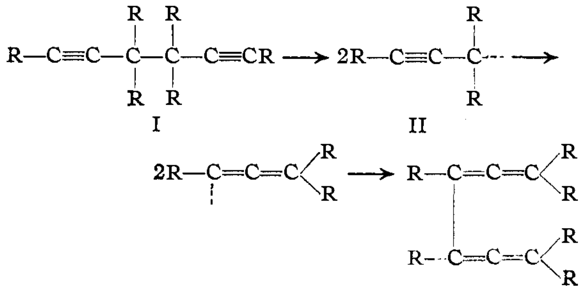
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

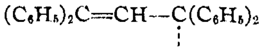
Rearrangement of Styryl Substituted Ethanes. XI[1]

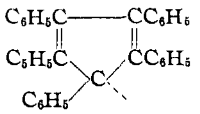
BY C. S. MARVEL, MAX B. MUELLER AND W. J. PEPPEL[2]

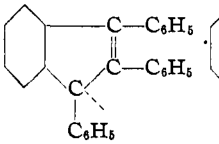
An investigation[1] of the rearrangement of certain types of acetylenic hexa-substituted ethanes and closely related compounds has shown that, whereas these molecules have many properties which are like those of the hexaarylethanes, they do not undergo reversible dissociation to give free radicals. Instead, they readily rearrange to give stable hydrocarbons. The rearrangement appears to involve: first, a dissociation of the ethane (I) to give free radicals (II); second, a 1,3-shift of the free valence similar to an allyl rearrangement to give a second free radical (III); and, finally, a recombination of these radicals to give the stable hydrocarbon (IV). We were interested in learning whether a similar rearrangement would occur in olefinic hydrocarbons of a closely related type and began this investigation of styryl substituted ethanes. A recent publication of Wittig and Kosach[3] has anticipated some of our experiments, hence we are reporting our results and withdrawing from a further study of compounds of this type.

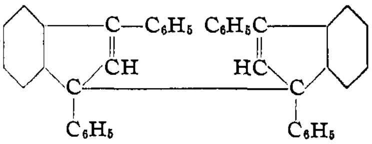

I II III IV

Ziegler and his students[4] have found that derivatives of the tetraphenylallyl type (V) and pentaphenylcyclopentadienyl (VI) exist mainly as the free radicals rather than as the corresponding ethanes. Much earlier Kohler[5] had found that triphenylindenyl (VII) existed at least in part as the free radical. More recently work in this Laboratory[6] demonstrated that bis-1,1′-(1,3-diphenylindenyl) (VIII) dissociated reversibly to give free radicals in boiling xylene solution. Wittig and Obermann[7] have demonstrated that tetra-(diphenylvinyl)-ethane (IX) which is a colorless stable hydrocarbon at room temperature gives a yellow-green solution in hot xylene and therefore undoubtedly is dissociated in part.


$$(C_6H_5)_2C{=}CH{-}\underset{\vdots}{C}(C_6H_5)_2$$
V


VI


VII


VIII

$$[(C_6H_5)_2C{=}CH]_2CHCH[CH{=}C(C_6H_5)_2]_2$$
IX

All of these results indicate that aryl substituted olefinic residues in an ethane nucleus tend to weaken the central bond just as do aryl and acetylenic groups. The aryl substituted olefinic types listed above are all vinylogs[8] of the hexaarylethanes (or triarylmethyls). It is, therefore, difficult to know what effect the olefin group itself may be exerting in these molecules.

In the present work we undertook the preparation of hexa-β-styrylethane (X) in order to compare it with its vinylog hexaphenylethane (XI). Tri-β-styrylcarbinol was prepared from β-styryllithium and dibenzalacetone. It crystallized as a monohydrate from moist dioxane but the anhydrous carbinol was obtained from benzene solution. Reduction of the carbinol in glacial acetic acid by means of vanadous chloride, according to the method developed by Conant and his students[9] for the conversion of triarylcarbinols to the corresponding hexaarylethanes, gave a red colored solution. The color faded rapidly and then a white hydrocarbon crystallized from the solution.

$$(C_6H_5CH{=}CH)_3CC(CH{=}CHC_6H_5)_3 \qquad (C_6H_5)_3CC(C_6H_5)_3$$
X XI

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[1] For the tenth communication on this subject see Sparks, Peppel and Marvel, THIS JOURNAL, **59**, 1351 (1937).

