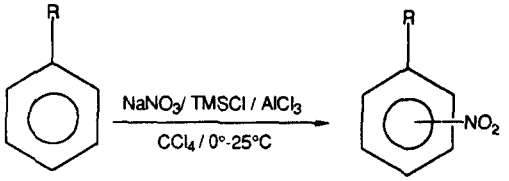
Aluminum Chloride Catalyzed Nitration of Aromatics with Sodium Nitrate/Chlorotrimethylsilane[1]

George A. Olah,* Pichika Ramaiah, Graham Sandford, Alexander Orlinkov, G.K. Surya Prakash*
Loker Hydrocarbon Research Institute and Department of Chemistry, University of California, Los Angeles, California 90089-1661, USA
Received 10 August 1993; revised 10 November 1993

A mixture of sodium nitrate and chlorotrimethylsilane in the presence of anhydrous aluminum trichloride is a convenient nitration system for aromatic compounds. Nitryl chloride is formed as an intermediate in the reactions.

The nitration of aromatics is well reviewed.[2] Nitration of arenes with metal nitrates in the presence of Lewis acids was reported by Topchiev.[3] This reaction, however, generally gives poor yields because of its heterogeneous nature. The chemistry of nitryl chloride has been extensively investigated.[4] It was applied to a variety of chemical transformations of aromatic and aliphatic compounds. Friedel–Crafts type nitration using nitryl chloride and aluminum trichloride was first reported[4a] by Price and Sears and studied more extensively by Kuhn and Olah.[2b] The aromatics nitrated were usually electron-rich compounds. Kuhn and Olah have also used[2b] for the nitration of some deactivated aromatics nitryl chloride/titanium tetrachloride in nitromethane solution. Nitryl chloride is prepared by oxidation of nitrosyl chloride with ozone[5] or reaction of chlorosulfuric acid with nitric acid.[4a] These methods are, however, somewhat inconvenient and potentially hazardous. A thorough search of the literature has revealed that preparation of nitryl chloride from chlorotrimethylsilane and sodium nitrate had not been reported. It was recently reported by Lee at al. that the reaction of chlorotrimethylsilane with sodium nitrate and nitrite generates nitryl and nitrosyl chloride, respectively.[6] However, they did not report the preparation, isolation and uses of nitryl chloride from the reaction between chlorotrimethylsilane and sodium nitrate. A mixture of chlorotrimethylsilane and sodium nitrite has been used for deoximation of aldoximes and ketoximes and for nonaqueous diazotization.[6]

We report now a convenient and simple method for nitration using in situ generated nitryl chloride in a one-step, $AlCl_3$ catalyzed reaction of aromatics with sodium nitrate and chlorotrimethylsilane.



R = H, Me, Br, Cl, F, CF_3, COOMe 62-97%

Chlorotrimethylsilane initially reacts with sodium nitrate to form trimethylsilyl nitrate ($TMSONO_2$)[7] which then reacts further with excess chlorotrimethylsilane to form in situ nitryl chloride. Trimethylsilyl nitrate was indeed isolated[8] when chlorotrimethylsilane was reacted with metal nitrates.

$$TMSCl + NaNO_3 \longrightarrow TMS\text{-}O\text{-}NO_2$$

$$TMS\text{-}O\text{-}NO_2 + TMSCl \longrightarrow Cl\text{-}NO_2 + TMS\text{-}O\text{-}TMS$$

Although $TMSONO_2$ itself can act as a nitrating agent under acidic conditions, it can easily decompose to NO_2 and $(TMS)_2O$. In the presence of excess TMSCl, nitryl chloride formation is preferred.

It was known from the literature[3] that sodium nitrate can react with aluminum trichloride to give the nitronium salt $NO_2^+ AlCl_4^-$, formed via intermediate nitryl chloride. We have now isolated nitryl chloride from the reaction between chlorotrimethylsilane and sodium nitrate. The formation of nitryl chloride takes about 3 hours at 0 °C. It could be trapped, for example, with methyl acrylate, giving at room temperature nearly quantitatively the addition compound.

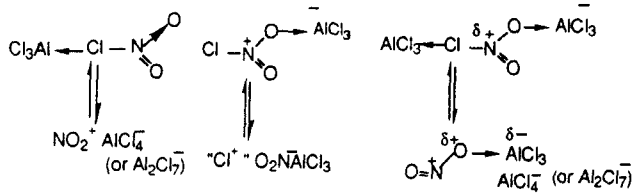
Nitryl chloride is activated by coordination with aluminum trichloride. It can either nitrate or chlorinate aromatic compounds depending how the N–Cl bond is polarized and cleaved. Nitryl chloride was found to be a

Table. Nitration of Aromatics with Nitryl Chloride and $AlCl_3$ in Carbon Tetrachloride

Substrate	Reaction Conditions temp. (°C)/time (h)	Yield[a] (%)	Isomer Distribution (%)			Product(s)[b]	bp (°C)/Torr or mp (°C)
			2-nitro	3-nitro	4-nitro		
benzene	0/2	97	–	–	–	*nitrobenzene*	210–211/760
toluene	0/1	90	42	3	55	2-, 3- and 4-nitrotoluene	110–112/2[c]
bromobenzene	0/3	93	45	–	55	2-bromo and 4-bromonitrobenzene	118/5[c]
chlorobenzene	0/2	88	35	–	65	2-chloro and 4-chloronitrobenzene	98–100/0.5[c]
fluorobenzene	0/4	86	16	–	84	2- and 4-fluorobenzene[d]	120/8[c]
trifluoromethylbenzene	r.t./5	82	10	88	2	2-, 3- and 4-trifluoromethylbenzene[d]	–
naphthalene	r.t./2	62	–	–	–	1-nitronaphthalene	60
methyl benzoate	r.t./6	78	7	93	–	*3-nitromethylbenzoate*	76–77

[a] Yield of isolated products.
[b] All products were identified by spectral data and compared with authentic samples.
[c] Mixture of isomers.
[d] Determined by ^{19}F NMR spectroscopy.

very reactive nitrating agent for aromatics, more powerful than dinitrogen pentoxide, when used with threefold excess of aluminum trichloride. The results obtained are summarized in the Table.



