

The semicarbazone melted at 228–229°; the mixture with an authentic sample showed no depression.

The ultraviolet absorption properties of the ketone ($\epsilon_{285 \text{ m}\mu} = 26,000$, in ethanol) and of the semicarbazone ($\epsilon_{305 \text{ m}\mu} = 46,000$, in dioxane) closely agreed with those of the authentic preparations.¹³

We are indebted to Dr. N. H. Coy of the Vitamin Laboratory of E. R. Squibb and Sons for the spectrographic measurements, and to Miss Mildred Moore for able technical assistance.

The microanalyses were carried out by J. F. Alicino, Fordham University.

Summary

The crystalline, levorotatory product obtained by reduction of 7-ketocholesteryl acetate with aluminum isopropylate is a mixture of 7(α)- and 7(β)-hydroxycholesterol containing up to 20% of the latter epimer. Free 7(α)-hydroxycholesterol,

in contradistinction to its esters, is only slightly dextrorotatory. It cannot be as readily obtained in crystalline form as the β -epimer or the epimeric mixture.

7(β)-Benzoxycholesteryl benzoate on hydrolysis with sodium methylate in the cold yields quantitatively 7(β)-benzoxycholesterol. The position of the benzoxy group was proved by its reductive removal, since the monoester, unlike its epimer, 7(α)-benzoxycholesterol, is not amenable to conversion into 7-dehydrocholesterol.

Two by-products of the reduction of 7-ketocholesteryl acetate, a dicholestadienyl ether and $\Delta^{4,6}$ -cholestadienone-3, have been isolated. Possible mechanisms for the formation of the latter compound are discussed.

NEW BRUNSWICK, N. J.

RECEIVED JULY 1, 1942

[CONTRIBUTION FROM RÖHM AND HAAS COMPANY, INC., AND RESINOUS PRODUCTS & CHEMICAL CO.]

The Chemistry of Acrylonitrile. I. Cyanoethylation of Active Methylene Groups

BY HERMAN ALEXANDER BRUSON

The reactions of acrylonitrile with amines,¹ phenols,² hydrogen sulfide,³ butadiene⁴ and halogens⁵ have been described almost exclusively in the patent literature. Concerning the chemical behavior of acrylonitrile with other types of compounds, very little is known.

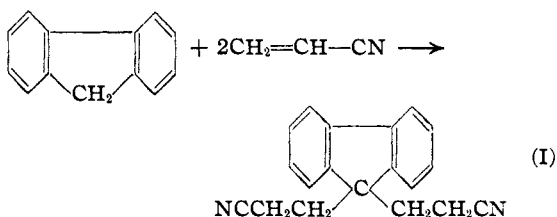
Because of its extremely reactive double bond, acrylonitrile condenses readily with a variety of organic compounds having labile hydrogen atoms or active methylene groups. These reactions occur in the presence of small quantities of alkaline condensing agents and are of the Michael type. The unique property of acrylonitrile in this respect is that it seeks out every available reactive hydrogen atom and by direct addition introduces the $-\text{CH}_2-\text{CH}_2-\text{CN}$ group in place thereof.

A powerful alkaline catalyst which is effective for promoting the cyanoethylation of many types of organic compounds is trimethylbenzylammonium hydroxide which is employed in the form

of an aqueous 40% solution known as "Triton B" (Trade Mark). In some cases sodium or potassium methylate, 30% methanolic potassium hydroxide, or even aqueous 40% sodium hydroxide are effective, but the solubility of "Triton B" and its high degree of alkalinity renders it particularly effective where the other alkalies either fail to initiate the reaction at all or to give good yields.

In this paper, the condensation of acrylonitrile with compounds having the reactive methylene or methenyl grouping $\text{C}=\text{C}-\overset{\text{H}}{\text{C}}-\text{C}=\text{C}$ in a carbocycle is described.⁶ Such a grouping is present in fluorene, indene, cyclopentadiene, anthrone, the fulvenes and many of their substituted derivatives.

