trichlorobenzene to potassium nitrate and sulfur trioxide of one to eight to twenty for eighteen hours at 135°.

EXPERIMENTAL

1,3,5-Tribromo-2,4-dinitrobenzene. 1,3,5-Tribromobenzene (31.5 g., 0.1 mole) was added portionwise to a solution of 155 g. of commercial white fuming nitric acid, assay 95%, in 62 g. of concd. sulfuric acid at room temperature, allowing the autogenous temperature to rise no higher than 60°. Within 10 min. after the addition was complete the reaction mixture was cooled and the solid collected, washed, and dried. 1,3,5-Tribromo-2,4-dinitrobenzene was obtained in 98% yield, m.p. 191°; recrystallized, m.p. 192°.

Anal.[6] Calcd. for $C_6H\,Br_3N_2O_4$: C, 17.80; H, 0.25; Br, 59.22. Found: C, 17.91; H, 0.22; Br, 59.08.

1,3,5-Trichloro-2,4,6-trinitrobenzene. Potassium nitrate (40.4 g., 0.4 mole) was added to 266.5 ml. (1.0 mole) of 30% oleum at 65° with external cooling to maintain this temperature. The resulting mixture of potassium salts and nitration solution was then heated to 110°, becoming clear at 95°. 1,3,5-Trichlorobenzene (9.0 g., 0.005 mole) was added with stirring. The temperature was raised to 130–135° and held for 18 hr. After cooling to room temperature the viscous mixture was slowly poured onto three times its volume of flaked ice. The solid which separated was collected, washed free of acid, dried, and recrystallized from chloroform. 1,3,5-Trichloro-2,4,6-trinitrobenzene was obtained in 73% yield, m.p. 190°.

Anal. Calcd. for $C_6Cl_3N_3O_6$: C, 22.75; Cl, 33.65; N, 13.27. Found: C, 22.72; Cl, 33.62; N, 12.81.

1,3,5-Tribromo-2,4,6-trinitrobenzene. The above procedure was also used for nitration of 0.12 mole (48.5 g.) of 1,3,5-tribromo-2,4-dinitrobenzene employing instead 0.54 mole (54.5 g.) of potassium nitrate dissolved in 320 g. of 30% fuming sulfuric acid (1.2 moles of sulfur trioxide), heated at 125 ±1° for 9 hr. There was obtained after recrystallization from chloroform a 74% yield of 1,3,5-tribromo-2,4,6-trinitrobenzene, m.p. 297°, and 6% of 1,2,3,5-tetrabromo-4,6-dinitrobenzene, m.p. 232°.

Anal. Calcd. for $C_6Br_3N_3O_6$: C, 16.02; Br, 53.30; N, 9.34. Found: C, 16.30; Br, 53.45; N 9.16. Calcd. for $C_6Br_4N_2O_4$: C, 14.90; Br, 66.09; N, 5.79. Found: C, 15.02; Br, 65.81; N, 5.87.

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(6) Analyses by Oakwold Laboratories, Alexandria, Va.

Reactions of Dinitrogen Tetroxide with Alicyclic Sulfides

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The reactions of dinitrogen tetroxide with 1,4-dithiane and 1,3,5-trithiane have been investigated in connection with a general study of addition compounds of dinitrogen tetroxide with organic sulfides. Bell and Bennett[1] made a slight reference to the oxidation of 1,4-dithiane in ether solution by nitrous fumes to give predominantly 1,4-dithiane α-disulfoxide [*trans* isomer] and a little 1,4-dithiane β-disulfoxide [*cis* isomer], but they gave few experimental details. The results reported here shed some light on the intermediates formed in the course of the reaction. More especially, we would like to call attention to an unexpected isomerization of 1,4-dithiane α-disulfoxide to 1,4-dithiane monosulfone.

Dinitrogen tetroxide is known to oxidize alkyl sulfides to the corresponding sulfoxides.[2] Methyl phenyl sulfide has also been oxidized to methyl phenyl sulfoxide by means of dinitrogen tetroxide.[3] Addison and Sheldon[2] have shown also that dinitrogen tetroxide forms molecular addition compounds with alkyl sulfoxides. They suggested that the formation of such addition compounds may inhibit further oxidation of the sulfur by dinitrogen tetroxide and explain why the sulfoxides rather than sulfones are produced.

