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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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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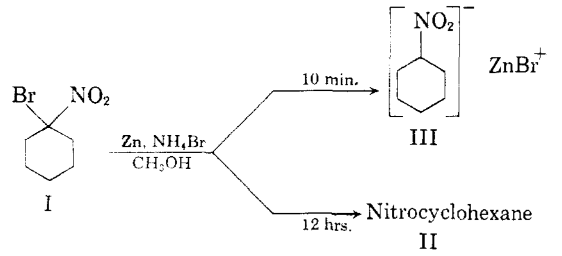

Reduction of 1-bromo-1-nitrocyclohexane (I) was then studied using an excess of zinc and ammonium bromide. In this case the only product isolated was cyclohexylamine hydrobromide (IV). When nitrocyclohexane is reduced under the same conditions cyclohexylamine hydrobromide is also formed. When, however, the reaction is stopped after only one hour, *N*-cyclohexylhydroxylamine (V) is formed as is reported in the literature.[2,3] The structure of the hydrobromide was confirmed by treatment with aqueous alkali and preparation of *N*-cyclohexylbenzamide (VI) from the resulting free amine.

EXPERIMENTAL

1-Bromo-1-nitrocyclohexane was prepared in 60% yield according to the procedure of Iffland and Criner.[4] Melting points and boiling points are uncorrected. Analyses by Mr. E. M. Hubbard and associates and by Galbraith Laboratories, Knoxville, Tenn.

Zinc reduction of 1-bromo-1-nitrocyclohexane (I), (*a*) *To nitrocyclohexane* (II). 1-Bromo-1-nitrocyclohexane (20.8 g., 0.10 mole) was mixed with 250 ml. of methanol and 17.6 g. (0.18 mole) of ammonium bromide, 11.6 g. of 90% zinc dust (0.16 mole) added and heating of the mixture begun. As in Klager's experiment, a white precipitate formed almost immediately with concomitant disappearance of the zinc dust. However, the reaction was not stopped at this point but allowed to reflux for 12 hr. further. At the end of the reaction a white solid was still present. After cooling, this solid was removed by filtration, washed with methanol, dried (Abderhalden), and analyzed.

Anal. Found: C, 0.70, 1.08; H, 2.46, 2.76; N, 9.35, 9.65; Br, 56.36, 56.53; Zn, 27.57, 27.87.

The filtrate was evaporated to small volume and the residue partitioned between ether and water. The ether solution was washed once with water, dried over sodium sulfate and evaporated to small volume. The residue was distilled yielding 5.7 g. (44.1%) of nitrocyclohexane, b.p. 16 mm. 88–90°, $n_D^{25°}$ 1.4612.

Anal. Calcd. for $C_6H_{11}NO_2$: C, 55.79; H, 8.58. Found: C, 56.09; H, 8.69.

(*b*) *To cyclohexylamine hydrobromide* (IV). To a mixture of 14.5 g. (0.07 mole) of 1-bromo-1-nitrocyclohexane and 34 g. (0.35 mole) of ammonium bromide in 400 ml. of methanol was added 23.3 g. (0.32 mole) of 90% zinc dust in small portions. After the initial reaction had subsided, the mixture was heated at reflux for 16 hr. The mixture was filtered and the solvent evaporated. The residue was dissolved in cold methanol and filtered. Crystallization from ether-methanol afforded 3.0 g. (24%) of cyclohexylamine hydrobromide. Evaporation of the mother liquor afforded another 5.0 g. of crude material. A benzamide prepared in the usual way from the free amine[5] had a melting point of 148.5–149.3°, mixed melting point with an authentic sample of *N*-cyclohexylbenzamide, 148.5–149.2°.

Reduction of nitrocyclohexane. (*a*) *To N-cyclohexylhydroxylamine* (V). To a solution of 12.9 g. (0.10 mole) of nitrocyclohexane in 250 ml. of methanol was added 39.2 g. (0.40 mole) of ammonium bromide and 21.8 g. (0.30 mole) of 90% zinc dust. After the initial exothermic reaction had subsided the mixture was heated at reflux for 1 hr. The mixture was then filtered and the filtrate evaporated to dryness. The residue was dissolved in ether-methanol, the solution was filtered and crystallization effected from methanol-hexane. The crystals were filtered, washed with hexane and air dried yielding 7.0 g. (60.8%) of *N*-cyclohexylhydroxylamine, m.p. 136.5–138° with sublimation (lit.,[6] m.p. 137°).

(*b*) *To cyclohexylamine hydrobromide* (IV). To a solution of 6.45 g. (0.05 mole) of nitrocyclohexane in 150 ml. of methanol was added 29.4 g. (0.30 mole) of ammonium bromide and 13.1 g. (0.18 mole) of 90% zinc dust. After the initial exothermic reaction had subsided, the mixture was heated at reflux for 16 hr. The mixture was then filtered and the filtrate evaporated to dryness. The residue was redissolved in cold methanol, the solution filtered, and ether added to the filtrate. The resulting crystals were filtered, washed with ether and air dried yielding 4.12 g. (46%) of cyclohexylamine hydrobromide. The benzamide prepared from a portion of this sample had a melting point of 148–149° and when mixed with authentic *N*-cyclohexylbenzamide, a melting point of 148.2–149.2°.

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Syntheses of 1-Benzylnaphthalenes

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The syntheses of substituted 1-benzylnaphthalenes may be effected by the action of benzylmagnesium chloride solution on the corresponding tetralones. The tertiary alcohols, which, are the initial reaction products, are easily dehydrated by distillation in vacuum during purification to olefins (IIa–g), 3,4-dihydro-1-benzylnaphthalenes and/or the double bond isomers, 1-benzal-1,2,3,4-tetrahydronaphthalenes (*cf.* Howell and Robertson[1]). These may be dehydrogenated with sulfur to the corresponding 1-benzylnaphthalenes (IIIa–g) as shown in the following scheme:

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[1] W. N. Howell and A. Robertson, *J. Chem. Soc.*, 587 (1936).