



its conjugate acid in solution. The latter conclusion is of only qualitative value, however, in view of the marked oxygen effect.

#### EXPERIMENTAL

*N,N*-Dimethyl-*m*-toluidine was obtained from Eastman Kodak Co. and was purified by drying with magnesium sulfate and distillation through a 25-cm. vacuum-jacketed Vigreux column under an atmosphere of nitrogen. The boiling point was 211–212° at 760-mm. pressure, and the refractive index,  $n_D^{20}$ , was 1.5490. The amine was stored in sealed ampoules after distillation.

Pyridine was of reagent grade and was used without further purification. Commercial dioxane was purified and stored in the method given by Fieser.<sup>6</sup> Perchloric acid was of reagent grade.

Aqueous formaldehyde solutions were prepared by hydrolysis of paraformaldehyde in dilute phosphoric acid with subsequent distillation.

*Analytical.* The analysis of formaldehyde was carried out according to the method of de Jong<sup>7</sup> by addition to the reaction mixture of an excess of KCN followed by back titration of excess cyanide with mercuric nitrate using diphenyl carbazone as indicator. Mercuric nitrate solutions were prepared using triply distilled mercury as a primary standard,<sup>8</sup> and KCN solutions were checked against these. The reaction mixtures were quenched prior to analysis by addition of an excess of base. Reaction vessels were simple volumetric flasks.

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(6) L. F. Fieser, *Experiments in Organic Chemistry*, D. C. Heath and Co., Boston, 1955, p. 285.

(7) J. I. de Jong, *Rec. trav. chim.*, **72**, 356 (1953).

(8) I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis*, Vol. 2, Interscience, New York, 1949, p. 338.

### Reactions of (1-Nitrocyclohexyl)methanol

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Although (1-nitrocyclohexyl)methanol has been known for some time,<sup>1</sup> it appears to have been subjected to only one reaction, namely, catalytic reduction to the corresponding amino alcohol.<sup>2–4</sup> This paucity of published information regarding its chemical properties prompted the present investigation.

Attempts to prepare (1-nitrocyclohexyl)methyl bromide from (1-nitrocyclohexyl)methanol by treatment in the usual manner with phosphorus tribromide were unsuccessful as were attempts to prepare (1-nitrocyclohexyl)methyl iodide from the *p*-toluenesulfonate derivative of the alcohol by

(1) O. von Schiekh, Ger. Pat. **870,850** (March 16, 1953).

(2) M. S. Newman and W. M. Edwards, *J. Am. Chem. Soc.*, **76**, 1840 (1954).

(3) W. B. Wheatley, *J. Am. Chem. Soc.*, **76**, 2832 (1954).

(4) W. E. Noland, J. F. Kneller, and D. E. Rice, *J. Org. Chem.*, **22**, 695 (1957).

treatment with iodide ions. Failure of these nucleophilic displacement reactions to take place can be accounted for on the basis of the neopentyl-type structure of this primary alcohol.<sup>5</sup> However, (1-nitrocyclohexyl)methyl bromide was prepared by reaction of the alcohol with phosphorus tribromide in the presence of quinoline according to the method of Sommer *et al.*,<sup>6</sup> for the successful conversion of neopentyl alcohol to the corresponding bromide.

Oxidation of (1-nitrocyclohexyl)methanol with nitrogen dioxide in chloroform under reaction conditions similar to those reported for converting primary alcohols to aldehydes<sup>7,8</sup> gave, instead, 1-nitrocyclohexanecarboxylic acid. The structure of this acid was established by the elemental and infrared analyses. The infrared spectrum has typical carboxyl absorption at 3.87 to 5.80 $\mu$  as well as nitro absorption at 6.45 and 7.42 $\mu$ .<sup>9</sup> The crystalline nitro acid was stable when stored at 0° but was unstable at room temperature, slowly decomposing with the evolution of gas. Attempts to obtain the nitro aldehyde by an Oppenauer oxidation of the nitro alcohol in the presence of either acetone or cyclohexanone were unsuccessful as were attempts to prepare the nitro aldehyde by the reaction of the nitro alcohol with *N*-bromosuccinimide in carbon tetrachloride.<sup>10</sup>

Attempts to prepare the symmetrical ether, bis[(1-nitrocyclohexyl)methyl] ether, from (1-nitrocyclohexyl)methanol by dehydration under acidic conditions (sulfuric acid or *p*-toluenesulfonyl chloride<sup>11</sup>) and by the classical Williamson synthesis utilizing the potassium alcoholate and the nitro bromide were unsuccessful.

#### EXPERIMENTAL

*(1-Nitrocyclohexyl)methanol.* This compound, prepared according to Newman and Edwards<sup>2</sup> by the base-catalyzed condensation of nitrocyclohexane with paraformaldehyde, was purified by distillation; b.p. 100–102° (1 mm.),  $n_D^{25}$  1.4846. This nitro alcohol is reported<sup>3</sup> to boil at 136–137° (5.5 mm.) with  $n_D^{25}$  1.4853.

*(1-Nitrocyclohexyl)methyl p-toluenesulfonate.* A solution of 120 g. (0.75 mole) of (1-nitrocyclohexyl)methanol, and 150 g. (0.79 mole) of *p*-toluenesulfonyl chloride in 600 ml. of pyridine was kept at 10° for 3 days. The mixture was poured into water, and the white solid which formed was washed with dilute hydrochloric acid followed by water and then recrystallized from ethanol to give 220 g. (94% yield) of (1-nitrocyclohexyl)methyl *p*-toluenesulfonate, m.p. 57–58°,

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(6) L. H. Sommer, H. D. Blankman, and P. C. Miller, *J. Am. Chem. Soc.*, **76**, 803 (1954).

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