

(XIV) 9-( $\beta$ -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  $\beta$ -cyanoethyl radical.

2. The preparation and properties of bis-( $\beta$ -cyanoethyl)-fluorene, tris-( $\beta$ -cyanoethyl)-indene, bis-( $\beta$ -cyanoethyl)-anthrone, hexa-( $\beta$ -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-( $\beta$ -cyano-isopropyl)-fluorene.

PHILADELPHIA, PA.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

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

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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.<sup>1</sup> 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.

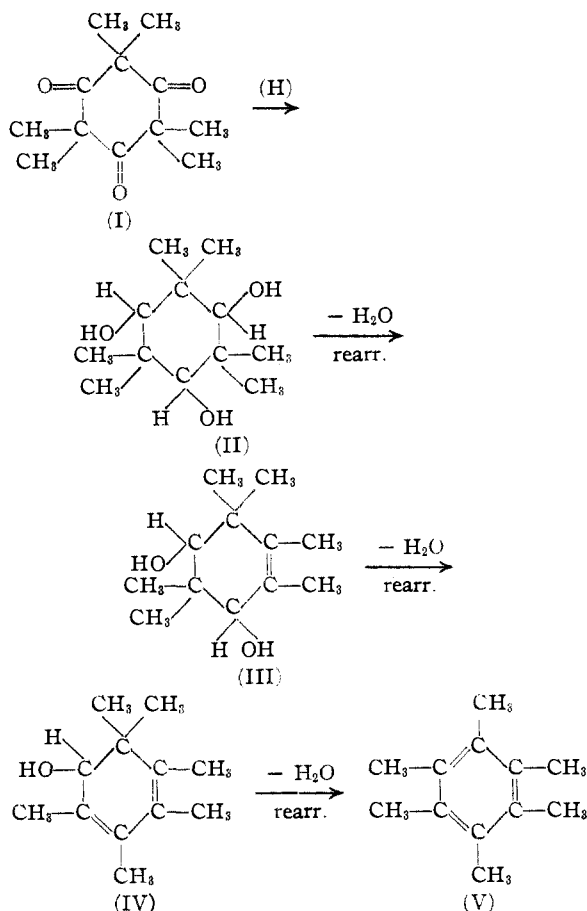
The cyclohexatriene (I) was reduced catalytically<sup>2</sup> in good yield to the cyclohexatriol (II), which was probably a mixture of two stereo-

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.

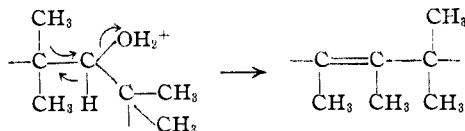
The conversion of the hexamethylcyclohexatriol (II) to hexamethylbenzene (V) probably involves

(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.



three separate reactions,<sup>3</sup> each consisting of the removal of a hydroxyl group (as a molecule of water from the oxonium ion formed by the addition of a proton to the hydroxyl), the shift of a methyl group with its attached electron pair, and the loss of a proton to form a double bond,<sup>4</sup> thus<sup>5</sup>



It is obvious that the monodehydration of (II) can give only one cyclic product (III). Of the hydroxyl groups in (III), the one in the  $\alpha$ -position to the double bond might be preferentially lost because of the possibility of allylic resonance in

(3) Although it would appear improbable that the three dehydrations and rearrangements take place simultaneously, the possibility is not entirely excluded; the triply charged oxonium ion required could probably be formed in low concentration, and such a reaction would involve considerable driving force in forming the aromatic ring.

(4) See especially Whitmore, *THIS JOURNAL*, **54**, 3274 (1932).

(5) Whitmore and Stahly, *ibid.*, **55**, 4153 (1933), found that *tert*-butylcarbinol, which is analogous to the section of (II) represented above, yields the expected olefin only under mild conditions; instead, a tertiary butyl group is eliminated as a carbonium ion. It is possible that this type of reaction occurs also with compound (II).

the resulting carbonium ion. Shift of a methyl group would give (IV), which contains conjugated double bonds. The third rearrangement should follow only the course giving hexamethylbenzene. In view of the several side reactions that one might expect to occur in the conversion of (II) to (V), it is not surprising that the yield of hexamethylbenzene is only 20%.

### Experimental

**1,1,3,3,5,5-Hexamethylcyclohexatriol-2,4,6.**—This substance was prepared by the reduction<sup>2</sup> of hexamethylcyclohexatrione-1,3,5 (15.3 g.) over copper chromite for five hours at 200 atm. at 200°. The triketone took up approximately three molecular equivalents of hydrogen. An alcoholic suspension of the reduction product yielded on filtering 7.0 g. of silky white crystals, m. p. 242–246° after some softening at 170°. Evaporation of the filtrate yielded 7.7 g. of slightly gummy solid; total yield of crude product, 14.7 g. (93%). After several recrystallizations from alcohol or, better, from acetone, the crystals melted at 251.0–251.5°. The substance could also be purified by sublimation.

*Anal.*<sup>6</sup> Calcd. for C<sub>12</sub>H<sub>24</sub>O<sub>3</sub>: C, 66.63; H, 11.18. Found: C, 66.85; H, 11.03.

**Dehydration and Rearrangement of 1,1,3,3,5,5-Hexamethylcyclohexatriol-2,4,6.**—To 15 cc. of ice-cold concentrated sulfuric acid was added 1.00 g. of 1,1,3,3,5,5-hexamethylcyclohexatriol-2,4,6. The color of the mixture became pale yellow and then reddish to red-brown during two hours. At one point there seemed to be very little suspended material; then the quantity of fine white platelets appeared to increase. After standing for two days at room temperature, the mixture was extracted with purified ligroin (b. p. 54–64°). After washing, drying and removing the ligroin under partial pressure, there was left an oil which solidified completely to 0.15 g. (19.4%) of white crystalline solid, m. p. 164–165°; a mixed melting point with a sample of Eastman Kodak hexamethylbenzene (m. p. 164–165°) was the same. The sulfuric acid layer was poured over crushed ice and the oily mixture extracted with ether. Upon washing the ether with sodium bicarbonate solution, drying and evaporation, there remained a trace of unidentified material.

In another experiment, 1,1,3,3,5,5-hexamethylcyclohexatriol-2,4,6 (1.00 g.) was warmed over a steam-bath with 85% phosphoric acid. From a ligroin extract of the mixture was obtained a very small amount of impure hexamethylbenzene and small amounts of solids which decomposed at about 200° and were perhaps phosphoric esters. An experiment carried out using thionyl chloride yielded only tarry material.

### Summary

1,1,3,3,5,5-Hexamethylcyclohexatriol-2,4,6 on treatment with sulfuric acid undergoes partly a triple dehydration and rearrangement of the neopentyl type, yielding hexamethylbenzene.

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(6) Microanalysis by Saul Gottlieb, Columbia University, New York, N. Y.