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.

DEPARTMENT OF CHEMISTRY
DUKE UNIVERSITY
DURHAM, N. C.
RECEIVED DECEMBER 18, 1950

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).

SCHOOL OF CHEMISTRY AND PHYSICS
THE PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNSYLVANIA
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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).

RESEARCH LABORATORY ETHYL CORPORATION
DETROIT, MICHIGAN
RECEIVED JANUARY 5, 1951

Synthesis of Cycloheptanone by a Nitromethane Condensation Sequence

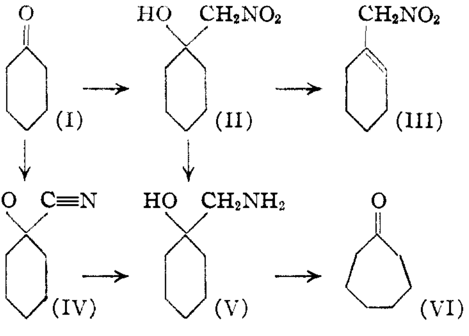
BY HYP J. DAUBEN, JR., HOWARD J. RINGOLD,[1] ROBERT H. WADE AND ARTHUR G. ANDERSON, JR.

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).



alcohol by catalytic hydrogenation of cyclohexanone cyanhydrin (I→IV→V) suffers from certain difficulties in both steps and from the low over-all yield (39–49%).[2b,c,3] The present studies show that the necessary intermediate, 1-(aminomethyl)-cyclohexanol, may be derived expediently in quantity and in considerably better over-all yield (68–75%) by another route, catalytic hydrogenation of 1-(nitromethyl)-cyclohexanol derived from cyclohexanone by base-catalyzed condensation with nitromethane (I→II→V).

The difficulties involved in effecting the condensation of nitromethane with cyclohexanone[4,5,6,7] have been resolved recently by Grob and von Tscharner[6] in their use of a molar equivalent of the condensing agent, ethanolic sodium ethoxide, instead of a fractional amount. Their yield (75%) of 1-(nitromethyl)-cyclohexanol appreciably exceeds that obtained by the substitution of equivalent quantities of either sodium methoxide in methanol (42%) or potassium *t*-butoxide in *t*-butanol (38%), presumably due to the greater solubilities of the condensation product salts in the respective solvents, but slightly better conversion (78–82%) may be realized by the use of excess nitromethane and a simplified isolation procedure. Diethylamine has also proven to be an effective condensing agent for the preparation of 1-(nitromethyl)-cyclohexanol under appropriate conditions (45–54%), in contrast to earlier results,[4,5] and piperidine in the presence of an internal desiccant has been found to furnish only 1-(nitromethyl)-cyclohexene (III) in 54% yield.

Nightingale and co-workers[7] have recently reported that high pressure hydrogenation of 1-(nitromethyl)-cyclohexanol using Raney nickel in methanol at 80° formed only cleavage (hydrogenolysis or reversal) and coupling products.[8] In our studies low pressure hydrogenation of the nitroalcohol at room temperature in ethanol using either Raney nickel or platinum oxide has been found to be sluggish but productive of low yields (<35%) of 1-(aminomethyl)-cyclohexanol. Utilization of Raney nickel catalyst in acetic acid or acetic acid–ethanol solvent[9] has given excellent and reproducible results when the temperature of the very exothermic reduction was controlled at 25–35°; hydrogenation under a few atmospheres pressure occurred smoothly at a moderate rate and 1-(aminomethyl)-cyclohexanol was isolated (as its acetic acid salt) in 86–91% yields. Diazotization converted the aminoalcohol into cycloheptanone in 59–65% yield, in agreement with the results of Tchoubar.[2c]

The nitromethane sequence (I → II → V → VI) for the synthesis of cycloheptanone from cyclohexanone possesses the advantages over the cyanhydrin sequence (I → IV → V → VI) of superior over-all yield (39–49%), more convenient manipulations, and adaptability to large scale preparation.