In the presence of a catalytic amount of "Triton B," acrylonitrile readily condenses with fluorene to yield *bis*-9,9-(β -cyanoethyl)-fluorene (I).



(1) British Patent 404,744 (1934), 457,621 (1936). I. G. Farbenindustrie; Hoffmann and Jacobi. U. S. Patents 1,992,615 (1935), 2,017,537 (1935).

(2) German Patent 670,357 (1939); Langley and Adams. THIS JOURNAL, 44, 2326 (1922).

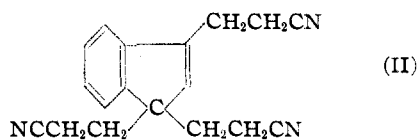
(3) German Patent 669,961 (1939); U. S. Patent 2,163,176.

(4) Wolfe. U. S. Patent 2,217,632 (1940).

(5) Long. U. S. Patent 2,231,363 (1941); Lichty. U. S. Patent 2,231,838 (1941); D'anni. U. S. Patent 2,231,360 (1941).

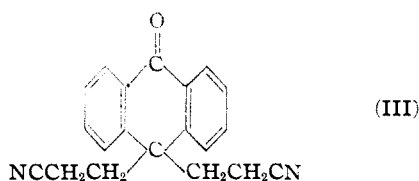
(6) See also Bruson. U. S. Patent 2,280,058 (1942).

Indene likewise adds acrylonitrile in the presence of "Triton B" to yield a liquid di-cyano-ethylation product and crystalline tris-(β -cyanoethyl)-indene very probably, (II) even when 1:1

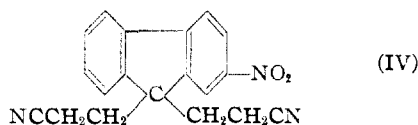


molecular proportions of the reactants are employed.

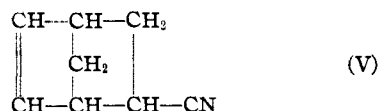
Anthrone similarly adds two moles of acrylonitrile to form meso-bis-(β -cyanoethyl)-anthrone (III).



These reactions take place at room temperature with evolution of heat. In order to prevent excessive polymerization of the acrylonitrile and to allow the condensation to proceed smoothly to completion, resort to cooling and the use of inert solvents such as dioxane or tertiary butanol have been found helpful, particularly if the reactive methylene compound is a high melting solid. In dioxane solution for example, 2-nitro-fluorene condenses readily with acrylonitrile in the presence of "Triton B" to form bis-9,9-(β -cyanoethyl)-2-nitro-fluorene (IV) almost quantitatively.



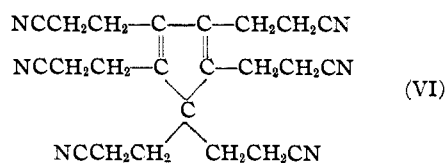
The reaction of acrylonitrile with cyclopentadiene was of particular interest because in the absence of a catalyst, a Diels-Alder adduct (V)



is formed by 1,4-addition. This adduct is a colorless, relatively low boiling liquid and forms spontaneously and almost quantitatively with considerable evolution of heat when the two components are mixed in equimolecular proportions.

However, in the presence of "Triton B" as the catalyst, the formation of the Diels-Alder type of adduct is so far repressed that each of the six hydrogen atoms in the cyclopentadiene molecule

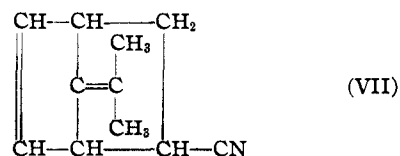
adds to acrylonitrile to form a crystalline hexacyanoethylation product (VI) melting at 203°,



accompanied by a mixture of lower poly-cyano-ethylation products of cyclopentadiene, boiling much higher than the Diels-Alder adduct.

