uct, after recrystallization from alcohol (50% yield), melted at 220° with decomposition.

Anal. Calcd. for $C_8H_4ClNO_2S_2$: C, 39.10; H, 1.64; S, 26.10. Found: C, 39.37; H, 2.12; S, 26.48.

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Synthesis and Properties of Trimethylhydrazine

BY J. B. CLASS AND J. G. ASTON

We have recently performed the first successful synthesis of trimethylhydrazine, the simplest member of the trisubstituted hydrazine series. Previous attempts by Klages and co-workers[1] indicated the impracticability of chloramine coupling and methylation means, so we attempted and succeeded in reducing N,N-dimethyl-N′-methylenehydrazine with $LiAlH_4$.

Identification of the product resulted from equivalent weight determinations by electrometric titration with HCl (equivalent weight: calcd., 74.13; found, 74.53, 74.59). A cryoscopic determination in water gave a molecular weight of 67.2 (calcd. 74.13) indicating one equivalent per molecule. A satisfactory combustion has not yet been obtained due to the compound exploding in the combustion tube.

Trimethylhydrazine is a colorless liquid possessing a strong, fish-like odor. Unlike hydrazine and the other known methylhydrazines, *it is relatively stable to the atmosphere.* The compound fumes on dilution with water, the process of solution being strongly exothermic. The low boiling point of 59°, which is lower than that of the methyl and dimethylhydrazines, indicates that the hydrogen bonding characteristic of hydrazine is further decreased by introducing a third methyl group.

A preliminary determination of its physical constants gave the following: b.p. 59° (740 mm.); d^{18}_4 0.814; n^{18}_{D} 1.406; *MR* calcd. 23.60, found 22.39; pK_b 7.0 (determined by electrometric titration using a glass electrode).

[1] F. Klages, G. Nober, F. Kircher and M. Bock, *Ann.*, **547**, 1 (1941).

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Structure of the Hexachlorocyclohexane Melting at 145°

BY G. CALINGAERT,[1] A. J. KOLKA AND H. D. ORLOFF

A hexachlorocyclohexane melting at 145° has been prepared[2,3] and shown to have zero dipole moment.[3] This material was considered to be a new isomer (ζ) of benzene hexachloride (1,2,3,4,5,6-hexachlorocyclohexane), and a steric structure that would have zero dipole moment was postulated.[3] Subsequently the structure proposed for the "ζ" isomer was assigned to the ε isomer of benzene hexachloride,[4] thus leaving no convincing evidence for or against any particular structure for the hexachlorocyclohexane melting at 145°.

Five steric isomers of benzene hexachloride have been isolated[5,6] and their structure established by X-ray diffraction,[7] electron diffraction,[8] and measurement of their dipole moments.[9] Because only two of the possible steric isomers of benzene hexachloride can have zero dipole moment, and both of these (β and ε) have been identified, the product reported to be the "ζ" isomer of benzene hexachloride must be a hexachlorocyclohexane other than a 1,2,3,4,5,6-positional isomer.

Of the other positional isomers of hexachlorocyclohexane, only two can have steric isomers possessing zero dipole moment. These are 1,1,3,3,5,5-hexachlorocyclohexane, capable of existence in only one steric structure, and the 1,1,2,4,4,5-isomer, which can theoretically have two zero dipole forms out of three possible steric isomers. Dehydrochlorination of 1,1,3,3,5,5- and 1,1,2,4,4,5-hexachlorocyclohexane can yield only 1,3,5- and 1,2,4-trichlorobenzene, respectively.

The preparation of the hexachlorocyclohexane melting at 145° was repeated in this Laboratory, and the purified material was dehydrochlorinated with 10% alcoholic potassium hydroxide solution by the method of Kauer, *et al.*[6] The product was proved to consist of only 1,2,4-trichlorobenzene by examination of its infrared absorption spectrum. It is concluded that the hexachlorocyclohexane melting at 145° is 1,1,2,4,4,5-hexachlorocyclohexane.

[1] Hobart College, Geneva, New York.

[2] Sabatier and Mailhe, *Bull. soc. chim.*, **29**, 977 (1903); *Ann. chim. phys.*, [8] **10**, 534 (1907); Beveridge, British Patent 573,712.

[3] Bastiansen and Hassel, *Acta Chem. Scand.*, **1**, 683 (1947).

[4] Bastiansen, Ellefsen and Hassel, *ibid.*, **3**, 918 (1949).

[5] Van der Linden, *Ber.*, **45**, 231 (1912).

[6] Kauer, DuVall and Alquist, *Ind. Eng. Chem.*, **39**, 1335 (1947).

[7] Dickinson and Bilicke, THIS JOURNAL, **50**, 764 (1928); Bijvoet, *Rec. trav. chim.*, **67**, 777 (1948); van Vloten, Kruissink, Strijk and Bijvoet, *Nature*, **162**, 771 (1948); *Acta Cryst.*, **3**, 139 (1950); van Bommel, Strijk and Bijvoet, *Proc. Koninkl. Nederland Akad. Wetenschap*, **53**, 47 (1950).

[8] Hassel and Ottar, *Acta Chem. Scand.*, **1**, 929 (1947); Bastiansen, Ellefsen and Hassel, *ibid.*, **3**, 918 (1949).

[9] Hetland, *Acta Chem. Scand.*, **2**, 678 (1948); Amble and Hassel, *Research*, **3**, 52 (1950); Lind, Hobbs and Gross, THIS JOURNAL, **72**, 4474 (1950).

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Synthesis of Cycloheptanone by a Nitromethane Condensation Sequence

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Large scale preparation of cycloheptanone from cyclohexanone by the diazomethane method[1a] presents the difficulties of preparation and use of large amounts of diazomethane and of fractional distillation of a product mixture of homologous cyclic ketones and epoxides. The alternative method of ring enlargement, diazotization of 1-(aminomethyl)-cyclohexanol (V), produces cycloheptanone conveniently and in moderate yield (60%)[2] but the synthesis of the requisite amino-

[1] Atomic Energy Commission Predoctoral Fellow, 1948–1950.

[1a] E. P. Kohler, M. Tishler, H. Potter and H. T. Thompson, THIS JOURNAL, **61**, 1059 (1939).

[2] (a) M. Tiffeneau, P. Weill and B. Tchoubar, *Compt. rend.*, **205**, 54 (1937); (b) B. Tchoubar, *ibid.*, **212**, 195 (1941); (c) B. Tchoubar, *Bull. soc. chim. France*, 160, 164, 169 (1949).