Experimental

1-(Nitromethyl)-cyclohexanol (II). (a) **Sodium Ethoxide Method.**—Slightly improved yields were obtained by the use of excess (0.5 equiv.) nitromethane in the Grob–von Tscharner procedure[6] and isolation of the product facilitated without loss of yield[10] by work-up of only the filtered sodium salt with lesser quantity of acetic acid (1.2 equiv.); 78–82% yield, b.p. 132–133° (18.5 mm.), $n^{25}\text{D}$ 1.4835. Comparable conversions were obtained in large runs (5–6 moles).

(b) **Diethylamine Method.**—A mixture of cyclohexanone (100 g., 1.02 moles), excess nitromethane (250 ml., 4.08 moles) and diethylamine (18.3 g., 0.25 mole) in 50% ethanol (500 ml.) was allowed to stand at room temperature for three days. The dark amber solution was diluted with ice–water mixture (500 ml.), the layers separated and the aqueous phase extracted with ether. The combined layers were washed with 10% hydrochloric acid (2 × 100 ml.), sodium bicarbonate, saturated sodium chloride and dried with magnesium sulfate. Concentration followed by distillation gave 1-(nitromethyl)-cyclohexanol in 45% yield (72.8 g., b.p. 131–133° (19 mm.), $n^{25}\text{D}$ 1.4844), a forerun of unreacted cyclohexanone containing little, if any, 1-(nitromethyl)-cyclohexene, and a black non-volatile residue (*ca.* 10 g.).[11]

1-(Nitromethyl)-cyclohexene (III).—Cyclohexanone (56.7 g., 0.58 mole), nitromethane (66.7 g., 1.09 moles) and piperidine (3 ml.) were allowed to stand over excess anhydrous magnesium sulfate (25 g.) at room temperature for six days. Distillation of the filtered and concentrated reaction mixture furnished 1-(nitromethyl)-cyclohexene in 54% yield (44.1 g., b.p. 110–118° (25 mm.), $n^{20}\text{D}$ 1.4838) and 20% unreacted cyclohexanone.

1-(Aminomethyl)-cyclohexanol (V).—Catalytic hydrogenation of 1-(nitromethyl)-cyclohexanol in acetic acid solvent with Raney nickel catalyst at low pressures produced a markedly exothermic reaction, particularly at its initiation and when large quantities (100–500 g.) were reduced. Moderation of the reduction temperature by external cooling was essential to prevent deactivation of the catalyst and excessive diminution of the yield as the result of extensive hydrogenolysis.

A solution of 1-(nitromethyl)-cyclohexanol (100 g., 0.63 mole) and glacial acetic acid (300 ml.) in a two-liter, heavy-walled stainless steel hydrogenation flask, fitted with an external coil of copper tubing through which a regulated stream of cold water could be circulated,[12] was placed in a

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(3) M. W. Goldberg and H. Kirchensteiner, *Helv. Chim. Acta*, **26**, 288 (1943).

(4) H. B. Fraser and G. A. R. Kon, *J. Chem. Soc.*, 604 (1934).

(5) H. B. Hass and E. F. Riley, *Chem. Revs.*, **32**, 383 (1943).

(6) C. A. Grob and W. von Tscharner, *Helv. Chim. Acta*, **33**, 1070 (1950).

(7) D. V. Nightingale, F. B. Erickson and N. C. Knight, *J. Org. Chem.*, **15**, 782 (1950).

(8) *Cf.* E. F. Degering and R. I. Hoaglin, *Proc. Indiana Acad. Sci.*, **52**, 119 (1943).

(9) *Cf.* J. B. Tindall, U. S. Patent 2,347,621 (*C. A.*, **39**, 88 (1945)).

(10) Separate handling of the material remaining in the filtrate produced no additional nitroalcohol product. Elimination of the filtrate concentration step avoids the danger of explosion of the sodium salt of nitromethane; *vid.*, J. F. Controulis, M. C. Rebstock and H. M. Crooks, THIS JOURNAL, **71**, 2465 (1949).

(11) Diethylamine under these reaction conditions apparently also catalyzes further reactions of the nitroalcohol product (*cf.* H. B. Hass and J. F. Bourland, U. S. Patent 2,343,256 (*C. A.*, **38**, 2969 (1944)); M. S. Larrison and H. B. Hass, U. S. Patent 2,383,603 (*ibid.*, **40**, 347 (1946)) and the length of reaction time must be varied for each catalyst concentration for maximum nitroalcohol formation, *e.g.*, 5 mole per cent. diethylamine produced 54% nitroalcohol in 14 days.

