barium diphenyl disulfonate in 100 cc. of water. On filtration and evaporation to dryness the salt was obtained.

It was purified from methyl alcohol and norite. All fractions gave the same rotation.

Rotation. (Dried *in vacuo* at 110°) 0.2363 g. made up to 10 cc. with pyridine gave α_D −0.71; $l = 1$; $[\alpha]^{0}_{D}$ −30°. Essentially the same rotation was observed at room temperature.

Anal. Calcd. for $C_{54}H_{54}O_{10}N_4S_2$: S, 6.52. Found: S, 6.41.

Attempts were also made to obtain the morphine, cinchonine, cinchonidine and quinine salts but in each case only oils were obtained.

Summary

Diisoduryl disulfonic acid has been resolved. Diphenyl 3,3′-disulfonic acid could not be resolved. These two compounds represent a pair which illustrate strikingly that the stereoisomerism in the diphenyl series cannot be defined by type formulas.

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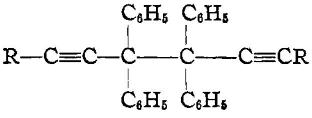
Rearrangements of Polyines. VI. Tetra-biphenyl-di-tertiary-butylethinylethane

BY JUNE CHIEN-YU TSAO AND C. S. MARVEL

It has been shown that hexa-substituted ethanes containing acetylenic groups on the central ethane carbon atoms readily undergo rearrangement to give more stable hydrocarbons.[1] The ease with which this rearrangement occurs appears to be dependent on the strength of the carbon–carbon single bond in the central ethane linkage.

$$[R-C\equiv C]_3-CC-[C\equiv C-R]_3$$

A



$$\begin{array}{c} C_6H_5\;\;C_6H_5 \\ R-C\equiv C-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-C\equiv CR \\ C_6H_5\;\;C_6H_5 \end{array}$$

B

None of the hexa-alkylethinylethanes (type A) undergo this rearrangement except under the influence of heat.[2] On the other hand all of the tetra-aryl dialkylethinylethanes (type B) which have been investigated[3] have changed to isomeric hydrocarbons at room temperature or below.

A remarkable increase in the degree of dissociation of hexaarylethanes[4] and of tetraaryldialkylethanes[5] has been observed when a biphenyl group has been introduced in place of a phenyl group in these molecules. This

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(1) See THIS JOURNAL, **55**, 3712 (1933), for the previous paper in this field.

(2) (a) Salzberg and Marvel, *ibid.*, **50**, 1737 (1928); (b) Ozanne and Marvel, *ibid.*, **52**, 5267 (1930); (c) Davis and Marvel, *ibid.*, **53**, 3840 (1931).

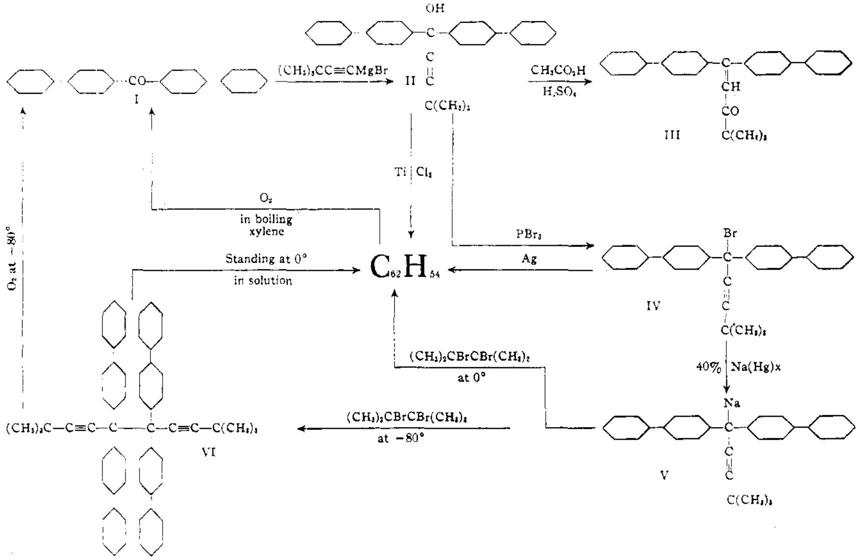
(3) (a) Stampfli and Marvel, *ibid.*, **53**, 4057 (1931); (b) Munro and Marvel, *ibid.*, **54**, 4445 (1932); (c) Harmon and Marvel, *ibid.*, **55**, 1716 (1933).

