818. *Aromatic Substitution. Part II.* Nitration of Aromatic Compounds with Nitronium Tetrafluoroborate and Other Stable Nitronium Salts.*

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A new method of nitration of aromatic compounds has been developed by use of stable nitronium salts, first, with nitronium tetrafluoroborate.

MOISSAN and LEBEAU,[1] using material which probably contained some nitryl fluoride,[2] obtained evidence of formation of nitrobenzene from benzene. Using pure nitryl fluoride, now readily prepared, Hetherington and Robinson[3] have surveyed its nitrating properties towards organic compounds, alone or dissolved in an inert liquid. Of the organic compounds used some were inert (aliphatic hydrocarbons and deactivated aromatic compounds such as nitrobenzene), some were nitrated normally, and some were destroyed (*e.g.*, aniline, which rapidly gave tars). As expected, those undergoing nitration gave the same nitro-compounds as result from the use of mixed acids. Hetherington and Robinson postulated that the nitration is due to the nitronium ion NO_2^+, formed by dissociation of the nitryl fluoride in the liquid undergoing treatment. During investigation of the mechanism of nitration Goddard, Hughes, and Ingold[4] isolated some nitronium salts, $[NO_2^+]X^-$, *e.g.*, the perchlorate, hydrogen disulphate, neutral disulphate, neutral nitronium trisulphate, and fluorosulphonate. The ionic constitutions assigned were spectroscopically established. The compounds isolated were not sufficiently stable for use as nitrating agents and as yet nothing has been published about the kinetics of reaction of these compounds. Woolf and Emeléus[5] treated oxy-salts with bromine trifluoride and nitrogen oxide, and so obtained a number of nitronium salts, such as the tetrafluoroborate, hexafluorostannate, hexafluorophosphate, hexafluoroarsenate, hexafluoroantimonate, and tetrafluoroaurate, but did not refer to their use as nitrating agents. So nothing has been known hitherto about the use of stable nitronium salts as nitrating agents.

We have found that some nitronium salts, first, nitronium tetrafluoroborate,[6] and then the hexafluorosilicate, hexafluoroantimonate, and hexafluorophosphate, are useful nitrating agents.

Of the stable nitronium salts it seems that the tetrafluoroborate is the most convenient. It can be prepared by Aynsley, Hetherington, and Robinson's method[2] from nitryl fluoride and boron trifluoride, or without the use of elementary fluorine by Schmeisser and Elischer's method,[7] by the reaction of dinitrogen pentoxide with hydrogen fluoride and boron trifluoride in nitromethane. Nitronium tetrafluoroborate, which is a white crystalline compound, is stable in the absence of moisture and is adaptable as a nitrating agent for common use. For instance, with it we have nitrated the compounds listed in the Table, with the yields stated. For the experimental methods see the Experimental section. In the case of nitrogen-containing compounds such as diethyl- and dimethyl-aniline or pyridine the basic nitrogen atom reacts first with the nitronium salt., and isolation of nitrated compounds is complicated.

Nitronium hexafluorosilicate, hexafluoroantimonate, and hexafluorophosphate behave similarly as nitrating agents (see Table), but because of the greater difficulty of preparing them are less important.

Nitration with nitronium tetrafluoroborate follows the general scheme :

$$ArH + NO_2^+BF_4^- \longrightarrow Ar{\cdot}NO_2 + HF + BF_3$$

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* Part I, *Chem. Ber.*, 1956, **89**, 866.

[1] Moissan and Lebeau, *Compt. rend.*, 1905, **140**, 1573, 1621.

[2] Aynsley, Hetherington, and Robinson, *J.*, 1954, 1119.

[3] Hetherington and Robinson, *J.*, 1954, 3512.

[4] Goddard, Hughes, and Ingold, *J.*, 1950, 2559.

[5] Woolf and Emeléus, *J.*, 1950, 1050.

[6] Oláh and Kuhn, *Chem. and Ind.*, 1956, 98.

[7] Schmeisser and Elischer, *Z. Naturforsch.*, 1952, **7b**, 583; G. P. 918,506/1955.

