Aromatic Nitration with Potassium Nitrate or Nitric Acid and Boron Trifluoride Monohydrate[1]

George A. Olah,* Qi Wang, Xing-ya Li, Imre Bucsi

Donald P. and Katherine B. Loker Hydrocarbon Research Institute and the Department of Chemistry, University of Southern California, Los Angeles, California 90089-1661, USA

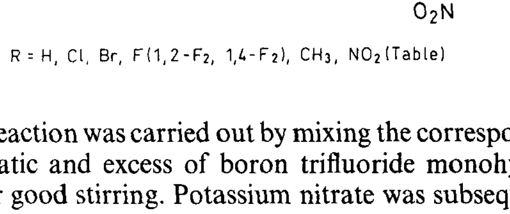
Received 18 October 1991; revised 31 March 1992

Potassium nitrate/boron trifluoride monohydrate and nitric acid/boron trifluoride monohydrate have been found to be efficient reagents for the nitration of aromatic compounds. Benzene and a series of substituted benzenes were nitrated with excellent yields.

Nitration of aromatics can be carried out by a variety of nitrating agents, primarily with nitric acid (or its derivatives) and metal nitrates.[2] While metal nitrates with bidentate nitrate ligands are extremely reactive and react with aromatics without catalysts, metal nitrates with monodentate nitrate ligands react only under Lewis acid or Brønsted acid catalysis.[2] Topchiev[3] first explored the nitration of aromatic hydrocarbons with metal nitrates in the presence of Lewis acids. The yields of the nitration were generally 30 % (based on the amount metal nitrate used). The heterogeneous nature of the reaction was considered in part responsible for the low yields.

We have developed[4] a homogeneous nitration system using silver nitrate/boron trifluoride in acetonitrile solution. The aromatics nitrated were generally relatively electron rich compounds. Silver can be recovered after reaction and recycled. There are also several reports of using inorganic nitrates in conjunction with trifluoroacetic acid,[5] polyphosphoric acid,[6] and sulfuric acid[7] to nitrate arenes. The yields in these reactions are usually low. For example, nitration of chlorobenzene with potassium nitrate/polyphosphoric acid gave only 39% of nitrated products.

Boron trifluoride monohydrate is a superacid, with acidity exceeding that of 100% sulfuric acid.[8] Catalytic use of this acid has so far been limited.[9-11] Based on our continued interest in superacids,[12] we have been investigating the application of boron trifluoride monohydrate as a relatively inexpensive acid catalyst system. We report now the study of nitration of aromatics by potassium nitrate or nitric acid and boron trifluoride monohydrate. These systems were found to be highly efficient new nitrating agents.



R = H, Cl, Br, F(1,2-F_2, 1,4-F_2), CH_3, NO_2 (Table)

The reaction was carried out by mixing the corresponding aromatic and excess of boron trifluoride monohydrate under good stirring. Potassium nitrate was subsequently added to the stirred mixture forming an emulsion. With more reactive aromatics, 2 or 5 equivalents of arene was used in relation to potassium nitrate. The reactions were usually carried out at ambient temperature, followed by aqueous quenching and usual workup giving the nitro products. Yields obtained, summarized in Table 1, are usually good to excellent. The yield of the reaction of deactivated aromatics can be improved by using excess nitrating agent. For example, while 81 % of 1,3-dinitrobenzene is obtained by nitrating excess nitrobenzene, quantitative nitration can be achieved with 3 equivalents of potassium nitrate in boron trifluoride monohydrate. However, no trinitrobenzene was obtained when the nitration of 1,3-dinitrobenzene was attempted under similar conditions. In the case of toluene, 14 % of dinitro compounds were also obtained even when 10 equivalents of toluene was used, indicative of a fast reaction with incomplete mixing.