(4) Schlenk, Weickel and Herzenstein, *Ann.*, **372**, 1 (1910); *Ber.*, **43**, 1753 (1910).

(5) Conant and Schultz, THIS JOURNAL, **55**, 2098 (1933).

fact has suggested that the synthesis of tetrabiphenyl-di-*tert*-butylethinylethane (VI) would make it possible to test in a critical way the idea that the weakness of the central ethane linkage is the principal causative factor in this type of polyine rearrangement.

The reactions involved in the present study are as follows



Most of the reactions were carried out by methods which have been discussed in earlier papers of this series. It is of great interest to note that no evidence for the existence of tetradiphenyl-di-*tert*-butylethinylethane (VI) could be obtained until the reaction between the sodium derivative (V) and tetramethylethylene bromide was carried out at about −80°. The desired hydrocarbon was not isolated, for even at this low temperature the rearrangement to the more stable isomeric hydrocarbon $C_{62}H_{54}$ (VII) took place rapidly. Evidence which supports our view that the desired ethane was present in the cold solution was obtained by oxidation experiments. When the ethane was prepared at about −80°, a solution which absorbed oxygen with great avidity was obtained. After oxidation was complete, the only product which could be isolated from this solution was di-biphenyl ketone (I).

The rearranged hydrocarbon $C_{62}H_{54}$ was not only obtained when solutions of the true ethane were allowed to stand until rearrangement had occurred but was also produced by the reduction of the carbinol (II) by titanium trichloride and by the action of silver on the bromide (IV). These last reactions have previously been shown to give rearrangement products from the corresponding phenyl substituted derivatives.[6] A

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[6] (a) Salzberg and Marvel, THIS JOURNAL, **50**, 2840 (1928); (b) Sweet and Marvel, *ibid.*, **54**, 1184 (1932).

solution of the rearranged hydrocarbon, $C_{62}H_{54}$, did not absorb oxygen at room temperature. When its solution in boiling xylene was treated with oxygen, oxidation did occur and di-biphenyl ketone was obtained in slightly less than 50% yields. This is further evidence that in this type of rearrangement at least half of the molecule retains its original structure.[3c]

The similarity of the properties of tetra-biphenyl-di-*tert*-butylethinylethane with those of tetra-biphenyl-di-*tert*-butylethane is of interest. Conant and Schultz[5] have found that this latter hydrocarbon is dissociated in benzene solution at 5° to the extent of nearly 75%, is extremely sensitive to oxygen, and its solutions are colored even at −78°. Oxidation of both compounds by oxygen gives di-biphenyl ketone. The compound with the two acetylenic groups seems to be more sensitive to oxygen, since it oxidized very rapidly at about −80°.

Experimental

Dibiphenyl-*tert*-butylethinylcarbinol.—This carbinol was prepared from 110 cc. of 1.875 *N* ethylmagnesium bromide solution, 20 g. of *tert*-butylacetylene and 60 g. of dibiphenyl ketone according to the usual procedure for such reactions.[2a] The dibiphenyl ketone was so insoluble in ether that it was necessary to add it in an ether suspension rather than in solution. The ketone was added in 20-g. portions suspended in 500 cc. of ether and the addition required about two days. The reaction mixture was filtered to recover about 30 g. of unreacted ketone and the ether solution was then worked up in the usual fashion. The crude carbinol obtained by evaporating the ether solution weighed 40 g. and melted at 170–171°. It was recrystallized three times from petroleum ether (b. p. 65–110°) and then melted at 172–173° in a capillary tube and at 180–181° on a Maquenne block. The yield of purified product was 36 g. (85% of the theoretical amount based on the unrecovered ketone).

