After drying in a vacuum desiccator there was obtained 2.4 g. (60% of the theoretical amount) of a white crystalline product; m. p. 58–59°.

Anal. Subs., 0.2431: CO_2, 0.6152; H_2O, 0.1502. Subs., 0.2011: 3.9 cc. of 0.1540 *N* $AgNO_3$. Calcd. for $C_{19}H_{23}Br$; C, 68.85; H, 6.99; Br, 24.13. Found: C, 69.00; H, 6.91; Br, 24.15.

The filtrates from this bromo compound were evaporated to dryness and the residue was heated with acetone and then recrystallized. A few colorless crystals melting at 169–174° were obtained. The product contained bromine but not enough material was isolated for further identification.

***Sym*.-diphenyl-tetra-*tert*.-butylethynylethane.**—A solution of 2.048 g. of phenyl-di-*tert*.-butylethynylbromomethane in 10 cc. of absolute ether was shaken with 2 g. of molecular silver for twenty-four hours. The solution was filtered and evaporated under reduced pressure almost to dryness. To the residue was added 8 cc. of absolute alcohol and the evaporation was continued until crystals began to form. The mixture was cooled to 0° for a few hours and filtered. The yield of hydrocarbon was 0.75–0.9 g. (40–50% of the theoretical amount). After recrystallization from ether and alcohol it melted at 98–99°.

Anal. Subs., 0.2010: CO_2, 0.6700; H_2O, 0.1670. Calcd. for $C_{38}H_{46}$: C, 90.85; H, 9.24. Found: C, 90.91; H, 9.22.

A solution of 0.4 g. of the ethane in 15 cc. of bromobenzene at about 100° was shaken in an atmosphere of oxygen for six hours. No absorption of oxygen was observed. The solution did turn yellow at 100° but the color did not disappear on cooling.

Effect of Heat on the Hydrocarbon.—A solution of 0.2 g. of the ethane in 4 cc. of hexane was heated in a sealed tube at 100° for one hour. The solution became light yellow and the color remained when the solution was cooled.

A solution of 0.22 g. of the ethane in 4 cc. of absolute alcohol was heated in a sealed tube to 100° for one hour. The solution became intensely yellow. The color did not disappear on cooling. On working up the solution 0.14 g. of the ethane was recovered.

A solution of 0.4 g. of the ethane in 15 cc. of xylene was refluxed gently for one hour. The solution turned dark red in color. When the solution was evaporated and the residue crystallized from alcohol and ether, 0.19 g. of the ethane was recovered. There was some oily residue which did not crystallize. A solution of 0.2 g. of the ethane in xylene was heated in a sealed tube to 140° for one hour. The color was yellow when air was thus excluded. From this reaction 0.1 g. of the ethane was recovered.

Cleavage of the Ethane with Alkali Metals.—A solution of 0.55 g. of the ethane in 10 cc. of dry ether was shaken with 5 cc. of liquid sodium–potassium alloy in an atmosphere of dry nitrogen. The solution turned red in about thirty seconds and was very deeply colored in one and one-half minutes. After twenty-four hours an excess of moist carbon dioxide was passed in until the solution became clear. The mixture was heated with 50 cc. of water containing 5 g. of potassium hydroxide. The mixture was heated to evaporate the ether and then cooled and filtered. The solution was cooled to 0°, acidified with dilute hydrochloric acid and a white precipitate of organic acid separated. After repeated crystallization from petroleum ether and methyl alcohol (using Norite to decolorize each solution), there was obtained a small amount of acid, m. p. 154–156°. This was found to be identical with phenyl-di-*tert.*-butylethynylacetic acid described below.

A solution of 1 g. of the ethane in 10 cc. of dry ether was shaken with 8 cc. of 40% sodium amalgam in an atmosphere of dry nitrogen. After about twenty seconds the surface of the alloy was tinged with red and the solution was yellow. After about eighty seconds the solution turned red. After shaking for twenty hours the mixture was decomposed with moist carbon dioxide and the acid isolated as described above. The yield of crude acid, which was still yellow in color, was 0.73 g. (56% of the theoretical amount). The recrystallized material melted at 154–156°. In the crystallization it was found that much of the yellow color was absorbed on the filter paper on allowing the crude material to stand in a funnel.

Anal. Subs., 0.2031: CO_2, 0.6040; H_2O, 0.1467. Calcd. for $C_{20}H_{24}O_2$: C, 81.08; H, 8.17. Found: C, 81.11; H, 8.08. *Neutral equivalent.* Subs., 0.1025: 2.85 cc. of 0.1215 *N* NaOH. Calcd. for $C_{20}H_{24}O_2$: 296.2. Found: 293.4.