[2] Chemical Foundation Fellow in Organic Chemistry.

[3] Wittig and Kosach, *Ann.*, **529**, 167 (1937).

[4] Ziegler and others, *ibid.*, **434**, 34 (1923); **445**, 266 (1925).

[5] Kohler, *Am. Chem. J.*, **40**, 217 (1908).

[6] Goebel and Marvel, THIS JOURNAL, **55**, 3712 (1933).

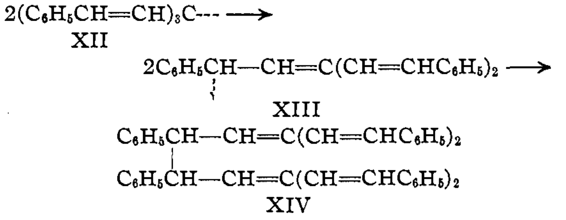
[7] Wittig and Obermann, *Ber.*, **68**, 2214 (1935).

[8] Fuson, *Chem. Rev.*, **16**, 1 (1935).

[9] Conant and Sloan, THIS JOURNAL, **45**, 2466 (1923); Conant and Small, *ibid.*, **47**, 3071 (1925).

This hydrocarbon corresponded in composition to the expected hexa-β-styrylethane. It was stable in air and did not change on long standing in the solid state. It slowly changed, however, to a yellowish tarry substance when its benzene solution was boiled, but the carbinol also behaved in this manner. The hydrocarbon gave deeply colored products soluble in ether when it was treated with liquid sodium-potassium alloy. However, treatment of the colored solution of the alkali metal derivatives with carbon dioxide did not yield crystalline acidic products. The alkali metal derivatives behaved more like addition products in which the alkali metal had attacked a double bond than like an alkali metal alkyl which should result from cleavage of the hydrocarbon.

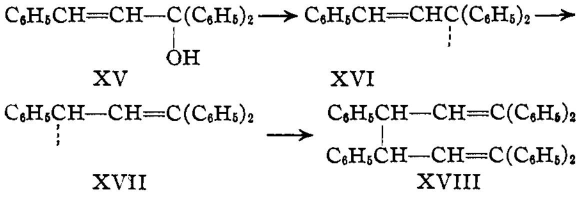
These properties of the new hydrocarbon led us to believe that it was not the hexa-β-styrylethane which we sought but some rearrangement product. It seems probable that reduction of the carbinol gave first tri-β-styrylmethyl (XII), which would account for the original reddish color formed in the reduction mixture, and that the radical then rearranged itself by a 1,3-shift of the free electron to yield the isomeric radical (XIII) which reassociated to give a stable hydrocarbon (XIV).



$$\underset{\text{XII}}{2(C_6H_5CH{=}CH)_3C{\cdots}} \longrightarrow \underset{\text{XIII}}{2C_6H_5\underset{\vdots}{C}H{-}CH{=}C(CH{=}CHC_6H_5)_2} \longrightarrow \underset{\text{XIV}}{\begin{array}{l} C_6H_5CH{-}CH{=}C(CH{=}CHC_6H_5)_2 \\ \;\;\;\;\;\;\;\;\;| \\ C_6H_5CH{-}CH{=}C(CH{=}CHC_6H_5)_2 \end{array}}$$