EXPERIMENTAL

1,4-Dithiane was prepared by the method of Masson,[4] which involves the reaction between potassium sulfide and ethylene dibromide in ethanol solution. The product which we obtained by this procedure melted at 111–112°[5] (lit.[4] 111°). Commercial nitrogen dioxide was dried by passing it through a glass tube filled with phosphorus (V) oxide and sand. Solid dinitrogen tetroxide (m.p. −11.5°, lit.,[6] m.p. −11.2°) was then collected in a trap cooled with Dry Ice and stored in a refrigerator until needed. Eastman White Label 1,3,5-trithiane (m.p. 216–218°, lit.[7] m.p. 216°) was used without further purification.

About 1 g. of 1,4-dithiane was dissolved in a few ml. of chloroform. A large excess of dinitrogen tetroxide was distilled into this solution and the entire mixture held at 0° for about 12 hr. At the end of this time, the system was composed of a deep blue solution with a white precipitate on the bottom of the container. The excess oxides of nitrogen were removed with an aspirator, at room temperature, and the white solid residue were collected and stored over Drierite in a desiccator. After this treatment, the white solid was odorless and decomposed at 225–230°. This same product was obtained by mixing 1,4-dithiane and dinitrogen tetroxide in the absence of a solvent. When this white, solid product (prepared by either method) was recrystallized from 95% ethanol, it produced a mixture of 1,4-dithiane α-disulfoxide (m.p. 263–265° dec., lit.[1] m.p. 263°) and 1,4-dithiane β-disulfoxide (m.p. 242–243° dec., lit.,[1] m.p. 235–250°). The isomers were separated by the fractional crystallization method described by Bell and Bennett.[1] The mixture was composed of 93–94% of the α-disulfoxide and 6–7% of the β-disulfoxide. The yield of the combined α- and β-disulfoxides was quantitative based upon the amount of 1,4-dithiane used.

Anal. Calcd. for $C_4H_8S_2O_2$ (α- or β-form): C, 31.6%; H, 5.3%. Found: for the α-isomer, C, 31.7%; H, 5.5%; for the β-isomer, C, 31.6%; H, 5.3%.[8]

Decomposition points of mixtures of these products with

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(1) E. Bell and G. Bennett, *J. Chem. Soc.*, 1798 (1927).

(2) C. Addison and C. Sheldon, *J. Chem. Soc.*, 2705 (1956).

(3) Von L. Horner and F. Hubenett, *Ann.*, **597**, 193 (1953).

(4) O. Masson, *J. Chem. Soc.*, **49**, 233 (1886).

(5) All melting and decomposition points are uncorrected.

(6) W. Giauque and J. Kemp, *J. Chem. Phys.*, **6**, 40 (1938).

(7) A. Hofmann, *Ber.*, **3**, 584 (1870).

(8) Analyses performed by Galbraith Microanalytical Laboratories, Knoxville, Tennessee.

authentic reference samples of the disulfoxides confirmed their identities. The reference samples of the disulfoxides were prepared by the oxidation of 1,4-dithiane in glacial acetic acid with hydrogen peroxide by the method of Bell and Bennett.[1]

Addition of excess dinitrogen tetroxide to some of the 1,4-dithiane α-disulfoxide, at 0° for 12 hr., followed by removal of the excess dinitrogen tetroxide, gave a white, solid, addition compound which decomposed at 225–230°. The composition of the addition product was variable, presumably because of incomplete reaction resulting from heterogeneity of the process. The pure addition compound is believed to have a 1:1 dinitrogen tetroxide to sulfoxide mole ratio. When this solid addition compound was heated to 150–190°, it was found that 1,4-dithiane monosulfone (m.p. 205–207°, lit.,[9,10] m.p. 200°, 203°) sublimed out of the solid.

Anal. Calcd. for $C_4H_8S_2O_2$: C, 31.6%; H, 5.3%. Found: C, 31.7%; H, 5.4%.[8]

The yield of the monosulfone was 39% of theory based upon the amount of 1,4-dithiane α-disulfoxide used.

When 1,4-dithiane β-disulfoxide was treated with dinitrogen tetroxide in the same manner as described for the α-disulfoxide, a white, solid, addition product was obtained. The composition of this product as obtained was variable. The substance began to decompose at 125°, and no sublimation product was observed.