As potassium nitrate in boron trifluoride monohydrate liberates nitric acid, we also carried out nitrations using nitric acid itself and boron trifluoride monohydrate. The results of nitration using nitric acid are comparable to those using potassium nitrate. (Table). Deactivated arenes such as nitrobenzene and 1,3,5-trifluorobenzene were nitrated in very high yields. In the case of toluene, dinitration again occurred, but only to a limited extent (5 %). The difference compared to potassium nitrate may be attributed to better mixing with nitric acid. The good reactivity of the studied new nitrating systems potassium nitrate/boron trifluoride monohydrate and nitric acid/boron trifluoride monohydrate is due to the high acidity of boron trifluoride monohydrate. Nitronium ion formation is facilitated by the ability of boron trifluoride monohydrate to bind an additional mole of water formed in the ionization of nitric acid. The nitronium ion may also be protosolvated[13] in the highly acidic medium.

All aromatics used were obtained from Aldrich, and used without further purification. BF_3 was obtained from Matheson Gas products. $BF_3 \cdot H_2O$ was prepared according to a reported procedure.[10] The authentic compounds of the products used for comparison except 2,4,6-trifluoronitrobenzene were purchased from Aldrich Chemical Company. 2,4,6-Trifluoronitrobenzene was obtained form PCR Incorporated, Florida.

NMR spectra were obtained on a Varian Associates Model VXR-200 NMR spectrometer. Mass spectra were obtained in a Finnigan Incos-50 GC-MS instrument. GC analyses were performed on a Varian (model 3700) gas chromatograph using a quartz column coated with DBWAX.

Nitration of Aromatics with Potassium Nitrate and Boron Trifluoride Monohydrate; General Procedure:

To a well stirred solution of $BF_3 \cdot H_2O$ (10 mL) and the aromatic compound (50 or 20 mmol) was added slowly KNO_3 (1.01 g, 10 mmol) over a period of 5 min. The mixture was then stirred for 2 h at r. t. followed by quenching with ice water. The quenched mixture was extracted with CH_2Cl_2 (3 × 30 mL), the combined organic extracts were washed with aq. 10% $NaHCO_3$ solution to remove any acid, dried ($MgSO_4$) and evaporated in a rotary evaporator. The product was further purified, if necessary, by either distillation or recrystallization and subjected to GCMS and NMR analyses (Table).

Table. Nitration of Aromatics with Potassium Nitrate or Nitric Acid and Boron Trifluoride Monohydrate

Substrate	Nitrating Agent[a]	Aromatics/ MNO_3 (mol ratio)	Product	Yield[b] (%)	Isomer Distribution (%)[c]			bp (°C)/Torr or mp (°C)	
					2-Nitro	3-Nitro	4-Nitro	found	reported[14]
benzene	A	5:1	nitrobenzene	88				86–88/15	210–211/760
	B	5:1		92					
toluene	A	10:1	2-, 3- and 4-nitrotoluene	83[d]	54	2	44	–	–
	B	10:1		93[e]	54	2	44		
chlorobenzene	A	5:1	2-chloro- and 4-chloronitrobenzene	91	30		70	–	–
	B	5:1		92	31		69		
bromobenzene	A	5:1	2-bromo- and 4-bromonitrobenzene	96	41		59	–	–
	B	5:1		95	37		63		
fluorobenzene	A	5:1	2-fluoro- and 4-fluoronitrobenzene	87	12[g]		88[g]	–	–
1,4-difluorobenzene	A	2:1	2,5-difluoronitrobenzene	82				86–88/15	206.5/760
	B	2:1		81					
1,2-difluorobenzene	A	2:1	3,4-difluoronitrobenzene	92				82–84/15	76–80/11
	B	2:1		88					
1,3,5-trifluorobenzene	A	2:1	2,4,6-trifluoronitrobenzene[h]	84				65–67/10	172/760
	B	2:1		82					
nitrobenzene	A	2:1	1,3-dinitrobenzene	81				87–88	88–89
	A	1:3		98					
	B	1:3		98					

[a] A = $KNO_3/BF_3 \cdot H_2O$, B = $HNO_3/BF_3 \cdot H_2O$.

[b] Yield of isolated products. All products were characterized by spectral data and comparison with authentic samples.

[c] Determined by GC.

[d] A sum of 14% of 2,4- and 2,6-dinitrotoluenes (75:25) were identified and estimated by GC with calibration.

[e] A sum of 5% of 2,4- and 2,6-dinitrotoluenes (79:21) were detected.