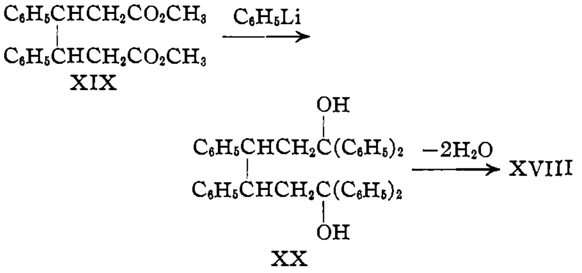
Attempts to prove that the hydrocarbon obtained by the reduction of tri-β-styrylcarbinol really had the structure represented by formula XIV were not entirely successful. Ozonolysis gave benzoic acid and non-crystalline acidic products. Apparently ozone acted on this arylated olefinic derivative to cause secondary reactions which prevented the formation of clean-cut oxidation products. This same difficulty has been experienced repeatedly in attempts to ozonize analogous rearrangement products in the acetylenic series.[10]

In order to simplify the problem of proving the structure of the final hydrocarbon, β-styryldiphenylcarbinol (XV) was reduced with vanadous chloride. The reduction product was again a stable hydrocarbon and its structure (XVIII) was shown by an independent synthesis to be that expected if a 1,3-rearrangement as postulated above had occurred.



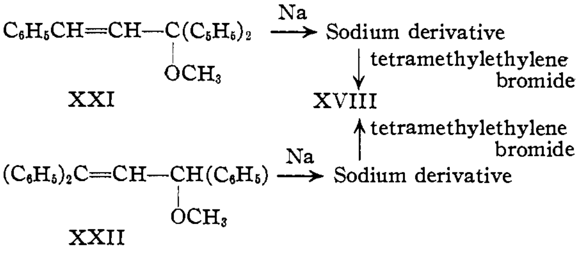
$$\underset{\text{XV}}{C_6H_5CH{=}CH{-}\underset{\underset{OH}{|}}{C}(C_6H_5)_2} \longrightarrow \underset{\text{XVI}}{C_6H_5CH{=}CH\underset{\vdots}{C}(C_6H_5)_2} \longrightarrow \underset{\text{XVII}}{C_6H_5\underset{\vdots}{C}H{-}CH{=}C(C_6H_5)_2} \longrightarrow \underset{\text{XVIII}}{\begin{array}{l} C_6H_5CH{-}CH{=}C(C_6H_5)_2 \\ \;\;\;\;\;\;\;\;\;| \\ C_6H_5CH{-}CH{=}C(C_6H_5)_2 \end{array}}$$

The 1, 1, 3, 4, 6, 6 - hexaphenylhexadiene - 1, 5 (XVIII) was synthesized from dimethyl β,β'-diphenyladipate (XIX) by the reactions



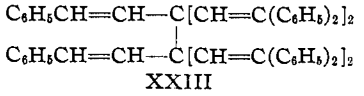
$$\underset{\text{XIX}}{\begin{array}{l} C_6H_5CHCH_2CO_2CH_3 \\ \;\;\;\;\;\;\;\;\;| \\ C_6H_5CHCH_2CO_2CH_3 \end{array}} \xrightarrow{C_6H_5Li} \underset{\text{XX}}{\begin{array}{l} \;OH \\ \;| \\ C_6H_5CHCH_2C(C_6H_5)_2 \\ \;\;\;\;\;\;\;\;\;| \\ C_6H_5CHCH_2C(C_6H_5)_2 \\ \;| \\ \;OH \end{array}} \xrightarrow{-2H_2O} \text{XVIII}$$

Wittig and Kosach[3] also have attempted to prepare diphenylstyrylmethyl (XVI) and have found that it rearranges and couples to give 1,1,3,4,6,6 - hexaphenylhexadiene - 1,5 (XVIII). Their evidence for this is that treatment of the sodium alkyl obtained from either the methyl ether of diphenylstyrylcarbinol (XXI) or the methyl ether of phenyl-(diphenylvinyl)-carbinol (XXII) with tetramethylethylene bromide gives the same product (XVIII).