Anal. Calcd. for $C_{31}H_{28}O$: C, 89.35; H, 6.80. Found: C, 89.85, 89.95; H, 6.85, 6.9.

Rearrangement of the Carbinol.—The carbinol underwent the Meyer and Schuster rearrangement[7] when treated with sulfuric acid in acetic acid. Two grams of carbinol in 10 cc. of glacial acetic acid was treated with 1 cc. of concentrated sulfuric acid and 1.5 g. of the unsaturated ketone (III) melting at 142° was obtained. Recrystallization of the unsaturated ketone from petroleum ether (b. p. 65–110°) raised the melting point to 144–145°.

Anal. Calcd. for $C_{31}H_{28}O$: C, 89.35; H, 6.8. Found: C, 89.18; H, 7.06.

Di-biphenyl-*tert*-butylethinylbromomethane.—Treatment of 6 g. of the carbinol in 100 cc. of dry ether with 2 g. of phosphorus tribromide at 0° for about six hours in the usual fashion[2a] gave 4 g. of crude bromide. Recrystallization of this product four times from a mixture of absolute alcohol and absolute ether gave 1.5 g. of product which melted at 135–136°.

Anal. Calcd. for $C_{31}H_{27}Br$: Br, 16.67; mol. wt., 479. Found: Br, 16.79, 16.89; mol. wt. (Rast), 538.

The bromide was sensitive toward moisture and on standing in the air changed to the yellow unsaturated ketone which was formed by the rearrangement of the carbinol by the action of acids.

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(7) Meyer and Schuster, *Ber.*, **55**, 819 (1922).

Action of Silver on the Bromide.—The ether solution of the bromide prepared from 6 g. of carbinol and 2 g. of phosphorus tribromide was shaken with 5 g. of molecular silver for about sixty hours. The solution was filtered and the solvent removed. The residue was recrystallized four times from absolute alcohol and absolute ether. The yield was 2 g. of a product which softened at 130° and decomposed at 135–148° in a capillary tube. On the Maquenne block the compound melted at 166°.

Anal. Calcd. for $C_{62}H_{54}$: C, 93.18; H, 6.82; mol. wt., 798. Found: C, 92.38, 92.69; H, 6.87, 7.00; mol. wt. (cryoscopic in benzene), 711, 799.

This hydrocarbon was stable in the air for short periods and could be kept for months in a vacuum desiccator. On long standing in the air, it turned yellow.

Action of Titanium Trichloride on the Carbinol.—A solution of 4 g. of the carbinol in 10 cc. of alcohol was heated with 20 cc. of 20% solution of titanium trichloride for about two hours.[6b] From the reaction mixture 3 g. of product melting at 128–140° was obtained. After recrystallization from absolute alcohol and ether, 1.8 g. of the hydrocarbon $C_{62}H_{54}$, m. p. 166° (Maquenne block), was obtained.

Di-biphenyl-*tert*-butylethinylmethyl-sodium.—The ether solution of the bromide prepared from 6 g. of the carbinol was shaken with 16 cc. of 40% sodium amalgam in an atmosphere of dry nitrogen for about twenty-four hours. The solution became warm within five minutes and was deep red in color within an hour. The alkyl was not isolated but was used in solution. Pure bromide was used in some experiments and toluene and petroleum ether were also used as solvents. Several attempts were made to convert the sodium alkyl to the corresponding acid and carbomethoxy derivative by treatment with dry carbon dioxide and methyl chlorocarbonate, respectively. No crystalline products were obtained.

Tetra-biphenyl-di-*tert*-butylethinylethane.—In a nitrogen atmosphere a toluene solution of the above sodium derivative prepared from 1 g. of the bromide was cooled to about −80° by means of carbon dioxide snow and acetone. To the cold solution was added dropwise about 10 cc. of a 20% solution of tetramethylethylene bromide in ether. The red color of the sodium alkyl disappeared in about thirty minutes.