(12) Less efficient but adequate cooling was also obtained by the use of a one-liter Pyrex bottle provided with a similar copper tubing coil and immersed in a surrounding water-bath.

reciprocating type shaking apparatus and cooled by a strong stream of water through the external coil before addition of the W-4 Raney nickel catalyst[13] (3–4 g.). While continuing the external cooling, hydrogen was admitted from a large low pressure hydrogen reservoir and shaking begun. Rapid circulation of water was necessary during the first 30–60 minutes of reduction to restrict the temperature to 35° but thereafter the optimum temperature of 25–35° could be maintained by slow or occasional water circulation. Absorption of hydrogen at 10–25 p.s.i. took place at a steady rate until approximately theoretical absorption had occurred (17.7 lb. in 14.5 hrs.; theoretical, 16.8 lb.). After filtration (filter-cel) and washing (ethanol) of the catalyst, the solvent was removed completely from the filtrate under reduced pressure on a steam-bath, ether (200 ml.) added to the viscous residue and the mixture triturated to induce crystallization. The first crop of 1-(1-hydroxycyclohexyl)-methylammonium acetate (acetic acid salt of V) (93.9 g., m.p. 115–118° (uncor.)) separated on standing in a refrigerator and a second crop (13.8 g., m.p. 108–113° (uncor.); total yield 107.7 g., 91%) was obtained after removal of the dissolved nickel from an aqueous solution of the concentrated filtrate by saturation with hydrogen sulfide, concentration and treatment with ether. Comparable yields (86–87%) were obtained in larger runs (350 g.) or by hydrogenation in 15% acetic acid–85% ethanol solvent but rate decreased to about one-half in the diluted solvent. Recrystallization of a small portion of the salt from acetic acid–ether raised the melting point to 122–123°. Characterization of the product was accomplished by the preparation of derivatives from the free amine: picrate, large yellow plates from absolute ethanol, m.p. 168–170° (uncor.) (reported,[20] 164°); hydrochloride, colorless plates from ether–hydrogen chloride, m.p. 215–216° (uncor.) (reported,[20] 190°) (Calcd. for $C_7H_{16}ONCl$: Cl, 21.37. Found: Cl, 21.40).

Cycloheptanone (VI).—Ring enlargement of 1-(1-hydroxycyclohexyl)-methylammonium acetate by diazotization, essentially according to the procedures of Tchoubar[20] and of Ruzicka and co-workers,[14] gave 59–65% yields on 0.5–1.5 mole runs; b.p. 68–74° (17 mm.), $n^{20}{}_D$ 1.4620; 2,4-dinitrophenylhydrazone, m.p. 146° (uncor.); semicarbazone, m.p. 160–161° (uncor.).

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[13] A. A. Pavlic and H. Adkins, THIS JOURNAL, **68**, 1471 (1946).

[14] L. Ruzicka, Pl. A. Plattner and H. Wild, *Helv. Chim. Acta*, **26**, 1631 (1943).

SEATTLE 5, WASH. RECEIVED DECEMBER 15, 1950

Preparation of 1,1,1,3,3,3-Hexachloropropane

BY H. W. DAVIS AND A. M. WHALEY

Recently the authors reported the synthesis of 1,1,3,3-tetrachloropropane,[1] leaving the 1,1,1,3,3,3-hexachloropropane as the only remaining chloropropane, out of twenty-nine, to be prepared. This work describes the preparation of the above hexachloride from the chlorination of 1,1,1,3,3-pentachloropropane, prepared in turn from both 1,1,1,3- and 1,1,3,3-tetrachloropropane.

The chlorination of the pentachloride can give only two possible hexachlorides, namely, the missing one and the 1,1,1,2,3,3-hexachloropropane. The latter is known[2] and has the properties: b.p. 216°, $d^{34}{}_4$ 1.6980, $n^{17}{}_D$ 1.5250. Therefore, the hexachloride boiling at 206° cannot be 1,1,1,2,3,3-hexachloropropane but must be 1,1,1,3,3,3-hexachloropropane.