This unexpected reaction of cyclopentadiene can best be explained by a resonating system of double bonds making all the methylene and methenyl hydrogen atoms equally active, or by a mechanism involving a shift of the residual methylene hydrogen atom to a contiguous carbon atom as soon as the first cyanoethyl group is introduced, thus forming new reactive methylene groups successively around the cycle as each cyanoethyl group enters. When the resonating system is interrupted as for example by dimerization of the cyclopentadiene or by adduct formation with the loss of a double bond, then acrylonitrile no longer can add to the methenyl groups remaining. Neither dicyclopentadiene nor the adduct (V) reacted with acrylonitrile in the presence of Triton B. The peculiar shifting of a hydrogen atom in the cyclopentadiene nucleus has already been pointed out by Ziegler and Crössmann⁷ to explain the activity of various fulvenes.

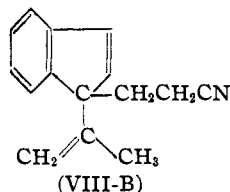
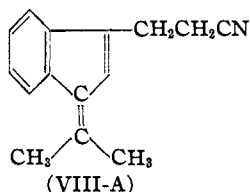
In order to test the activity of a resonating fulvene system toward acrylonitrile, dimethylfulvene was treated with acrylonitrile in the absence and in the presence of Triton B. In the former case, the expected crystalline Diels-Alder type adduct (VII) was isolated, but in the presence of Triton B higher cyanoethylation products of dimethyl-



fulvene were obtained in impure form. However, ω,ω -dimethylbenzofulvene⁸ reacted with acrylonitrile in the presence of Triton B to yield a crystalline cyanoethylation product, corresponding to the formula VIII-A or VIII-B, whereas without the Triton B only resinous adducts were obtained.

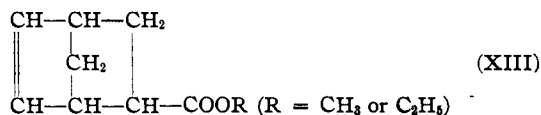
(7) Ziegler and Crössmann, *Ann.*, **511**, 89 (1934).

(8) Thiele and Merck, *ibid.*, **415**, 260 (1918).

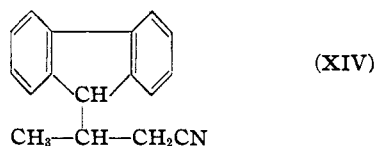


The pure poly-cyanoethylation products I, II, III and VI were each converted into their respective polycarboxylic acids IX, X, XI and XII by alkaline hydrolysis.

Attempts to replace acrylonitrile by acrylic esters such as methyl acrylate or ethyl acrylate in the above experiments so as to obtain the corresponding poly-(carbalkoxy-ethyl) derivatives were unsuccessful. Cyclopentadiene and the acrylic esters gave only the Diels-Alder type adducts (XIII) regardless of whether Triton B was used as the catalyst or not.



Crotononitrile reacted in the presence of Triton B with indene or cyclopentadiene to give poorly defined, resinous cyano-alkylation products. With fluorene, however, a crystalline cyano-alkylation product, XIV, was obtained.



Not only does acrylonitrile cyanoethylate each available hydrogen atom of carbocyclic compounds of the types described above, but also each reactive hydrogen atom of a methyl, methylene, or methenyl group which is contiguous to a nitro or carbonyl group as in the nitro-paraffins or ketones; furthermore as in the reactive methylene groups of malonic esters, malonamides, cyanacetic esters, cyanacetamides, benzyl cyanides, benzyl sulfonamides, α,β -unsaturated nitriles and amides. These will be described in later papers.

Experimental

(I) **Bis-9,9-(β -cyanoethyl)-fluorene.**—Acrylonitrile (111.3 g.) was added dropwise during the course of one hour to a rapidly stirred solution consisting of 166 g. of fluorene, 500 g. of dioxane, and 5 g. of aqueous 40% trimethylbenzylammonium hydroxide. The reaction temperature was maintained between 30 and 40° by occasional cooling with ice-water. The mixture was then stirred for three hours longer at room temperature to complete the