This solution was connected with a gas buret containing oxygen and the absorption of the gas was noted. The reaction mixture was shaken by hand to facilitate absorption. Within thirty minutes 187.7 cc. of oxygen was taken up and no more was absorbed when the mixture was allowed to stand at about −80° or after warming the mixture to room temperature.

The toluene solution was a yellow-orange in color and was acidic to moist litmus. No acid could be separated in sufficient quantity for identification by extracting with alkalies and reacidifying the aqueous extract. The toluene solution was evaporated and the residue treated with absolute alcohol. The solid thus obtained was washed with ether to remove the excess tetramethylethylene bromide. The residue (0.05 g.) after this treatment was found to be di-biphenyl ketone; m. p. 230–234°. When mixed with an authentic specimen of the ketone, this product did not depress the melting point.

The same experiment was repeated using 2 g. of bromide. After the addition of the tetramethylethylene bromide, the solution was divided into two equal portions. One portion was treated with oxygen as above and 158.5 cc. of oxygen was absorbed in twenty-six minutes. By allowing the reaction mixture to warm up to room temperature, a further 129.2 cc. of oxygen was absorbed. From the toluene solution a small amount of di-biphenyl ketone (0.049 g.) was isolated as before.

The other portion of the solution obtained in the above experiment was allowed to come to room temperature and to stand for about ten hours. After that time the solution would no longer absorb oxygen. On evaporating the solvent and recrystallizing the residue, about 0.5 g. of the hydrocarbon $C_{62}H_{54}$ was obtained. This product was not pure but recrystallization gave 0.1 g. of pure hydrocarbon, m. p. 166° (Maquenne block).

The reaction between di-biphenyl-*tert*-butylethinylmethyl-sodium and tetramethylethylene bromide was also carried out at room temperature and at 0°. The solutions thus obtained did not absorb oxygen and the only product which could be isolated from them was the rearranged hydrocarbon, $C_{62}H_{54}$.

Some Reactions of the Rearranged Hydrocarbon, $C_{62}H_{54}$.—A solution of 0.1 g. of the hydrocarbon $C_{62}H_{54}$ in 2 cc. of dry carbon tetrachloride did not decolorize two drops of a 5% solution of bromine in carbon tetrachloride.

Treatment of 1 g. of the hydrocarbon with 8 cc. of 40% sodium amalgam under nitrogen in ether solution produced a purple-red colored alkali metal derivative. No acid was isolated when this was treated with carbon dioxide. The color of this metal derivative was somewhat different from that of the sodium compound prepared from di-biphenyl-*tert*-butylethinylbromomethane.

The hydrocarbon $C_{62}H_{54}$ dissolved in petroleum ether would not absorb oxygen at room temperature. When a solution of 0.8 g. of the hydrocarbon in 100 cc. of boiling xylene was maintained in contact with oxygen for seven days, a total of 164 cc. of oxygen was absorbed. After the third day crystals began to separate. Toward the end of the period the solution became dark yellow in color. When no more oxygen was absorbed the solution was filtered and evaporated. From the residue 0.5 g. of the original hydrocarbon was recovered. The crystals which had separated from the xylene weighed 0.2 g. and melted at 230–234°. They were identified as di-biphenyl ketone. The yield of the ketone was about 50% based on the hydrocarbon which was used up in the reaction.

Summary

1. Tetra-biphenyl-di-*tert*-butylethinylethane has been prepared in solution. It is rapidly oxidized by oxygen at about −80° to yield di-biphenyl ketone. At 0° it rapidly rearranges to a stable isomer $C_{62}H_{54}$. The ease with which this change occurs is further evidence that weakness of the ethane linkage is the chief causative factor in this rearrangement.

2. The hydrocarbon $C_{62}H_{54}$ has also been obtained by the action of silver on di-biphenyl-*tert*-butylethinylbromomethane and by the reduction of di-biphenyl-*tert*-butylethinylcarbinol with titanium trichloride. This hydrocarbon in boiling xylene is slowly oxidized by oxygen to give about a 50% yield of di-biphenyl ketone.

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