Experimental

1,1,1,3,3-Pentachloropropane, b.p. 71–73° (16 mm.) was synthesized from 1,1,1,3- and 1,1,3,3-tetrachloropropane by chlorination of each at 80–100° with gaseous chlorine in the presence of ultraviolet light, followed by fractionation from the isomeric pentachlorides. This separation is comparatively easy as the possible pentachlorides boil at 180° ($CHCl_2–CH_2–CCl_3$), 199° ($CHCl_2–CHCl–CHCl_2$) and 192.4° ($CH_2Cl–CHCl–CCl_3$). The 1,1,1,3,3-pentachloride was then chlorinated similarly to yield a mixture of two hexachlorides from which was fractionated the 1,1,1,3,3,3-hexachloropropane, b.p. 206° (760 mm.), 89° (16 mm.), $n^{20}{}_D$ 1.5179, $d^{20}{}_4$ 1.6800, m.p. −27° ±0.5. *Anal.* Calcd. for $C_3H_2Cl_6$: Cl, 84.83; molecular refraction, 45.22. Found: Cl, 84.61; mol. refr., 45.23.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SOUTH CAROLINA
COLUMBIA, S. C. RECEIVED JANUARY 19, 1951

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[1] H. W. Davis and A. M. Whaley, THIS JOURNAL, **73**, 1382 (1951).

[2] H. J. Prins, *J. prakt. Chem.*, [2] **89**, 417–419 (1914).

Addendum to "A Spectrophotometric Investigation of the Interaction between Antimony(III) and -(V) in Hydrochloric Acid Solutions"

BY NORMAN DAVIDSON

Figure 3 of the above named article[1] exhibits values of the interaction constant, $k_1(\lambda)$, for mixed solutions of antimony(III) and -(V) in concentrated hydrochloric acid. Figure 4 gives the extinction coefficients of antimony(III) and -(V) at several hydrochloric acid concentrations (11–3.5 *F*). To aid other workers who wish to use the numerical values of these constants, we have prepared a tabular presentation of the data.[2]

It is noteworthy that Edwards, Voigt and Diehl[3] have presented data from which one can calculate values of $k_1(\lambda)$. These results are in general agreement with ours but give a more detailed picture of the effect of acidity on the interaction constant.

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[1] J. E. Whitney and N. Davidson, THIS JOURNAL, **71**, 3809 (1949).

[2] For detailed tables of data order Document 3039 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

[3] F. Edwards, A. Voigt and H. Diehl, *Proc. Iowa Acad. Sci.*, **55**, 247 (1948).

CONTRIBUTION NO. 1489 FROM THE
GATES AND CRELLIN LABORATORIES OF CHEMISTRY
PASADENA 4, CALIF. RECEIVED NOVEMBER 10, 1950

Reactions Involving Like-Charged Ions. II. The Rate of Disproportionation of Uranium(V) in Deuterium Oxide[1]

BY FREDERICK R. DUKE AND RICHARD C. PINKERTON

The kinetics of the disproportionation of uranium (V) ion in perchloric acid solutions has been studied by Heal[2a] and by Kern and Orleman.[2b] The conclusion from both investigations is that the reaction is second order in uranium(V) ion and first order in hydrogen ion. The reactions are formulated as

$$UO_2{}^+ + H^+ \overset{K}{\rightleftarrows} UOOH^{++} \qquad (1)$$

$$UO_2{}^+ + UOOH^{++} \xrightarrow{k} UO_2{}^{++} + UOOH^+ \qquad (2)$$

$$UOOH^+ \longrightarrow \text{stable U(IV) species} \qquad (3)$$

The rate-determining step (2) is noteworthy because reaction apparently occurs between two

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[1] Contribution No. 113 from the Institute for Atomic Research and Department of Chemistry, Iowa State College, Ames, Iowa. Work performed in the Ames Laboratory of the Atomic Energy Commission.

[2] (a) Heal, *Trans. Faraday Soc.*, **45**, 1 (1949); (b) Kern and Orleman, THIS JOURNAL, **71**, 2102 (1949).