condensation. At the end of this time, the dark brown solution obtained was neutralized with dilute hydrochloric acid and, without interrupting the stirring, 800 cc. of water was added to precipitate the product in granular form. The precipitate was filtered off and air dried; crude yield 250 g. Upon recrystallization once from 500 g. of ethanol, the product separated as yellowish crystals m. p. 118–119°; yield 201 g. or 74%. One more recrystallization from ethanol using Norite gave the pure compound as colorless needles m. p. 121°. *Anal.* Calcd. for $C_{19}H_{15}N_2$: C, 83.78; H, 5.92; N, 10.29. Found: C, 84.03; H, 5.76; N, 10.33. It is readily soluble in benzene, chloroform, acetone, ethyl acetate or dioxane at 25°. It is insoluble in ether, and is only slightly soluble in cold methanol or ethanol, but dissolves readily on heating.

(II) **Tris-1,1,3-(β -cyanoethyl)-indene.**—To a mixture of 69.5 g. of indene (0.6 mole), 100 g. of dioxane, and 4 g. of aqueous 40% trimethylbenzylammonium hydroxide there was added dropwise during two hours 95.4 g. of acrylonitrile (1.8 mole) while the reaction mixture was stirred and cooled to 25–30°. After the addition, the dark solution was stirred at room temperature for an hour and then acidified to litmus with dilute hydrochloric acid. The mixture was shaken with an equal volume of ethylene dichloride and a little water. The aqueous layer was discarded, and the ethylene dichloride layer washed with water and then evaporated to dryness under reduced pressure on a steam-bath. The residue was a dark red, viscous oil weighing 147 g. Upon distillation in high vacuum, two main fractions were obtained as follows

- I. 210–220° (2 mm.) 18 g. pale yellow oil
- II. 280–290° (1 mm.) 58 g. viscous reddish oil

Fraction I analyzed 12.76% N, corresponding to di-(β -cyanoethyl)-indene, $C_{18}H_{14}N_2$ (calcd.: N, 12.61).

Fraction II crystallized on standing. Upon recrystallization from ethanol using "Norite" for decolorizing, it separated in colorless crystals, m. p. 65°.

Anal. Calcd. for $C_{18}H_{14}N_2$: C, 78.50; H, 6.23; N, 15.26. Found: C, 78.80; H, 6.09; N, 15.39.

(III) **Meso-bis-(β -cyanoethyl)-anthrone.**—Acrylonitrile (15.9 g.) was added dropwise during thirty minutes to a stirred solution consisting of 29.1 g. of anthrone, 100 g. of dioxane and 3 g. of aqueous 40% trimethylbenzylammonium hydroxide while the reaction mixture was maintained at 40°. A deep red solution resulted. This was stirred for one hour longer at 35° and then allowed to stand eighteen hours. The mixture was then acidified with dilute hydrochloric acid whereupon the red color disappeared. The crystalline product was filtered off, washed and dried; yield 40 g. After crystallization from glycol monoethyl ether ("Cellosolve"), it formed colorless prisms, m. p. 215°. *Anal.* Calcd. for $C_{20}H_{16}N_2O$: C, 79.92; H, 5.37; N, 9.32. Found: C, 80.36; H, 5.45; N, 9.49.

(IV) **Bis-9,9-(β -cyanoethyl)-2-nitro-fluorene.**—To a solution of 20 g. of 2-nitrofluorene, 150 g. of dioxane and 2 g. of aqueous 40% trimethylbenzylammonium hydroxide there was added dropwise during twenty minutes 10.6 g. of acrylonitrile, while the reaction mixture was stirred and cooled to 35–40°. The mixture was then stirred for two hours longer and finally neutralized with dilute hydrochloric acid. The crystalline product was filtered off,

washed and dried; yield 21 g. Upon recrystallization from glycol monoethyl ether it formed yellow needles, m. p. 236–237°. *Anal.* Calcd. for $C_{10}H_{15}N_3O_2$: C, 71.90; H, 4.77; N, 13.12. Found: C, 72.40; H, 4.80; N, 13.09.