$$\begin{array}{lcl} \underset{\text{XXI}}{C_6H_5CH{=}CH{-}\underset{\underset{OCH_3}{|}}{C}(C_5H_5)_2} & \xrightarrow{Na} & \text{Sodium derivative} \\ & & \Big\downarrow \text{tetramethylethylene bromide} \\ & & \text{XVIII} \\ & & \Big\uparrow \text{tetramethylethylene bromide} \\ \underset{\text{XXII}}{(C_6H_5)_2C{=}CH{-}\underset{\underset{OCH_3}{|}}{C}H(C_6H_5)} & \xrightarrow{Na} & \text{Sodium derivative} \end{array}$$

The same authors also attempted to prepare distyryltetra-(diphenylvinyl)-ethane (XXIII) and obtained a product (XXIV) which they believe to be formed by a similar rearrangement.



$$\begin{array}{l} C_6H_5CH{=}CH{-}C[CH{=}C(C_6H_5)_2]_2 \\ \;| \\ C_6H_5CH{=}CH{-}C[CH{=}C(C_6H_5)_2]_2 \end{array}$$

XXIII

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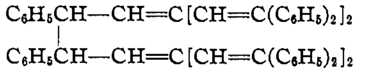
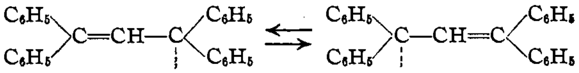
(10) Althausen and Marvel, THIS JOURNAL, **54**, 1174 (1932); Harmon and Marvel, *ibid.*, **55**, 1716 (1933); Ford, Thompson and Marvel, *ibid.*, **57**, 2619 (1935); Farley and Marvel, *ibid.*, **58**, 29 (1936).



$$\begin{array}{l} C_6H_5CH-CH=C[CH=C(C_6H_5)_2]_2 \\ | \\ C_6H_5CH-CH=C[CH=C(C_6H_5)_2]_2 \end{array}$$

XXIV

All the foregoing experiments indicate that it is very unlikely that any β-styryl substituted methyl will exist as a stable free radical. When a 1,3-shift of the odd electron in the free radical will give a second radical which is not of the triarylmethyl type, this rearrangement occurs and then coupling to give a stable hydrocarbon follows. Hence, the only types of olefinic substituted ethanes which can be expected to dissociate reversibly to give free radicals are those, such as the diphenylvinyl derivatives mentioned earlier in this paper, where a 1,3-shift of the free electron does not change the nature of the radical, *e. g.*



Experimental

Tri-β-styrylcarbinol.—A solution of β-styryllithium was prepared from 8.3 g. of β-bromostyrene and 4 g. of lithium according to the procedure of Wright,[11] filtered from the excess lithium and to it was added dropwise 90 cc. of a 10% solution of dibenzalacetone in dry benzene. The color of the solution changed from purple to brown during this addition. The reaction mixture was poured onto a mixture of ice and a saturated solution of ammonium chloride. The ether layer was separated, washed with water and dried. When the ether was evaporated at room temperature under reduced pressure, a sirupy residue remained. This was washed with low-boiling petroleum ether (b. p. 30–60°) and a solid residue was obtained. Recrystallization of this residue from dioxane gave 5 g. of a product, m. p. 110–111°. Analysis indicated this product was the monohydrate of the desired carbinol.

Anal. Calcd. for $C_{25}H_{22}O \cdot H_2O$: C, 83.56; H, 6.41. Found: C, 83.92; H, 6.67.

Four grams of the hydrate was dissolved in 50 cc. of dry benzene and the solution was boiled until the cloudiness due to the water had disappeared. The solution was concentrated to about 10 cc. and cooled. The yield of anhydrous carbinol was 2 g.; m. p. 120.5–121°.

Anal. Calcd. for $C_{25}H_{22}O$: C, 88.76; H, 6.51; mol. wt., 338. Found: C, 88.93; H, 6.54; mol. wt. (in benzene), 341.

