

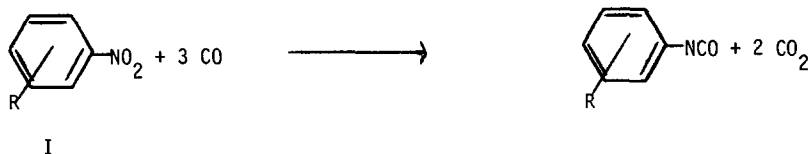
THE DIRECT CONVERSION OF AROMATIC NITRO COMPOUNDS
TO ISOCYANATES BY CARBON MONOXIDE

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Isocyanates have long been recognized for their broad utility in organic synthesis and in recent years they have achieved great commercial importance for the manufacture of polyurethanes. The conventional commercial synthesis of isocyanates consists of phosgenation of the corresponding amine (1). An interest in new routes to isocyanates led us to examine the following reaction:



Because of the significant advantages such a process would have over the phosgenation route, we have made a careful study of its feasibility. We now report the first direct synthesis of isocyanates from aromatic nitro compounds and carbon monoxide (2).

Previous workers have reported that the reaction of nitro compounds with hydrogen-free carbon monoxide yielded derivatives of azobenzene. Thus two different groups have reported the high temperature reaction of nitrobenzene with carbon monoxide to yield azobenzene as the principal product (3,4), while Kmiecik (5) has recently described the reductive coupling of nitro compounds by carbon monoxide in the presence of iron pentacarbonyl at 200° and 200 atm. Since completion of the work reported here, two patents (6) have appeared describing the formation of urethanes from nitro compounds, carbon monoxide, and alcohols in the presence of a metal carbonyl catalyst system.

We have found that the one-step conversion of aromatic nitro compounds to isocyanates can be realized by treating a solution of the nitro compound with carbon monoxide under pressure in the presence of a catalyst at temperatures below 200° and pressures as low as 200 atm. A sample procedure is as follows:

To a 250 ml glass-lined autoclave is charged 24.6 g (0.2 mole) nitrobenzene, 5.0 g 5% Rh/C (dried under N_2 at 350°), 0.4 g anhydrous ferric chloride, and 100 ml benzene. The autoclave is pressurized with CO (Air Products and Chemicals, Inc. C. P. grade) to 500 atm and the reaction mixture agitated at 190° for 5.5 hrs. After cooling, the autoclave is discharged under N_2 and the catalyst removed by filtration. The presence of phenyl isocyanate is shown by IR and VPC examination (100% conversion). Vacuum fractional distillation yields pure phenyl isocyanate, bp $57^\circ/15$ mm (8.3 g, 35% yield). An additional 6.2 g mixture of diphenylurea and 1,3,5-triphenylbiuret is obtained as a pot residue. The low material balance is due to mechanical problems, since the same material balance was obtained when the theoretical amount of phenyl isocyanate was subjected to the reaction conditions. No evidence for azobenzene, azoxybenzene, or any other product is obtained by VPC analysis.

Other nitro compounds which have been successfully converted to the corresponding isocyanates (7) include I where $R = \text{o-CH}_3$, p-CH_3 , m-Cl , m-CF_3 , and m-CN . The reactions have been conducted at pressures of 200-1350 atm and temperatures of 150° - 225° in a stainless steel, glass-lined or tantalum-lined autoclave. Benzene, chlorobenzene, cyclohexane, and 1,1,2-trichloro-1,2,2-trifluoroethane have been used as solvents. The catalyst system consists of a noble metal and a Lewis acid. The noble metal can be supported, unsupported, or in the form of a salt, oxide, or complex. Among the Lewis acid co-catalysts used successfully are ferric chloride, ferrous chloride, ferric bromide, aluminum chloride, aluminum bromide, stannic chloride, cupric chloride, and anhydrous hydrogen chloride. The highest yields have been obtained with palladium or rhodium on alumina or carbon with ferric chloride as co-catalyst.

Studies on the mechanism of this new reaction and some of the obvious extensions of this system will be reported in more detail at a later date.

References

1. For reviews of isocyanate preparations see, for example, R. G. Arnold, J. A. Nelson, and J. J. Verbanc, *Chem. Rev.*, 57, 47 (1957); C. V. Wilson, *Org. Chem. Bull.*, 35, 2 (1963).
2. This reaction is the subject of Netherlands Patent 6,513,844 (American Cyanamid Co.) June 29, 1966.
3. G. D. Buckley and N. H. Ray, *J. Chem. Soc.*, 1154 (1949).
4. F. R. Glaser and R. van Beneden, *Chem. Ing. Tech.*, 29, 512 (1947); *C. A.*, 51, 17023 (1947).
5. J. E. Kmiecik, *J. Org. Chem.*, 30, 2014 (1965).
6. British Patent 993,704 (to Imperial Chemical Industries, Ltd.), June 2, 1965.
Netherlands Patent 6,502,601 (to Imperial Chemical Industries, Ltd.), November 25, 1965
7. The products in each case were identified by IR and VPC analysis and by conversion to the corresponding diarylurea derivative. No effort was made to optimize conditions.