[CONTRIBUTION FROM THE HALL LABORATORY OF CHEMISTRY, WESLEYAN UNIVERSITY]

Tribenzylmethane

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In 1909 Schmerda[1] reduced tribenzylcarbinol with hydriodic acid in a heated sealed tube and obtained a hydrocarbon. On the basis of a single analysis and a single molecular weight determination he concluded that the substance was hexabenzylethane, $C_{44}H_{42}$. He prepared a nitro derivative of the hydrocarbon and reported its analysis, but apparently did not determine the molecular weight. He believed this substance to be hexanitrohexabenzylethane. In 1925 Trotman[2] obtained the same hydrocarbon as a by-product in a Grignard reaction. He reported an analysis, but no determination of the molecular weight, and believed the compound to be hexabenzylethane.

In the course of a study of certain ketones, in this Laboratory, a hydrocarbon was obtained which it was expected would prove to be tribenzylmethane, $C_{22}H_{22}$. Its melting point and its analysis indicated that it was identical with Schmerda's and with Trotman's compounds. Molecular weight determinations, by the cryoscopic method, with benzene and with acetic acid (the solvent used by Schmerda), and ebullioscopic molecular weight determinations with benzene showed it to be tribenzylmethane.

This conclusion was confirmed by three independent syntheses of the hydrocarbon. Tribenzylcarbinol yielded it when heated with hydriodic acid and red phosphorus in a sealed tube. Tribenzylacetophenone,[3] when acted upon by sodamide, gave the same product. Dibenzylacetophenone was reduced by heating in a sealed tube with hydriodic acid and red phosphorus and likewise gave tribenzylmethane. It is significant that in two of these syntheses the tribenzylmethyl radical was present in the starting materials, and was formed in the other case.

$$\left.\begin{array}{l} (C_6H_5CH_2)_3COH \xrightarrow{\text{red P} + \text{HI}} \\ (C_6H_5CH_2)_3CCOC_6H_5 \xrightarrow{\text{Na}-\text{NH}_2} \\ (C_6H_5CH_2)_2CHCOC_6H_5 \xrightarrow{\text{red P} + \text{HI}} \end{array}\right\} (C_6H_5CH_2)_3CH$$

A nitro derivative of this hydrocarbon was prepared according to Schmerda's directions. Its analysis and determinations of its molecular weight, ebullioscopically with acetone, and by Rast's method, with camphor, showed it to be trinitrotribenzylmethane.

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Experimental

Preparation of Tribenzylmethane

(A) The tribenzylcarbinol used in these experiments was prepared from dibenzyl ketone, and from ethyl phenylacetate, by the use of benzylmagnesium chloride.[4] Twenty grams (0.066 mole) of tribenzylcarbinol, placed in a Pyrex bomb tube with 50 cc. of 47% hydriodic acid (0.275 mole) and 3 g. (0.097 mole) of red phosphorus, was heated at 200° for twenty-four hours. After cooling, the hydriodic acid was poured away from the solid product, which was taken up in 250 cc. of ether. The ether solution was washed with water, with 6 *N* sodium hydroxide, with sodium thiosulfate solution, and again with water. It was dried with anhydrous sodium sulfate. After removal of the ether, the residue was twice recrystallized from ethyl alcohol and the white crystals melted at 82°. The yield was 70%.

(B) 19.6 g. of tribenzylacetophenone, a white solid, melting at 127.6°, and 14.6 g. of finely ground sodamide in 100 cc. of xylene, were refluxed in an oil-bath at 145–150° for forty hours. A red color developed in the solution. Water was added after cooling. The xylene layer was separated and the alkaline aqueous layer extracted with four 15-cc. portions of xylene. The xylene solutions were united, washed with water, and dried with anhydrous sodium sulfate. After removal of the xylene by heating and by a blast of dry air, a crystalline residue was obtained. It was recrystallized from benzene and from alcohol and yielded white crystals, melting at 81.8°. The percentage yield was not recorded, but it was observed to be considerably better than the yields of similar experiments run in toluene.

(C) Four grams (0.013 mole) of dibenzylacetophenone, a white solid melting at 76°,[5] 80 cc. (0.44 mole) of 47% hydriodic acid, and 4 g. (0.13 mole) of red phosphorus, were heated at 200°, in a bomb tube, for twenty-four hours. After cooling, the two layers were separated and the nonaqueous layer was diluted with 200 cc. of ether. The ether solution was treated, as indicated in (A), and ultimately yielded 1.5 g. of white crystals melting at 82°. The yield was 40%. Other experiments showed that the

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(1) Schmerda, *Monatsh.*, **30**, 387 (1909).

