

Nitryl Fluoride as a Nitrating Agent.

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Nitryl fluoride is shown to be an active nitrating agent, and its behaviour with typical organic compounds is described. It is somewhat selective in its attack, leaving such deactivated aromatic compounds as nitrobenzene, benzoic acid, and benzaldehyde largely unchanged. With substances of intermediate reactivity nitration is rapid and smooth: the products are those which would result from the use of mixed acids. Highly reactive materials like aniline, anisole, and quinoline are converted immediately into intractable tars. These results are compared with those obtained when nitryl chloride is used.

MOISSAN and LEBEAU (*Compt. rend.*, 1905, **140**, 1573, 1621), using material which probably contained some nitryl fluoride (see *J.*, 1954, 1119), obtained evidence of formation of ethyl nitrate from alcohol, of nitrobenzene from benzene, and of unspecified reactions with ether, chloroform, and turpentine. Using pure nitryl fluoride, now readily prepared, we have made a general survey of its nitrating properties by treating organic compounds, either alone or dissolved in an inert liquid. The materials and Pyrex vessels employed were dry (but not intensively dried) and the experiments were carried out without exposure to air. The results are recorded in a Table which gives, for convenience of comparison, the products obtained by Price and Sears (*J. Amer. Chem. Soc.*, 1953, **75**, 3276) in their experiments with nitryl chloride.

With nitryl fluoride.

Aliphatic compound		Product	
Ethyl alcohol		Ethyl nitrate, acetaldehyde, acetic acid	
<i>n</i> -Pentane		No reaction	
Chloroform		No reaction	
Carbon tetrachloride		No reaction	
Carbon disulphide		Very little reaction	
Aromatic compound		Solvent	Product
Benzene	—		Nitrobenzene (65%), <i>m</i> -dinitrobenzene (<5%)
Toluene	—		2 : 4-Dinitrotoluene (55%)
Bromobenzene	—		<i>p</i> - (60%) and <i>o</i> -Nitrobromobenzene (trace)
Nitrobenzene	—		<i>m</i> -Dinitrobenzene (trace)
Benzaldehyde	—		Benzoic acid (trace)
Phenol	CS ₂		<i>p</i> - (trace) and <i>o</i> -Nitrophenol (trace)
Naphthalene	C ₅ H ₁₂		1-Nitronaphthalene (35%)
Anthracene	CHCl ₃		9-Nitroanthracene
Salicylic acid	PhNO ₂		5-Nitrosalicylic acid
Benzoic acid	CS ₂		No reaction

(*m*-Cresol, anisole, diphenyl ether, aniline, furan, and quinoline gave tars.)

With nitryl chloride.

	Product (without solvent)	Solvent	Catalyst	Product (with solvent and catalyst)
Benzene	Nitrobenzene (27—35%)	HF	HF	Nitrobenzene (70%)
Benzene	—	CS ₂	AlCl ₃	Nitrobenzene (89%)
Toluene	—	"	"	<i>o</i> - (47%) and <i>p</i> -Nitrotoluene (24%)
Bromobenzene	—	"	"	<i>o</i> - (8%) and <i>p</i> -Nitrobromobenzene (67%)
Nitrobenzene ...	—	HF	BF ₃	No reaction
Benzaldehyde ...	—	CS ₂	AlCl ₃	No reaction
Phenol	—	"	"	<i>o</i> - (trace) and <i>p</i> -Nitrophenol (trace)
Naphthalene ...	—	"	"	1-Nitronaphthalene (31%)
Salicylic acid ...	—	PhNO ₂	AlCl ₃	5-Nitrosalicylic acid (10%)
Benzoic acid ...	—	CS ₂	AlCl ₃	No reaction

The behaviour of the organic compounds used falls into three patterns: (*a*) the inert, comprising aliphatic hydrocarbons and deactivated aromatic compounds such as nitro-

benzene; (b) the normally nitrated; (c) the destroyed, comprising highly reactive aromatic materials, such as aniline, which rapidly gave tar. As was expected, those undergoing nitration gave the same nitro-compounds as result from the use of mixed acids. We believe that the nitration is due to the nitronium ion, NO_2^+ , formed by dissociation of the nitryl fluoride in the liquid undergoing treatment. As may be seen from the Table, the products are qualitatively similar in character to those produced when nitryl chloride is employed. Unfortunately, only one quantitative comparison can be made, namely, in the reactions with benzene, where clearly the yield from nitryl chloride when used without a catalyst is about half that obtained with the fluoride. Other materials, *e.g.*, toluene, bromobenzene, and naphthalene, show more nitration with nitryl fluoride than with the chloride even when the latter is used with a catalyst. This suggests that nitryl fluoride stands higher than nitryl chloride in the series of nitrating agents of the type $\text{X}\cdot\text{NO}_2$, in which the nitrating power increases with the electron-accepting quality of X (see Gillespie and Millen, *Quart. Reviews*, 1948, 2, 278).