Reduction of Tri-β-styrylcarbinol with Vanadous Chloride.—A solution of 1 g. of the carbinol in 50 cc. of glacial acetic acid was treated with a solution of vanadous chloride prepared by boiling 1 g. of vanadium pentoxide with 30 cc. of 20% hydrochloric acid and 20 g. of amalgamated zinc. A bright red coloration spread through the solution as soon as the reducing agent was added to the carbinol solution, but the color faded quickly and a white precipitate separated. The solution was diluted with water and the precipitate was removed by filtration and crystallized from benzene. The yield was 0.3 g., m. p. 173–174°.

Anal. Calcd. for $C_{50}H_{42}$: C, 93.46; H, 6.54; mol. wt., 642. Found: C, 93.44; H, 6.55; mol. wt. (in benzene), 615, 626.

This colorless hydrocarbon did not oxidize in the air. Boiling a solution of the hydrocarbon in benzene caused it go over into a yellow non-crystalline sirup but the change was not due to oxidation. An ether solution of the hydrocarbon was treated with liquid sodium–potassium alloy. The solution turned deep red in color, indicating a reaction. The color was discharged when dry carbon dioxide was passed into the solution. However, no crystalline acid was obtained from the reaction mixture. When the hydrocarbon was ozonized in carbon tetrachloride solution and the ozonide was decomposed with hydrogen peroxide, benzoic acid was produced. A yellow non-crystalline product was also obtained but could not be characterized.

Reduction of β-Styryldiphenylcarbinol with Vanadous Chloride.—Styryldiphenylcarbinol was made by a modification of the method originally devised by Meyer and Schuster.[12] β-Styryllithium was substituted for their β-styrylmagnesium bromide. The yield was 43% of a product melting at 94.5–95° after crystallization from petroleum ether (b. p. 100–110°).

A solution of 1 g. of this carbinol in 30 cc. of glacial acetic acid was treated with a vanadous chloride solution as described before. No color changes were noted in this experiment. A white precipitate separated almost as soon as the reagents were mixed. The reaction mixture was diluted with water and the solid product was separated and crystallized from petroleum ether (b. p. 100–110°). The yield was 0.5 g. of a colorless hydrocarbon; m. p. 210–211° (uncorr.).

This hydrocarbon when mixed with a sample of the synthetic 1,1,3,4,6,6-hexaphenylhexadiene-1,5 described below melted at 209–211°. Wittig and Kosach[8] report the melting point at 211–212°.

1,1,3,4,6,6-Hexaphenylhexan-1,6-diol.—Three and a half grams of dimethyl meso-β,β'-diphenyladipate, prepared by the method of Oommen and Vogel,[13] was added in small portions to a solution of 9 g. of phenyllithium in 75–80 cc. of dry ether. The mixture was allowed to stand for several hours and then poured into an excess of cold water and shaken. The ether layer was separated and the ether evaporated. The residue was taken up in warm benzene and an equal volume of petroleum ether (b. p. 100–110°) was added. On cooling 4 g. of the diol (m. p. 193–194°) separated.

Anal. Calcd. for $C_{42}H_{38}O_2$: C, 87.7; H, 6.6 Found: C, 87.5; H, 6.8.

1,1,3,4,6,6-Hexaphenylhexadiene-1,5.—A suspension of 4 g. of the above glycol in 25 cc. of glacial acetic acid containing a few drops of concentrated hydrochloric acid was boiled for about two hours. On cooling a hydrocarbon crystallized. It was recrystallized from glacial acetic acid and it then melted at 210–211°.

Anal. Calcd. for $C_{42}H_{39}$: C, 93.68; H, 6.32. Found: C, 93.4; H, 6.2.

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(11) Wright, *J. Org. Chem.*, **1**, 457 (1936).

(12) Meyer and Schuster, *Ber.*, **55**, 815 (1922).

(13) Oommen and Vogel, *J. Chem. Soc.*, 2150 (1930).

Summary

Attempts to prepare hexa-β-styrylethane and di-β-styryltetraphenylethane have yielded isomeric stable hydrocarbons. In the second of these cases the hydrocarbon has been definitely identified as 1,1,3,4,6,6-hexaphenylhexadiene-1,5, showing that a 1,3-rearrangement had preceded the coupling reaction involved in the synthesis.