When a solution of 0.1 g. of the ethane in 10 cc. of ether was shaken with 3 cc. of 1% sodium amalgam in an atmosphere of dry nitrogen for three days, no color was developed. Practically all of the ethane (0.082 g.) was recovered on evaporation and crystallization of the residue.

Phenyl-di-*tert.*-butylethynylacetic acid.—To prove the structure of the acid obtained by splitting the ethane with alkali metals, phenyl-di-*tert.*-butylethynylacetic acid was prepared from phenyl-di-*tert.*-butylethynylbromomethane. This was accomplished by the action of 40% sodium amalgam on the bromide to give the sodium derivative of phenyl-di-*tert.*-butylethynylmethyl which, with carbon dioxide, gave the acid and also by the action of magnesium and carbon dioxide on the bromide.

A solution of 1 g. of phenyl-di-*tert.*-butylethynylbromomethane in 10 cc. of dry ether was shaken with 4 cc. of 40% sodium amalgam in an atmosphere of dry nitrogen for twenty-four hours. The solution was then treated with moist carbon dioxide as described under the splitting of the ethane. The acid was isolated as before and the yield was 0.6 g. (66% of the theoretical amount). This product after several recrystallizations from petroleum ether and methyl alcohol melted at 154–156° and showed no depression in melting point when mixed with the acids obtained by splitting the ethane with sodium–potassium alloy or 40% sodium amalgam.

Anal. Subs., 0.1890: CO_2, 0.5606; H_2O, 0.1344. Calcd. for $C_{20}H_{24}O_2$: C, 81.08; H, 8.17. Found: C, 81.05; H, 7.95. *Neutral equivalent.* Subs., 0.1006: 2.8 cc. of 0.1215 *N* NaOH. Calcd. for $C_{20}H_{24}O_2$: 296.2. Found: 295.0.

The same acid was obtained by the action of carbon dioxide and magnesium on the bromide. To a solution of 2 g. of phenyl-di-*tert.*-butylethynylbromomethane in 10 cc. of dry ether was added 0.15 g. of magnesium and about 0.01 g. of iodine. The mixture was stirred and a slow current of dry carbon dioxide was passed over the surface of the ether. More ether was added from time to time as it evaporated. After about five hours the mixture was decomposed with dilute hydrochloric acid and the organic acid was extracted from the ether with a solution of 5 g. of sodium hydroxide in 50 cc. of water. The acid was reprecipitated and the yield of crude acid was about 1 g. After recrystallization it melted at 154–156° and showed no depression in the melting point when mixed with the acid prepared from the ethane by splitting with alkali metals and treating with carbon dioxide.

When an attempt was made to prepare the Grignard reagent from the bromide first, and then to convert it to the acid by the action of carbon dioxide, only the ethane was obtained.

Reaction of Phenyl-di-*tert.*-butylethynylbromomethane and Silver in an Atmosphere of Oxygen.—A solution of 0.5 g. of the bromide in 5 cc. of ether was treated with 0.5 g. of molecular silver in an atmosphere of dry oxygen. The reaction mixture was shaken by hand from time to time. In about ten hours the reaction mixture had absorbed the theoretical amount of oxygen (18.4 cc. at 25° and 745 mm.) for the formation of a peroxide. In twelve hours a total of 25.5 cc. of oxygen was absorbed. No further absorption occurred in four hours more. The solution was evaporated under reduced pressure but only oily products were obtained.

Another run of 0.2 g. of the bromide was made and the reaction was discontinued when the theoretical amount of oxygen had been taken up by the reaction mixture. No crystalline products were isolated on evaporation of the solution.

Summary

1. *Sym.*-di-phenyl-tetra-*tert.*-butylethynylethane has been obtained by the action of silver on phenyl-di-*tert.*-butylethynylbromomethane.

2. The hydrocarbon reacts with 40% sodium amalgam or with liquid sodium–potassium alloy to give the alkali metal derivative of phenyl-di-*tert.*-butylethynylmethyl. The ethane does not react with 1% sodium amalgam.

3. The properties of this hydrocarbon are intermediate between those of hexa-*tert.*-butylethynylethane and of the hydrocarbon $C_{38}H_{38}$ obtained by the action of silver on diphenyl-*tert.*-butylethynylbromomethane.

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