[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF MISSOURI]

THE REACTION OF NITROPARAFFINS AND ALICYCLIC KETONES. I. THE PREPARATION OF NITROALKYLCYCLOHEXANOLS

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The purpose of the investigation was to prepare a series of α-nitroalkylcyclohexanols by the reaction of alicyclic ketones with nitroparaffins in the presence of sodium ethoxide or piperidine, and to reduce the nitro compounds to the corresponding amines with hydrogen and Raney nickel.

All efforts to prepare 1-nitromethyl-1-cyclohexanol from cyclohexanone and nitromethane by the procedure of Fraser and Kon (1), using their directions for the preparation of the sodium ethoxide catalyst, were fruitless. Hass and Riley (2) quoting Bourland reported similar negative results.

When the sodium ethoxide was prepared with a ratio of 1 g. of sodium to 11 cc. of absolute alcohol and used at once, it was possible to obtain 1-nitromethyl-1-cyclohexanol in 33% yield, if the reaction mixture was heated to 50° for an hour and a half.

The 3- and 4-methyl-1-cyclohexanone would not react with nitroethane or nitropropane when sodium ethoxide was used, but with piperidine as the catalyst, the corresponding α-nitroalkylcyclohexanols were obtained in yields of 5–13%. 2-Methyl-1-cyclohexanone did not react with nitroethane or nitropropane.

The reduction of 1-nitromethyl-1-cyclohexanol with hydrogen and Raney nickel at pressures ranging from 44 to 3000 p.s.i. was unsatisfactory; the product in each case was a mixture from which no pure 1-(aminomethyl)cyclohexanol or cyclohexanemethylamine could be isolated. The presence of methylamine, ammonia, and cyclohexanol among the reduction products indicated some hydrogenolysis.

Bis-(cyclohexanemethyl)amine, methylamine, and ammonia were isolated from the reduction of 1-nitromethyl-1-cyclohexene, and 4-methylcyclohexanemethylamine was obtained from 1-nitromethyl-4-methyl-1-cyclohexanol. Yields were poor.

These results were rather surprising, in view of the fact that several nitrocyclohexanes and nitrocyclohexenes were reduced with hydrogen and Raney nickel to the corresponding amines in good yield (3), and Lambert and Lowe (4) reported the reduction of 1,1-*bis*-(nitromethyl)cyclohexene to 1,1-*bis*-(aminomethyl)cyclohexane by this means.

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[1] Abstract of a portion of the Ph.D. dissertation of Floyd B. Erickson, August, 1949, and the Master's dissertation of Nina C. Knight, June, 1944.

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EXPERIMENTAL

Preparation of the sodium ethoxide catalyst. Clean, freshly cut sodium was added in small pieces to absolute alcohol in the ratio of 1 g. of sodium to 11 cc. of alcohol. This solution of sodium ethoxide was added at once to the nitro paraffin-cyclohexanone mixture.

1-(Nitromethyl)-1-cyclohexanol. A mixture of 30 cc. (0.29 mole) of cyclohexanone, 17 cc. (0.32 mole) of nitromethane, and 6 ml. of freshly prepared sodium ethoxide solution was heated at 50° for 1½ hours, and allowed to stand at room temperature for 36 hours. The solution was then acidified with dilute acetic acid and extracted with ether. The ether extract was washed with sodium bicarbonate solution, dried over Drierite, and fractionated; yield 14.5 g. (33.7%), b.p. 128–129° (17 mm.). If the mixture was not heated, the yield was 26%.

Anal. Calc'd for $C_7H_{13}NO_3$: C, 52.83; H, 8.17.
Found: C, 53.18; H, 8.22.

1-(Nitromethyl)-3-methyl-1-cyclohexanol was obtained similarly from 3-methylcyclohexanone. The mixture stood for 79 hours; yield, 29%, b.p. 98–102° (2 mm.).

Anal. Calc'd for $C_8H_{15}NO_3$: C, 55.45; H, 8.72.
Found: C, 55.72; H, 8.77.

1-(Nitromethyl)-4-methyl-1-cyclohexanol was obtained from 4-methylcyclohexanone. The mixture stood for one week; yield, 42%, b.p. 105–107° (4 mm.); m.p. 52–53°.

Anal. Calc'd for $C_8H_{15}NO_3$: C, 55.45; H, 8.72.
Found: C, 55.70; H, 9.00.

2-Methylcyclohexanone, cyclohexene-2-one-1, and 3-methylcyclohexene-2-one-1 did not react with nitromethane, nitroethane or 1-nitropropane with sodium ethoxide as the catalyst.

1-(α-Nitroethyl)-4-methyl-1-cyclohexanol. The procedure is essentially that of Fraser and Kon (1). 4-Methylcyclohexanone (67 cc., 0.45 mole), 45 cc. of nitroethane, and 4 cc. of piperidine were allowed to stand two weeks at room temperature. The nitroalkylcyclohexanol was isolated as already described; yield, 11.5 g. (13.7%), b.p. 125–128° (20 mm.), n_{D}^{20} 1.4565.

Anal. Calc'd for $C_9H_{17}NO_3$: C, 57.71; H, 9.09.
Found: C, 57.54; H, 9.13.

