[Contribution from the Chemistry Department, St. Olaf College]

THE REDUCTION OF ISOCYANATES AND ISOTHIOCYANATES WITH LITHIUM ALUMINUM HYDRIDE[1]

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The reaction of lithium aluminum hydride with compounds containing a carbonyl group adjacent to a nitrogen atom usually results in a hydrogenolysis of the carbon-oxygen bond (1–3). In a few instances, cleavage of the nitrogen-carbon bond has been observed (1, 4, 5) but this is not common. The purpose of this work was to determine which type of cleavage occurs in the reductions of isocyanates and isothiocyanates with the hydride. The formation of a methyl secondary amine was observed in every case, the reactions probably occurring according to the equations:

1. $4\ RNCO + 3\ LiAlH_4 \rightarrow LiAl[NR(CH_3)]_4 + 2\ LiAlO_2$
2. $4\ RNCS + 3\ LiAlH_4 \rightarrow LiAl[NR(CH_3)]_4 + 2\ LiAlS_2$
3. $LiAl[NR(CH_3)]_4 + 4\ H_2O \rightarrow 4\ RNH(CH_3) + LiAl(OH)_4$

The stoichiometry of equation 1 was established by reacting a known quantity of phenyl isocyanate with a standardized solution of lithium aluminum hydride. The amount of excess hydride was determined by measuring the volume of hydrogen given off on hydrolysis after the reduction was completed. The agreement with equation 1 was excellent, indicating an almost quantitative reduction.

Phenyl isocyanate, α-naphthyl isocyanate, ethyl isocyanate, phenyl isothiocyanate, and allyl isothiocyanate were reduced to the corresponding methyl amines in yields of 78–96%. The usual room temperature decomposition of the intermediate lithium aluminum salts with alkali, acid, or salt followed by ether extraction was not satisfactory. Hydrolysis with alkaline aqueous solutions at reflux temperature followed by steam-distillation or ether extraction gave high yields.

EXPERIMENTAL

Reduction of isocyanates and isothiocyanates. Freshly distilled isocyanate or isothiocyanate was weighed out in a separatory-funnel and diluted five-fold with an ether solvent. Diethyl ether was used in all experiments except with ethyl isocyanate where the solvent was diethylene glycol diethyl ether (Diethyl Carbitol). The solution was dropped slowly under nitrogen, with stirring, into a weighed amount of a standardized ether solution of lithium aluminum hydride. The reactions were smooth but vigorous and produced curdy white precipitates. The reaction mixture was refluxed for one-half to two hours. The excess hydride was decomposed with water and the reduction complex was hydrolyzed with 100 to 200 ml. of a 30% sodium hydroxide solution. The lithium aluminum salts usually did not break up until the ether was distilled off and the solution was boiled. The isolation of the individual products is given below.

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[1] Since this work was completed, a paper has appeared by Ried and Muller [*Chem. Ber.*, **85**, 4704 (1952)] describing the reduction of phenyl isocyanate and phenyl isothiocyanate. Our paper however presents a more detailed investigation of the reduction of these classes of compounds.

Phenyl isocyanate. An ether solution of 14.95 g. (0.126 mole) of phenyl isocyanate was added to 100 ml. of an ether solution containing 5.6 g. (0.147 mole) of lithium aluminum hydride. After alkaline hydrolysis and removal of ether the reaction mixture was refluxed, steam-distilled out of the reaction vessel, and extracted with ether. The ether solution was dried with calcium hydride and the crude product was obtained by evaporation of the ether. On redistilling, 11.52 g. (86%) of *N-methylaniline* was isolated, b.p. 86.5–87.5° at 17 mm., and n_D^{20} 1.5715; reported n_D^{20} 1.5714 (6). The tetranitro derivative melted at 127–127.5°; reported m.p. 128–129° (7).

1-Naphthyl isocyanate. An ether solution of 11.51 g. (0.068 mole) of 1-naphthyl isocyanate was added to 100 ml. of an ether solution containing 2.06 g. (0.054 mole) of lithium aluminum hydride. The white lithium aluminum complex dissolved completely on refluxing the solution after alkaline hydrolysis and removal of ether. The product was extracted with ether, dried over calcium hydride, and isolated as a crude product by evaporating off the ether. On redistilling, 9.7 g. (90%) of N-methyl-1-naphthylamine was isolated, b.p. 167.0–167.5° at 15 mm. and n_D^{20} 1.6722. The acetyl derivative was made, m.p. 94–95°; reported m.p. 93–94° (8).

Ethyl isocyanate. A Diethyl Carbitol solution of 9.2 g. (0.129 mole) of ethyl isocyanate was added to a solution of 4.55 g. (0.119 mole) of lithium aluminum hydride in 123 ml. of the Carbitol. Excess hydride was destroyed with 20 ml. of water. Solid sodium hydroxide, 100 g., was added and the solution cleared up completely on heating. The crude product was distilled directly out of the reaction vessel. After drying over potassium hydroxide, and redistilling, 5.92 g. (78%) of *methylethylamine*, b.p. 35–38°, was isolated. The *chloroplatinate* melted at 206–207.5°; reported m.p. 208° (9).

Phenyl isothiocyanate. The same reaction, isolation, and identification procedure was used here as for phenyl isocyanate. Phenyl isothiocyanate, 11.52 g. (0.085 mole), in ether was added to 100 ml. of an ether solution containing 5.2 g. (0.137 mole) of lithium aluminum hydride. The pure *N-methylaniline* weighed 8.77 g. (96%).

Allyl isothiocyanate. An ether solution of 9.70 g. (0.098 mole) of allyl isothiocyanate was added to 110 ml. of an ether solution containing 4.0 g. (0.105 mole) of lithium aluminum hydride. After alkaline hydrolysis the ether solvent was stripped off with all other materials up to a boiling point of 90°. The distillate was dried over calcium hydride and fractionated in a steel-helices packed column using toluene as a chaser. *Methylallylamine*, 5.64 g. (81%), b.p. 64–68°, was obtained. A *chloroplatinate* melted at 164–165°; reported m.p. 164° (10). A *picrate* melted at 113–113.5°.

Stoichiometry. This study was made using the usual vacuum line techniques. A sample, 3.104 g. (26.07 millimoles) of phenyl isocyanate was added *in vacuo* to a solution of 2.05 g. (53.9 millimoles) of lithium aluminum hydride in 37 g. of diethyl ether. The reaction mixture was stirred for two hours at room temperature. The excess hydride was decomposed with a dilute sulfuric acid solution. The hydrogen evolved, 3115 ml. S.T.P. (139 millimoles) was collected with a Toepler pump and measured in the vacuum line. This hydrogen is equivalent to 34.9 millimoles of hydride. Thus the molar ratio of isocyanate reacting with hydride was 4.09 to 3.00. This established ratio of reactants plus the approaching quantitative yields of N-methylaniline from both phenyl isocyanate and phenyl isothiocyanate in the larger scale reductions strongly suggests the stoichiometry shown for equations (1) and (2).

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SUMMARY

Alkyl and aryl isocyanates and isothiocyanates are reduced with lithium aluminum hydride to the corresponding methyl amines.

The stoichiometry of the reactions was indicated by a determined reaction

ratio of four moles of phenyl isocyanate to three moles of lithium aluminum hydride.

Compounds reduced were phenyl isocyanate, 1-naphthyl isocyanate, ethyl isocyanate, phenyl isothiocyanate, and allyl isothiocyanate.

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