(V) **3-Cyano-1,4-endomethylene-cyclohexene-5**.—To 33 g. of cyclopentadiene in a flask under a reflux condenser, there was added 26.5 g. of acrylonitrile. After standing for about ten minutes the mixture became warm and began to boil. The exothermal reaction lasted for about a half hour. The mixture was allowed to stand for four hours thereafter and then distilled in vacuum at 11 mm. A colorless oil came over at 80–85° (11 mm.), yield 49.5 g.; n_D^{25} 1.4876; d_4^{25} 1.0066. *Anal.* Calcd. for C_9H_9N : N, 11.76. Found: N, 11.70. It crystallizes in an ice-bath but is liquid at room temperature.

(VI) **Hexa-(β -cyanoethyl)-cyclopentadiene**.—Acrylonitrile (106 g.) was added dropwise during two hours to a stirred, cooled mixture of 66 g. of cyclopentadiene, 100 g. of dioxane, and 4 g. of aqueous 40% trimethylbenzylammonium hydroxide while the reaction temperature was maintained at 20–25°. The mixture was stirred three hours longer at 20°, then neutralized with dilute hydrochloric acid. During the condensation the mixture became almost black but bleached to a yellow color on the addition of the acid. The crystalline product was filtered off. It was a tan-colored powder; yield 34 g. Upon recrystallization from glycol monomethyl ether it separated in colorless needles, m. p. 203°. *Anal.* Calcd. for $C_{22}H_{24}N_6$: C, 71.84; H, 6.30; N, 21.86. Found: C, 71.80; H, 6.26; N, 21.93.

The original filtrate was washed with water, dried and distilled in vacuum. Only a small amount boiled below 90° at 11 mm. The bulk distilled from 100 to 280° (1 mm.) with some decomposition and considerable residue but a clean fractionation was not accomplished.

(VII) **3-Cyano-1,4-endo-isobutenylidene-cyclohexene-5**.—A mixture of 50 g. of dimethylfulvene and 25 g. of acrylonitrile was gently heated on a water-bath under reflux for several hours until no further refluxing occurred. The viscous reddish product was distilled in vacuum at 1 mm. At 95–100° (1 mm.) an amber-colored oil came over which gradually crystallized; yield 35 g. Upon recrystallization from petroleum ether using Norite for decolorization, the product was obtained as colorless crystals, m. p. 87°. Calcd. for $C_{11}H_{13}N$: C, 82.96; H, 8.24; N, 8.80. Found: C, 83.20; H, 8.03; N, 8.90.

VIII-A or VIII-B. **Cyanoethylated Dimethylbenzofulvene**.—To a solution of 44 g. ω,ω -dimethylbenzofulvene, 44 g. of dioxane and 3 g. of Triton B, acrylonitrile (15 g.) was added dropwise while stirring at 25–35°. The mixture was stirred for four hours after the exothermal reaction had ceased, and then neutralized with dilute hydrochloric acid, taken up in ethylene dichloride, and washed and dried *in vacuo* at 100°. The residual oil weighing 61 g. was distilled in vacuum at 1 mm. The main fraction came over at 180–230° (1 mm.) and solidified in the receiver; yield 13 g. Upon recrystallization from methanol the product was obtained as yellow crystals, m. p. 121°. Calcd. for $C_{16}H_{18}N$: C, 86.07; H, 7.23; N, 6.69. Found: C, 85.90; H, 7.11; N, 6.64.

(IX) **Bis-9,9-(β -carboxy-ethyl)-fluorene**.—A mixture of 16 g. of sodium hydroxide, 400 cc. of water and 40 g. of

(I) was boiled under reflux with rapid stirring, for twelve hours. The solution was bleached with charcoal, cooled, filtered, and the filtrate acidified hot with hydrochloric acid. The white precipitate (yield 41 g. air-dried) was recrystallized from ethanol. It separated in colorless crystals, m. p. 273–274°. *Anal.* Calcd. for $C_{19}H_{16}O_4$: C, 73.51; H, 5.85. Found: C, 73.70; H, 5.83.