(2) Trotman, *J. Chem. Soc.*, **127**, 88 (1925).

(3) An account of the preparation and properties of this new ketone will appear in a forthcoming paper.

(4) Klages and Heilmann, *Ber.*, **37**, 1456 (1904).

(5) Haller and Bauer, *Compt. rend.*, **149**, 8 (1909).

large excess of hydriodic acid employed is quite essential in order to produce the hydrocarbon with even moderate success.

Physical Properties of Tribenzylmethane

The melting point of the hydrocarbon prepared by Schmerda was given as 81°, Trotman gave 82–83°, while all the pure samples prepared in this Laboratory melted from 81.8–82°. The identity of the products of the syntheses given above was established by a series of mixed melting point determinations.

Anal. Calcd. for $C_{22}H_{22}$: C, 92.30; H, 7.69. Calcd. for $C_{44}H_{42}$: C, 92.63; H, 7.36. Found: C, 92.07, 91.95, 91.97, 92.19, 92.49, Schmerda 92.35, Trotman 92.4; H, 7.68, 7.60, 7.73, 7.70, 7.85, Schmerda 7.04, Trotman 7.7.

Mol. wt. Calcd. for $C_{22}H_{22}$: 286; for $C_{44}H_{42}$: 570. Found: mol. wt. (depression in benzene), 278.5, 285.2, 293.7; (depression in acetic acid), 297.4, 287.7; (McCoy method) 276.3, 262.7; av. of all, 283.1; found by Schmerda, 560.6.

The Nitro Compound

This derivative of the hydrocarbon was prepared by Schmerda's method, nitration with fuming nitric acid. It is a yellow crystalline solid softening at 74°, decomposing on further heating; Schmerda reported 75°. Like Schmerda's compound, our product dissolved in alcoholic potash with a blue to violet color which became redder upon warming.

Anal. Calcd. for $C_{22}H_{19}O_6N_3$: N, 9.97. Found: (modified Kjeldahl method) N, 9.95, Schmerda (Dumas method) 9.55.

Mol. wt. Calcd. for $C_{22}H_{19}O_6N_3$: 421; for $C_{44}H_{38}O_{12}N_6$: 740. Found: mol. wt. (McCoy method), 472, 462, 444; (Rast method) 421, 421, 421, 408, 430, 425, 421; av. of all, 432.5.

Conclusions

1. The compound obtained by Schmerda and by Trotman, and believed by them to be hexabenzylethane, is in reality tribenzylmethane.
2. This conclusion is based upon analyses, molecular weight determinations, and three quite independent syntheses.
3. A nitro compound, hitherto believed to be hexanitrohexabenzylethane, has been prepared, and analyses and molecular weight determinations show it to be *trinitrotribenzylmethane*.

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The Mechanism of Macropolymerization Reactions

BY WILLIAM CHALMERS

General Introduction

This paper sets forth a theoretical study of a group of reactions by which simple substances are transformed into derivatives of high molecular weight. Such changes are classified at present under the two headings of "polymerization" and "condensation." Polymerization has been defined as the union of like molecules to form a product of the same composition.[1] Yet the tendency of unsaturated molecules to attain a higher degree of saturation by interaction is not confined to those of the same species. The "heteropolymerization" process described by Wagner-Juaregg[2] involves two or more different compounds. Polymerization in the broader sense is thus a class of addition reaction in which all reactant molecules are unsaturated. Polymerizations leading to polymers of considerable complexity will be designated as "macropolymerizations" in the following.

Processes in which the aggregation of molecules takes place by condensation present some formal analogies with polymerization. Condensation' it is now currently accepted, implies the elimination of another substance. Carothers[3] has proposed that it be regarded as a sub-class of polymerization and that the products be named "polymers." The writer does not concur in this view. It will be seen that macropolymerizations are quite different in mechanism from what will be referred to as "multicondensations." Multicondensations rarely elaborate molecules containing more than twenty-five structural units (see the numerous papers of Carothers and co-workers[3]) whereas the true high polymers may have an order of polymerization exceeding a thousand.

To these previously recognized divisions should be added a third, of which the so-called "polymerization" of formaldehyde is an example. This is intermediate in nature between multicondensation and polymerization proper and may resemble either under certain conditions. Consideration of these "pseudopolymerizations" will be reserved for a later article.

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[1] Staudinger, *Ber.*, **53**, 1073 (1920).

[2] Wagner-Juaregg, *ibid.*, **63**, 3213 (1930).

[3] Carothers, THIS JOURNAL, **51**, 2548 (1929), and later papers.