

Electrophilic Substitution. II*

Friedel-Crafts Type Nitration Using Acetone Cyanohydrin Nitrate

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Abstract

Nitration of activated aromatic systems has been studied by using acetone cyanohydrin nitrate with boron trifluoride etherate in catalytic amounts. Products of typical electrophilic nitration were formed under non-oxidizing conditions.

Although nitration of aromatics is a well studied reaction the conditions employed are usually strongly acidic. Nitric acid is used alone or as a solution in organic solvent or in strong acid such as sulfuric acid.^{1,2} Nitrations with mixed anhydrides of nitric acid are also well documented.² Relatively little attention has been paid to nitrations of the Friedel-Crafts type with nitrate esters. Olah *et al.*³⁻⁵ have recently reported the use of methyl nitrate in conjunction with boron trifluoride for the selective nitration of various methylbenzenes.[†]

Because acetone cyanohydrin nitrate (1-cyano-1-methylethyl nitrate) is more stable and more readily prepared⁷ than methyl nitrate we have investigated the system acetone cyanohydrin nitrate/boron trifluoride etherate for the nitration of some activated aromatics. In addition to this we have reduced the amount of boron trifluoride to catalytic quantities so that we obtain higher yields and cleaner products. The use of boron trifluoride etherate also provides a simpler and cheaper source of catalyst than the use of boron trifluoride gas. Table 1 summarizes the results. It will be noted that the product distribution is similar to that obtained with the more usual nitrating agents.

* Part I, *Aust. J. Chem.*, 1975, **28**, 385.

† Nitrate esters have been used⁴ in conjunction with acids and other Lewis acid catalysts. Acetone cyanohydrin nitrate shows enhanced reactivity compared to methyl nitrate for synthesis of phenyl-nitromethanes.⁶

¹ Ingold, C. K., 'Structure and Mechanism in Organic Chemistry' 2nd Edn (Cornell University Press: Ithaca, New York, 1969); Olah, G. A., and Kuhn, S. J., in 'Friedel-Crafts and Related Reactions' (Ed. G. A. Olah) Vol. 3, Part 2, Ch. 43 (John Wiley: New York 1969).

² Hoggett, H. G., Moodie, R. B., Penton, J. R., and Schofield, K., 'Nitration and Aromatic Reactivity' (Cambridge University Press: New York 1971).

³ Olah, G. A., and Lin, H. C., *Synthesis*, 1973, 488.

⁴ Olah, G. A., and Lin, H. C., *J. Am. Chem. Soc.*, 1974, **96**, 2892.

⁵ Olah, G. A., Lin, H. C., Olah, J. A., and Narang, S. C., *Proc. Nat. Acad. Sci. U.S.A.*, in press.

⁶ Emmons, W. D., and Freeman, J. P., *J. Am. Chem. Soc.*, 1955, **77**, 4391.

⁷ Emmons, W. D., and Freeman, J. P., *J. Am. Chem. Soc.*, 1955, **77**, 4387.

When the product from nitration of *p*-xylene was examined by gas chromatography the presence of trace amounts of *p*-tolualdehyde and 4,4'-dimethyl-1,2-diphenylethane was noted. These compounds are formed in the injection port of the gas chromatograph by pyrolysis of *p*-methylphenylnitromethane (see Part I). The present procedure did not produce any detectable amounts of dinitro compounds although, under similar reaction conditions, methyl nitrate/boron trifluoride etherate gave a 5% yield of an equimolar mixture of 2,5-dinitro- and 2,6-dinitro-*p*-xylene. *p*-Xylene forms these same products during nitration with acetyl nitrate even when there is excess hydrocarbon present. The dinitro compounds appear not to be formed by the further nitration of nitro-*p*-xylene.

Table 1. Nitration by acetone cyanohydrin nitrate/boron trifluoride etherate

Compound	Yield (%)	Relative yield (%)		
		2-Nitro	3-Nitro	4-Nitro
Toluene	77.6	59.8	4.5	35.7
<i>o</i> -Xylene	75.2		60.3	39.7
<i>m</i> -Xylene	78.0	15.3		84.7
<i>p</i> -Xylene	90.0	—	—	—
Mesitylene	74.1	—	—	—
Anisole	73.1	72.4		27.6

Olah⁴ has examined the mechanism of the methyl nitrate/boron trifluoride reaction and concluded that free nitronium ion is not involved. In the case of acetone cyanohydrin nitrate, nucleophilic attack by the aromatic hydrocarbon is assisted by the expulsion of cyanide ion.

Experimental

All solvents, alkylbenzenes and anisole were commercially available highest purity materials. *p*-Xylene was purified by partial freezing. Acetone cyanohydrin nitrate was prepared by the method of Emmons and Freeman.⁷ Methyl nitrate was prepared from methanol and nitric acid/sulfuric acid.⁸

General Procedure for Nitration

To a solution of the aromatic substrate (0.1 mol) in acetonitrile (10 ml) was added acetone cyanohydrin nitrate (0.05 mol) and freshly distilled boron trifluoride etherate (0.2 ml). The reaction mixture was stirred for 3 h at room temperature before workup. The products were analysed by g.l.c. before and after distillation under vacuum.

Gas chromatography was performed on a Varian 1740 gas chromatograph with a flame ionization detector with a Disc Instrument 252-A integrator and a 10 ft by 1/8 in. column packed with 10% Carbowax 20M on Chromosorb W HMDS 100–120 mesh.

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⁸ Black, A. P., and Babers, F. H., *Org. Synth.*, 1943, Coll. Vol. II, 412.