(X) **Tris-1,1,3-(β -carboxy-ethyl)-indene**.—A mixture of 23 g. of potassium hydroxide, 225 cc. of water and 27 g. of (II) was stirred and boiled under reflux for three hours. The clear solution was bleached with charcoal, filtered and acidified with hydrochloric acid. The product separated as a resinous solid which became crystalline after being dissolved in hot water and allowed to separate slowly on cooling. After several recrystallizations from hot water, the melting point remained unchanged at 161–162°. *Anal.* Calcd. for $C_{13}H_{20}O_6$: C, 65.03; H, 6.07. Found: C, 64.80; H, 5.97.

(XI) **Bis-meso-(β -carboxy-ethyl)-anthrone**.—A mixture of 12 g. of sodium hydroxide, 120 cc. of water, 70 cc. of ethanol, and 27 g. of (III) was stirred rapidly and boiled under reflux for seven hours. The solution was cooled, filtered, and the filtrate acidified with hydrochloric acid. The product separated as an oil which rapidly solidified; yield 27 g. Upon recrystallization from dilute ethanol (75% H_2O + 25% ethanol) it separated in colorless flakes which sinter at 220° and decompose at 230°. *Anal.* Calcd. for $C_{20}H_{18}O_6$: C, 70.97; H, 5.36. Found: C, 71.10; H, 5.41.

(XII) **Hexa-(β -carboxy-ethyl)-cyclopentadiene**.—A mixture of 140 g. of sodium hydroxide, 1000 cc. of water and 184 g. of (VI) was boiled under reflux for eighteen hours. The dark solution was treated with Norite, filtered, and the filtrate acidified with concd. hydrochloric acid (350 g.) and cooled to 5°. The white crystalline precipitate was filtered off, washed on the filter with 200 cc. of ice-water and dried in an oven at 60°; yield 199 g. of crude acid containing 0.09% ash. It may be purified by recrystallization from four times its weight of water by chilling the solution to 5°. The purified analytical sample formed colorless crystals, m. p. 180–181°. It is readily soluble in alcohol and in warm water. *Anal.* Calcd. for $C_{23}H_{30}O_{12}$: C, 55.39; H, 6.07. Found: C, 55.40; H, 5.93.

(XIII) **3-Carbomethoxy-1,4-endomethylene-cyclohexene-5**.—A mixture of 33 g. of cyclopentadiene and 43 g. of methyl acrylate was placed in a flask under a reflux condenser. After standing for about thirty minutes the mixture began to boil. After boiling had ceased, the mixture was allowed to stand for twenty-four hours and was then distilled under reduced pressure. The product came over at 71–73° (8 mm.) as a colorless oil of strong characteristic valerian odor; yield 64 g. or 84%; n_D^{25} 1.4745; d_4^{25} 1.0543. *Anal.* Calcd. for $C_9H_{12}O_2$: iodine no., 167. Found: 170.

The corresponding ethyl ester (XIII, R is C_2H_5) was prepared in the same manner as above from ethyl acrylate and cyclopentadiene. It is a colorless oil of b. p. 84–85° (10 mm.), n_D^{25} 1.4675; d_4^{25} 1.0268. *Anal.* Calcd. for $C_{10}H_{14}O_2$: saponification no., 338. Found: 338. It is also formed in 85% yield instead of the expected poly-(carbomethoxy-ethyl) derivative when ethyl acrylate is added to cyclopentadiene containing "Triton B."

(XIV) 9-(β -Cyano-isopropyl)-fluorene.—To a stirred solution of 83 g. of fluorene, 250 g. of dioxane, and 10 g. of "Triton B," there was added dropwise 67 g. of allyl cyanide during the course of one hour while the exothermal reaction was maintained at 38–47° by intermittent cooling. The mixture was then heated at 45–50° for six hours longer, cooled, rendered acid to congo red indicator with dilute hydrochloric acid, taken up in its own volume of ethylene dichloride and washed thoroughly with water. The ethylene dichloride layer was evaporated to dryness and the residual dark oil distilled in vacuum. After a small forerun of unchanged fluorene, the main fraction boiled between 190° and 220° (1–2 mm.) and weighed 60 g. It formed a yellow balsam which gradually solidified to a crystalline mass. After recrystallization from methanol, the pure product was obtained as colorless crystals melting at 92–93°. *Anal.* Calcd. for $C_{17}H_{15}N$: C, 87.50; H, 6.49; N, 6.00. Found: C, 87.51; H, 6.38; N, 6.07.