URBANA, ILLINOIS RECEIVED DECEMBER 24, 1937

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Molecular Rearrangements in the Sterols. III. The Constitution of *i*-Cholesterol and of the Isomeric Ethers of Cholesterol

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In a paper recently published[3] from this Laboratory certain experimental results were reported on the action of anhydrous potassium acetate on cholesteryl *p*-toluenesulfonate in acetic anhydride solution. The preparation of a new isomer of cholesterol, designated as *i*-cholesterol, was described. Some important chemical properties of this new compound and of its acetate were also recorded. From the chemical behavior of these two new compounds the authors were led to the conclusion that in this reaction a molecular rearrangement occurred. Accordingly, they suggested a tentative formula, I, for *i*-cholesterol. They also pointed out that a close relationship exists between this new alcohol and the isomeric ethers of cholesterol discovered by Stoll.[4] In Part II[5] of this series this relationship was clarified, and evidence was submitted which shows conclusively that the abnormal ethers of cholesterol recently referred to in the literature as "*cis*-cholesteryl ethers" are in reality ethers of *i*-cholesterol.

We are now able to substantiate the validity of the formula suggested for *i*-cholesterol, I, by the series of reactions shown in the chart.

As shown in Part I[3] of this series *i*-cholesterol on oxidation in glacial acetic acid solution with chromic acid (CrO_3) gives a ketone which was isolated in the form of its oxime (m.p. 143–144°). From this oxime we have been able to prepare *i*-cholestanone, II, whose crystals melt at 110–111°, and have the specific rotation $[\alpha]^{25}\text{D}$ +64.9°. Treatment of this compound with dry hydrogen chloride dissolved in glacial acetic acid yields a crystalline chloro ketone, III, which is easily purified as such and which forms a characteristic oxime. This chloro ketone was found by determinations of the melting point and mixed melting point to be identical with the α-3-chlorocholestanone-6 prepared by Windaus and Dalmer[6] from cholesteryl chloride. Removal of hydrogen chloride by means of alkali produces the same "heterocholestenone," IV (m. p. 95–96°). Hydrogenation of samples of this unsaturated ketone obtained from both sources with palladium black gives the same cholestanone (m. p. 98–99°) identical with the compound prepared from cholestene by the method of Windaus.[6,7]

From these facts it can be seen that in *i*-cholesterol the hydroxyl group is in position 6 of the sterol molecule and that during its formation from cholesteryl *p*-toluenesulfonate a molecular rearrangement occurs. We think, therefore, that the structural formulas for *i*-cholesterol and the isomeric ethers of cholesterol first discovered by Stoll[4] are now established and that the recent arguments and contentions of Heilbron, *et al.*,[8] are untenable.

In conclusion we also would like to point out that in this new isomer of cholesterol there are interesting possibilities. The method of breaking the cyclopropane ring gives a new route to the preparation of many highly interesting compounds and further investigations in this direction are in progress.

Experimental Part

Preparation of α-3-chlorocholestanone-6 (III) from *i*-Cholestanone Oxime.—*i*-Cholestanone oxime (m. p. 143–144°) prepared by the method of Wallis, Fernholz and

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[1] Research Assistant on special funds from the Chemical Foundation.

[2] Research Fellow on special funds from the Rockefeller Foundation.

[3] Wallis, Fernholz and Gephart, THIS JOURNAL, **59**, 137 (1937).

[4] Stoll, *Z. physiol. Chem.*, **207**, 147 (1932).

[5] Ford and Wallis, THIS JOURNAL, **59**, 1415 (1937).

[6] Windaus and Dalmer, *Ber.*, **52**, 168 (1919); see also Mauthner and Suida, *Monatsh.*, **24**, 656 (1903).

[7] Windaus, *Ber.*, **53**, 492 (1920).

[8] Heilbron, *et al.*, *J. Chem. Soc.*, 406, 1459 (1937).