[f] Bp of the mixture of isomers obtained.

[g] Determined by ^{19}F NMR spectroscopy.

[h] MS: m/z (%) = 177 (31.1), 161 (4.2), 147 (56.7), 131 (21.6), 119 (55.6), 112 (4.2), 99 (9.2), 81 (100), 75 (17.5).
^{19}F NMR ($CDCl_3/CFCl_3$): $\delta = -99, -115$.

Nitration of Aromatics with Nitric Acid and Boron Trifluoride Monohydrate; General Procedure:

To a well stirred solution of $BF_3 \cdot H_2O$ (10 mL) and the aromatic compound (50 or 20 mmol) was added dropwise conc. HNO_3 (0.45 mL, 10 mmol) over a period of 5 min. The mixture was stirred for 2 h at r.t. followed by quenching with ice water. The quenched mixture was extracted with CH_2Cl_2 (3 × 30 mL), the combined organic extract was washed with aq. 10% $NaHCO_3$ solution to remove any acid, dried ($MgSO_4$) and evaporated in a rotary evaporator. The product was further purified, if necessary, by either distillation or recrystallization and subjected to GCMS and NMR analyses (Table).

Support of our work by the Office of Naval Research is gratefully acknowledged.

(1) Synthetic Methods and Reactions. 173. For Part 172, see: Olah, G.A.; Reddy, V.P.; Prakash, G.K.S. *Synthesis*, in press.

(2) Olah, G.A.; Malhotra, R.; Narang, S.C. *Nitration, Methods and Mechanism*; VCH Publishers, Inc.: New York, 1989.

(3) Topchiev, A.V. *Nitration of Hydrocarbons and Other Organic Compounds*; Pergamon Press: New York, 1959.

(4) Olah, G.A.; Fung, A.P.; Narang, S.C.; Olah, J.A. *J. Org. Chem.* **1981**, *46*, 3533.

(5) Crivello, J.V. *J. Org. Chem.* **1981**, *46*, 3056.

(6) Sastry, S.; Kudav, N.A. *Ind. J. Chem.* **1979**, *18B*, 198.

(7) Majumdar, M.P.; Kudav, N.A. *Ind. J. Chem.* **1976**, *14B*, 1012.

(8) Rochester, C.H. *Acidity Functions*; Academic Press: New York, 1970.
Farcasiu, D.; Ghenciu, A., *J. Catal.* **1992**, *134*, 126.

(9) For examples, see:
Yoneda, N.; Hasegawa, E.; Yoshida, H.; Aomura, K.; Ohtsuka, H. *Mem. Fac. Eng. Hokkaido Univ.* **1973**, *13*, 227; *Chem. Abstr.* **1973**, *79*, 146068.
Takai, H.; Okumura, Y. Imai, C. *Jpn. Kokai Tokkyo Koho* JP 6357537 (8857537); *Chem. Abstr.* **1989**, *110*, 195118.
Kolesnikov, I.M.; Mirgaleev, I.G.; Kruglyak, A. *Zh. Prikl. Khim. (Leingrad)* **1971**, *44*, 425; *Chem. Abstr.* **1971**, *74*, 125002.

(10) Larsen, J.W.; Chang, L.W. *J. Org. Chem.* **1979**, *44*, 1168.
Cheng, J.C.; Maioriello, J.; Larsen, J.W. *Energy & Fuels* **1989**, *3*, 321.

(11) For example, see: Jung, J.A.; Peress, J.; Gelgein, A.P. Eur Patent, 17441 (1980); *Chem. Abstr.* **1981**, *94*, 156336.

(12) Olah, G.A.; Prakash, G.K.S.; Sommer, J. *Superacid*, Wiley-Interscience: New York, 1985.

(13) Olah, G.A.; Prakash, G.K.S.; Lammertsma, K. *Research on Chemical Intermediate* **1989**, *12*, 141.

(14) PCR Incorporated 1988–1989 Research Chemical Catalog, P.O. Box 1466, Gainesville, Florida, 32602, p. 73.
"Catalog Handbook of Fine Chemicals 1990–1991". Aldrich Chemical Company, Milwaukee.