Benzene and toluene are nitrated in nearly quantitative yield at 0 °C. The isomer distribution of the nitration of toluene is similar to that of previously reported Friedel–Crafts nitration with an *o/p* ratio of 0.76.[2b] Reaction of naphthalene gave both 1-nitro- and 1-chloronaphthalene. 1-Nitronaphthalene was isolated in 62% yield. The reaction also proceeds well with deactivated aromatics. In these cases, such as methyl benzoate, however, more than 3 equiv of aluminum trichloride is necessary. Even under these conditions nitrobenzene and benzaldehyde are not satisfactorily nitrated, indicating that strong complexation of the polar substituent groups interfere with the activation of nitryl chloride. When fluorobenzene was reacted in acetonitrile, it gave only ring chlorinated products. However, in carbon tetrachloride an 86% yield of *o*- and *p*-nitrofluorobenzene was obtained.

Typical Procedure of Nitration:

Chlorotrimethylsilane (5.4 g, 50 mmol) was added dropwise to a heterogeneous suspension of $NaNO_3$ (1.87 g, 22 mmol), the aromatic compound (20 mmol) to be nitrated and powdered $AlCl_3$ (8.8 g, 66 mmol), stirred in anhydr. CCl_4 (50 mL) at ice-bath temperature for 2–3 h. The stirring was continued at r.t. to complete the reaction (see Table). The solvent and the byproduct hexamethyldisiloxane were then removed under reduced pressure and the residue was extracted with Et_2O (2 × 20 mL). The organic layer was washed with ice-cold aq sodium hydrogen carbonate (5%) (2 × 25 mL) until the washings were neutral. The organic layer was then further washed with brine and dried ($MgSO_4$). The residue obtained after removal of solvent under reduced pressure was distilled or recrystallized to furnish the products. GC/MS of the samples was compared with that of authentic samples. The yield is based on consumed aromatic compound.

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

(1) Synthetic Methods and Reactions. Part 186. For part 185, see: Olah, G.A.; Wang, Qi; Neyer, G. *Synthesis* **1994**, 276.

(2) (a) Olah, G.A.; Malhotra, R.; Narang, S.C.; *Nitration: Methods & Mechanisms*; VCH: New York, 1989.
(b) Kuhn, S.J.; Olah, G.A. *J. Am. Chem. Soc.* **1961**, *83*, 4564.

(3) Topchiev, A.V. *Nitration of Hydrocarbons and Other Organic Compounds*; Pergamon: New York and London, **1959**, p 299.

(4) (a) Sears, C.; Price, C.C. *J. Am. Chem. Soc.* **1953**, *75*, 3276.
(b) Goddard, D.R.; Collis, M.J. *J. Chem. Soc.* **1958**, 1952.
(c) Goddard, D.R. *J. Chem. Soc.* **1958**, 1955.
(d) Collis, M.J.; Gintz, F.P.; Goddard, D.R.; Hebdon, E.A.; Minkoff, G.J. *J. Chem. Soc.* **1958**, 438.
(e) Bachman, B.C.; Hokama, T. *J. Org. Chem.* **1960**, *25*, 178.
(f) Muller, E.; Padeken, H.G. *Chem. Ber.* **1966**, *99*, 2971.
(g) Schlubach, H.; Braun, A. *Liebigs Ann. Chem.* **1959**, *627*, 28.
(h) Shechter, H.; Conrad, F.; Daulton, A.L.; Kapan, R.B. *J. Am. Chem. Soc.*, **1952**, *74*, 3052.
(i) Shechter, H. *Rec. Chem. Prog.* **1964**, *25*, 55.
(j) Shin, C.; Yonezawa, Y.; Narukawa, H.; Najo, K.; Yoshimura, J. *Bull. Soc. Chim. Jpn.* **1972**, *45*, 3595.

(5) Schumacher, H.J.; Sprenger, G. *Z. Anorg. Chem.* **1929**, *182*, 139.

(6) (a) Lee, J.G.; Kwak, K.H.; Hwang, J.P. *Tetrahedron Lett.* **1990**, *31*, 6677.
(b) Lee, J.G.; Cha, H.T. *Tetrahedron Lett.* **1992**, *33*, 3167.

(7) (a) Schmidt, M.; Schmidbaur, H. *Angew. Chem.* **1959**, *71*, 220.
(b) Voronkov, M.G.; Roman, V.K.; Maletina, E.A. *Synthesis* **1982**, 277.
(c) Narang, S.C.; Ph.D. Thesis; Flinders University, Adelaide, South Australia, 4887.

(8) (a) Kimura, M.; Kajita, K.; Onoda, N.; Morosawa, S. *J. Org. Chem.* **1990**, *55*, 4887.
(b) Kimura, M. Jpn. Pat. 90174728 (1990); *Chem. Abstr.* **1990**, *113*, 190888.