The salt-like character of nitronium tetrafluoroborate was proved by our electric conductivity measurements. Nitronium tetrafluoroborate has a specific conductivity (κ) in 0·02% nitromethane solution of $0{\cdot}75 \times 10^{-4}\ \Omega^{-1}$ cm.$^{-1}$; the solvent, nitromethane, has $\kappa = 3{\cdot}18 \times 10^{-6}\ \Omega^{-1}$ cm.$^{-1}$; thus the specific conductivity of the pure electrolyte is $0{\cdot}72 \times 10^{-4}\Omega^{-1}$cm.$^{-1}$. In 0·2% solution, nitronium fluoroborate has $\kappa = 6{\cdot}3 \times 10^{-4}\ \Omega^{-1}$ cm.$^{-1}$; the pure electrolyte has $0{\cdot}68 \times 10^{-3}\ \Omega^{-1}$ cm.$^{-1}$.

Compound nitrated	Yield (%) of mononitro-product	Method
	By use of NO_2BF_4	
Benzene	87	A
Toluene	88	A
Nitrobenzene	85·5	B
Fluorobenzene	82	A
Chlorobenzene	77	A
Bromobenzene	90·5	A
Iodobenzene	88	A
o-Dichlorobenzene	91·5	A
Naphthalene	93	C
Anthracene	98	C
Thiophen	91·5	C
Furan	14 *	C

Compound nitrated	Yield (%) of mononitro-product	Method
	By use of $(NO_2)_2SiF_6$	
Benzene	93	A
Nitrobenzene	82	B
	By use of NO_2SbF_6	
Benzene	84	A
	By use of NO_2PF_6	
Benzene	90	A

* With much decomp.

The new nitration by the stable nitronium salts gives a direct preparative proof of the electrophilic character of nitration through the NO_2^+ cation. It also made it possible to examine the kinetics of nitration in very advantageous circumstances: results of the kinetic investigations will be reported later.

EXPERIMENTAL

Nitronium Tetrafluoroborate (cf. Schmeisser and Elischer [7]).—To a solution of dinitrogen pentoxide (108 g., 1 mole) in nitromethane (150 g.) at −20° is added anhydrous hydrogen fluoride (20 g., 1·0 mole). The solution is then saturated with boron trifluoride. Nitronium tetrafluoroborate separates and is collected and dried *in vacuo* over phosphoric oxide (yield, 125 g., 94%) (Found: F, 56·8; N, 10·5. Calc. for O_2NF_4B: F, 57·1; N, 10·5%). The salt is stable in absence of moisture but is hygroscopic (with subsequent decomposition) and when heated decomposes at *ca.* 170° without melting or subliming.

Nitronium Hexafluorosilicate (cf. Schmeisser and Elischer [7]).—Replacing the boron trifluoride in the above preparation by silicon fluoride (52 g., 0·5 mole) gives the hexafluorosilicate (107·6 g., 92%) (Found: F, 48·3; N, 12·2; Si, 11·7. Calc. for $O_4N_2F_6Si$: F, 48·7; N, 12·0; Si, 12·0%).

Nitronium hexafluoroantimonate (Found: F, 39·9; N, 5·2; Sb, 42·6. Calc. for O_2NF_6Sb: F, 40·4; N, 5·0; Sb, 43·2%) and hexafluorophosphate (Found: F, 59·3; N, 7·1; P, 16·0. Calc. for O_2NF_6P: F, 59·7; N, 7·3; P, 16·2%) were prepared as described by Woolf and Emeléus.[5]

Nitrations.—*Method A.* To 0·2 mole of the dry aromatic compound was added, in small portions with ice–salt cooling and stirring, 0·1 mole of the nitronium salt. A very exothermic reaction took place. Then the mixture was allowed to warm to room temperature and kept for some hours. The mixture was washed free from acid, dried ($CaCl_2$), and distilled.

Method B. In the case of deactivated aromatic rings the reaction was effected at 20—130°.

Method C. For solid or highly sensitive ring systems, the reaction was effected in 5—10% ether solution.

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