Dinitrogen tetroxide reacts rapidly with 1,3,5-trithiane at 0° to cleave the trithiane ring and to yield sulfur-containing, volatile products and a yellow, solid residue which was insoluble in a variety of organic solvents.

The oxidation of 1,4-dithiane by dinitrogen tetroxide to 1,4-dithiane α-disulfoxide and a small amount of 1,4-dithiane β-disulfoxide was to be expected from earlier work.[1,2,3]

Because dinitrogen tetroxide could be added to pure 1,4-dithiane α-disulfoxide to produce the white solid which decomposed at 225–230°, and by simple recrystallization of this solid the 1,4-dithiane α-disulfoxide could be recovered, no molecular rearrangement occurs at room temperature when the disulfoxide unites with the dinitrogen tetroxide. Such behavior is characteristic of a rather stable Lewis acid-base type addition compound. The production of 1,4-dithiane monosulfone as a sublimation product of this white solid was unexpected, as no analogous reaction has previously been reported. The yield of the monosulfone is not higher than it is perhaps because heterogeneity of the reactions system prevents the completely quantitative formation of the dinitrogen tetroxide-α-sulfoxide addition compound. The failure of the addition compound between dinitrogen tetroxide and 1,4-dithiane β-disulfoxide to give the monosulfone upon sublimation is also interesting.

Because Lewis acids like aluminum chloride in benzene[11] and chlorine water[12] are known to cleave the 1,3,5-trithiane ring, it is not surprising that dinitrogen tetroxide produces a similar result.

The oxidation of 1,4-dithiane to 1,4-dithiane α-disulfoxide and 1,4-dithiane β-disulfoxide provides a method for the synthesis of these products which is superior to the hydrogen peroxide method. The dinitrogen tetroxide procedure gives a quantitative yield of the disulfoxides. A slight excess of hydrogen peroxide is likely to cause further oxidation to the trioxide of disulfone. Furthermore, the dinitrogen tetroxide procedure is faster and involves simple laboratory manipulations.

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(9) E. Fromm and B. Ungar, *Ber.*, **56**, 2286 (1923).

(10) E. Bell and G. Bennett, *J. Chem. Soc.*, 86 (1928).

(11) S. Lee and G. Dougherty, *J. Org. Chem.*, **4**, 48 (1939).

(12) S. Lee and G. Dougherty, *J. Org. Chem.*, **5**, 81 (1940).

Reduction of Bromonitro Compounds with Zinc. An Amplification

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In 1955 Klager[1] reported the reduction of methyl 4-nitro-4-chloropentanoate and of 1-bromo-1-nitrocyclohexane with zinc. Under the conditions employed, a white precipitate formed which could not be adequately characterized because of its insolubility. Analyses on the precipitate obtained directly from the reaction mixture gave variable results. Subsequent treatment of this precipitate with aqueous hydrochloric acid afforded the corresponding ketones, methyl 4-ketopentanoate and cyclohexanone. Klager postulated the structure of this precipitate to be a zinc complex of the ketoxime. The object of the present work was to elucidate the course of this reduction and, if possible, to shed some light on the structure of the precipitate.

It was decided to use 1-bromo-1-nitrocyclohexane as a model compound and to make one change in the reaction–substitution of ammonium bromide for ammonium chloride. In this way any possible ambiguity in the halogen analyses is eliminated. In Klager's work the variability of analysis of the precipitate indicated the possibility that this solid was a transient species and, while the appearance of the reaction mixture was unchanged after the initial solid formation, that actually a change in composition of the solid was occurring.

The reduction of 1-bromo-1-nitrocyclohexane (I) was then repeated. In this case however, the mixture of zinc, ammonium bromide, and 1-bromo-1-nitrocyclohexane in methanol was allowed to reflux for twelve hours instead of ten minutes. Two products were isolated, an insoluble white solid which proved to be inorganic, and nitrocyclohexane (II). On the basis of this information and that obtained by Klager, one may postulate a structure for the organic precipitate (III) isolated by Klager. This zinc salt of the nitroparaffin would be expected to undergo a Nef-type reaction[2] when treated with aqueous acid to yield cyclohexanone. And upon further refluxing in methanol the zinc salt might be expected to abstract a proton from methanol to form nitrocyclohexane.

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(1) K. Klager, *J. Org. Chem.*, **20**, 1348 (1955).

(2) H. B. Hass and E. F. Riley, *Chem. Revs.*, **32**, 373 (1943).