The same product is obtained by using crotononitrile in place of allyl cyanide.

Acknowledgment.—The analyses of the above products were performed by Mr. C. W. Nash, and much of the experimental work was done by Mr. Thomas Riener of these Laboratories.

Summary

1. Acrylonitrile condenses in the presence of strong bases, notably aqueous trimethylbenzylammonium hydroxide ("Triton B") as a catalyst, with reactive carbocyclic methylene or methenyl compounds such as fluorene, indene, anthrone, cyclopentadiene and fulvenes to replace each reactive hydrogen atom by a β -cyanoethyl radical.

2. The preparation and properties of bis-(β -cyanoethyl)-fluorene, tris-(β -cyanoethyl)-indene, bis-(β -cyanoethyl)-anthrone, hexa-(β -cyanoethyl)-cyclopentadiene, and the corresponding carboxylic acids obtained therefrom by hydrolysis are described, as well as the cyanoethylation product of dimethylbenzofulvene and certain Diels-Alder type adducts of acrylonitrile and acrylic esters.

3. Allyl cyanide or crotononitrile condensed with fluorene to a 9-(β -cyano-isopropyl)-fluorene.

PHILADELPHIA, PA.

RECEIVED JULY 23, 1942

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Rearrangement of 1,1,3,3,5,5-Hexamethylcyclohexatriol-2,4,6 to Hexamethylbenzene

BY ERLE B. AYRES AND CHARLES R. HAUSER

In another investigation in this Laboratory a method was developed for the synthesis of hexamethylcyclohexatriene-1,3,5 (I) in an over-all yield of approximately 25% starting with ethyl isobutyrate and isobutyryl chloride.¹ It seemed possible that the cyclohexatriene (I) might be reduced to the triple neopentyl system, 1,1,3,3,5,5-hexamethylcyclohexatriol-2,4,6 (II), which might be made to undergo a triple dehydration and rearrangement to form hexamethylbenzene (V). This transformation, which represents a new route from an aliphatic to an aromatic compound, has been realized.

The cyclohexatriene (I) was reduced catalytically² in good yield to the cyclohexatriol (II), which was probably a mixture of two stereo-

(1) The methods are described by Hudson and Hauser (*THIS JOURNAL*, 61, 3567 (1939)). Better yields were subsequently obtained (Hudson, Ph.D. Thesis, Duke University (1941)) as follows: for ethyl isobutyryl isobutyrate, 74%; for ethyl 2,2,4,4,6-pentamethyl-3,5-diketooheptanoate, 72%; for hexamethylcyclohexatriene-1,3,5, 52%.

(2) The authors are indebted to Dr. Homer Adkins of the University of Wisconsin for carrying out this reduction.

isomers; in one of the isomers the three hydroxyl groups are arranged on one side of the ring, and in the other, two hydroxyl groups are on one side and the third hydroxyl on the opposite side of the ring. In the present study no attempt has been made to separate the two isomers after a substance was obtained the melting point of which was not raised by further recrystallization. The cyclohexatriol was dissolved in sulfuric acid, giving a colored mixture from which practically pure hexamethylbenzene in approximately 20% yield was extracted with ligroin. Other products were present in the sulfuric acid layer but were not identified in the present investigation. The rearrangement was also carried out in warm phosphoric acid, but the yield of hexamethylbenzene was very low. Treatment of the cyclohexatriol with thionyl chloride gave only tarry material from which no hexamethylbenzene could be isolated.

The conversion of the hexamethylcyclohexatriol (II) to hexamethylbenzene (V) probably involves