1-(α-Nitroethyl)-3-methyl-1-cyclohexanol was obtained from 3-methylcyclohexanone in 9.4% yield, b.p. 131–136° (20 mm.), n_{D}^{20} 1.4727.

Anal. Calc'd for $C_9H_{17}NO_3$: C, 57.71; H, 9.09.
Found: C, 57.41; H, 9.08.

1-(α-Nitropropyl)-4-methyl-1-cyclohexanol was obtained from 1-nitropropane and 4-methylcyclohexanone in 10.6% yield, b.p. 135–140° (21 mm.); n_{D}^{20} 1.4488.

Anal. Calc'd for $C_{10}H_{19}NO_3$: C, 59.70; H, 9.51.
Found: C, 59.74; H, 9.34.

1-(α-Nitropropyl)-3-methyl-1-cyclohexanol was obtained from 1-nitropropane and 3-methylcyclohexanone in 5% yield, b.p. 130–135° (20 mm.); n_{D}^{20} 1.4550.

Anal. Calc'd for $C_{10}H_{19}NO_3$: C, 59.70; H, 9.51.
Found: C, 59.75; H, 9.64.

With piperidine as the catalyst, 2-methylcyclohexanone reacted with neither nitroethane nor 1-nitropropane.

Reduction of 1-(nitromethyl)-1-cyclohexanol with hydrogen and Raney nickel catalyst. The nitro compound (38 g.) was dissolved in 100 cc. of anhydrous methanol and placed in the copper liner of a rocking steel autoclave with 3 g. of Raney nickel, at an initial hydrogen pressure of 3000 lbs. Absorption of hydrogen began at 80° and this temperature was maintained until the pressure was constant; the reduction was complete in five hours.

The catalyst was separated and the methyl alcohol was distilled. The residue was dissolved in ether and extracted with dilute hydrochloric acid. The aqueous acid layer and the ether layer were separated and processed by the usual procedures to yield, respectively, a mixture of high-boiling amines and cyclohexanol. The amine fraction was converted to the hydrochloride, but no one pure amine could be separated from the mixture. The amine hydrochlorides melted over a wide range and analyses indicated that the principal product was probably *bis*-(cyclohexanemethyl)amine. The methyl alcohol distillate was neutralized with conc'd hydrochloric acid and evaporated to dryness to yield ammonium chloride and methylamine hydrochloride. The latter melted at 125–126° and did not depress the melting point of an authentic sample. The cyclohexanol was identified by its *phenylurethan*, m.p. 82–83°.

The reduction was repeated with an initial hydrogen pressure of 44 lbs., but the product was an intractable mixture.

Reduction of 1-(nitromethyl)-1-cyclohexene. The nitro olefin (21.7 g.) dissolved in 100 cc. of methanol was reduced as described above. Only small amounts of pure compounds could be separated from the mixture of amines.

The amine fraction yielded *bis*-(cyclohexanemethyl)amine; methylamine and ammonia were isolated from the methanol distillate. The yield of crude *bis*-(cyclohexanemethyl)-amine hydrochloride was 45%.

The *bis*-(cyclohexanemethyl)amine distilled at 120–121° (2 mm.).

Anal. Calc'd for $C_{14}H_{27}N$: C, 80.38; H, 12.92.
Found: C, 80.23; H, 13.13.

Bis-(cyclohexanemethyl)amine hydrochloride crystallized from alcohol as plates, m.p. 264–265°.

Anal. Calc'd for $C_{14}H_{27}N \cdot HCl$: C, 68.4; H, 11.4.
Found: C, 68.32; H, 11.54.

The reduction was repeated in an ethanol-glacial acetic acid solution at an initial hydrogen pressure of 1490 p.s.i., but no pure compound could be isolated from the amine fraction.

Reduction of 1-(nitromethyl)-4-methyl-1-cyclohexanol. 4-Methylcyclohexanemethylamine hydrochloride, m.p. 266–267° d., was isolated from the amine fraction.

Anal. Calc'd for $C_8H_{17}N \cdot HCl$: C, 58.71; H, 11.01.
Found: C, 58.57; H, 11.08.

SUMMARY

Nitromethane will react with cyclohexanone, 3-methylcyclohexanone, and 4-methylcyclohexanone with sodium ethoxide as the catalyst to form the corresponding 1-nitromethyl-1-cyclohexanol.

Nitroethane and 1-nitropropane will react at room temperature with cyclohexanone, 3-methylcyclohexanone, and 4-methylcyclohexanone to form the corresponding 1-(α-nitroalkyl)-1-cyclohexanol in low yield.

A mixture of amines was obtained from the reduction of 1-nitromethyl-1-cyclohexanol with hydrogen and Raney nickel catalyst.

4-Methylcyclohexanemethylamine was obtained from the reduction of 1-nitromethyl-4-methyl-1-cyclohexanol.

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REFERENCES

(1) FRASER AND KON, *J. Chem. Soc.*, **137**, 604 (1934).
(2) HASS AND RILEY, *Chem. Revs.*, **32**, 384 (1943).
(3) NIGHTINGALE AND TWEEDIE, *J. Am. Chem. Soc.*, **66, 1968 (1944).**
(4) LAMBERT AND LOWE, *J. Chem. Soc.*, 1519 (1947).