Synthetic Methods and Reactions VIII[1]. Nitrofluorination of Alkenes

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We would like to report a convenient general method of nitrofluorination of alkenes. Although β-nitrofluoroalkanes are useful intermediates for the preparation of β-fluoroalkylamines, as well, via dehydrofluorination of β-nitroalkenes, nitrofluorination was until now scarcely studied[2,3]. Knunyants[2] and Titov[3] achieved *nitrofluorination* of some unbranched alkenes when nitrating them with nitric acid in anhydrous hydrogen fluoride solution. It is, however, usually inconvenient to use hydrogen fluoride as solvent, especially in the reaction of reactive, branched alkenes which readily polymerize and undergo other side reactions in the system.

The reaction of nitronium tetrafluoroborate with excess alkenes was used to initiate cationic polymerization in our preceeding work[4]. Smit and coworkers[5] reported the reaction of nitronium tetrafluoroborate (NO_2BF_4) with an equimolar amount of cyclohexene in acetonitrile/sulfur dioxide solution at −70°, which gave upon workup 40% of 3-nitrocyclohexene. We have found that *nitrofluorination* of alkenes can be carried out in 70% hydrogen fluoride/pyridine (pyridinium polyhydrogenfluoride) solution using nitronium tetrafluoroborate as nitrating agent under mild reaction conditions. To carry out the reaction, into a solution of nitronium tetrafluoroborate in 70% hydrogen fluoride/pyridine solution (in a polyethylene flask) is added the corresponding alkene. It was found that the reaction is applicable to a wide variety of alkenes and the corresponding nitrofluorinated products can be isolated in good yield. The data obtained are summarized in the Table. A typical example of the reaction is the nitrofluorination of cyclohexene.

1-Fluoro-2-nitrocyclohexane:
Into 70% hydrogen fluoride/pyridine solution (70 ml) maintained in a polyethylene flask at −70°, nitronium tetrafluoroborate (14 g, 0.1 mol) was dissolved. Then, cyclohexene (4.2 g, 0.05 mol) was added to the stirred solution in ten minutes, at −70°. After that the reaction mixture was warmed up to 0° during ten minutes, and then the reaction was continued for one hour at 0°. The reaction mixture was poured into ice-water and extracted with ether. The ether layer was washed with water, aqueous $NaHCO_3$, and water and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was distilled, and 1-fluoro-2-nitrocyclohexane was obtained; yield: 5.1 g, 70%; b.p. 50°/30 torr.
^{1}H-N.M.R. $\delta = 5.07$ (broad d, $J_{HF} = 50$ Hz, $—C\underline{H}F$), 4.83 (m, $—C\underline{H}NO_2$), 3.3–1.13 ppm (broad m, other ring protons).
^{19}F-N.M.R. $\phi = 187.5$ (m).

All yields reported in the Table are of isolated products, characterized by N.M.R. and I.R. spectroscopy and by correct elemental analyses.

Table. Nitrofluorination of Alkenes[a]

Alkene	Reaction Temperature	Reaction Time (hr)	Product	Yield (%)	b.p.
Ethene[b]	20°	1	1-Fluoro-2-nitroethane	60	60°/15 torr[c]
Propene[b]	20°	1	2-Fluoro-1-nitropropane	65	33°/4 torr[c]
2-Butene[b]	20°	0.5	2-Fluoro-3-nitrobutane	60	37°/4 torr
1-Hexene	0°	1	2-Fluoro-1-nitrohexane	65	45°/3 torr
Chloroethene[b]	20°	2	1-Chloro-1-fluoro-2-nitroethane	40	41°/10 torr[c]
1,1-Dichloroethene	20°	2	1,1-Dichloro-1-fluoro-2-nitroethane	45	48°/10 torr[c]
Cyclohexene	0°	1	1-Fluoro-2-nitrocyclohexane	70	50°/3 torr
	20°	0.3		80	

[a] Reactions were carried out with nitronium tetrafluoroborate in 70% HF/30% pyridine solution.
[b] The reaction was carried out in a pressure bomb.
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