Pyridine does not fall into any of the behaviour patterns mentioned above since, besides the volatile 3-nitropyridine which distils forward, there is left in the reaction vessel a viscous brown liquid. This undoubtedly contains fluorine and sets to a gum, on the surface of which appear white crystals. According to the analytical evidence these crystals and the polymer are very similar material, and are probably a hydrofluoride of 3-nitropyridine. Both substances react immediately with water to form an orange-brown precipitate which dissolves in acetone to give a clear orange solution. The solid is 2 : 6-dihydroxy-3-nitropyridine. This shows that water not only hydroxylates the two substances but also removes fluorine from them.

EXPERIMENTAL

Preparation of Nitryl Fluoride.—This was prepared, as previously described (*J.*, 1954, 1119), by passing a stream of fluorine (about 4 g./hr.) diluted with nitrogen (1 : 1 by vol.) over well-dried sodium nitrite. The nitryl fluoride was fractionated in a vacuum to free it from fluorine and nitrogen peroxide and stored in a bulb fitted with a "break-seal," whence it could be obtained after attaching the bulb to the rest of the apparatus.

Treatment of the Organic Compounds.—This was done in a Pyrex all-glass train, carrying a number of traps, which before use was carefully dried. When the organic material was a liquid, it was treated, in lots of about 5 c.c., by bubbling nitryl fluoride vapour through it; when a solid or a too reactive liquid, the compound was dissolved in an inert solvent such as *n*-pentane, carbon disulphide, chloroform, or nitrobenzene. Usually the reaction was very exothermic and to moderate its vigour the trap was cooled in ice. The treatment took only a few minutes to complete, after which the apparatus was flushed out with nitrogen to remove the excess of nitryl fluoride together with any hydrogen fluoride retained by the organic product; this was subsequently purified by such conventional means as fractionation, steam-distillation, and crystallisation.

Individual Reactions.—*Ethyl alcohol*: reaction was very vigorous, the alcohol boiling with the heat of reaction. Some alcohol-ethyl nitrate azeotropic mixture (b. p. 71.85°) distilled forward and was collected in the next trap. Other products were acetaldehyde and acetic acid from the oxidation of the alcohol.

n-Pentane, chloroform, and carbon tetrachloride: the liquids became yellow but, on distillation, the original liquid was recovered unchanged. The colour was caused by the release of nitrogen dioxide.

Carbon disulphide: in contradistinction to the behaviour with nitryl chloride, there appeared to be some action, too little, however, to justify investigation.

Benzene: a very exothermic reaction began at room temperature; the benzene boiled even when surrounded by ice, and became deep yellow. Fractionation yielded nitrobenzene (b. p. 210°; 65%) and *m*-dinitrobenzene (m. p. 89°; <5%).

Toluene: a very exothermic reaction began at room temperature and deposited a yellow solid from a yellow solution. Recrystallised from ether the solid proved to be 2 : 4-dinitrotoluene (Found: C, 46.1; H, 3.4; N, 15.7. Calc. for $\text{C}_7\text{H}_8\text{O}_4\text{N}_2$: C, 46.2; H, 3.3; N, 15.7%), m. p. 69° (yield 55%).

Naphthalene: treatment in *n*-pentane gave a yellow solid. Unchanged naphthalene was

leached out with *n*-pentane, and the nitro-compound, recrystallised from chloroform, was 1-nitronaphthalene (m. p. 61°; dark red solution with concentrated sulphuric acid; yield 30—40%).

Anthracene: treatment in chloroform solution caused a mildly exothermic reaction. The solution became brown and a precipitate was formed which, recrystallised from alcohol, proved to be 9-nitroanthracene (15%) (Found: C, 74.6; H, 3.5; N, 5.9. Calc. for $C_{14}H_9O_2N$: C, 75.3; H, 4.0; N, 6.3%).

Bromobenzene: reaction was so vigorous that reactants had to be cooled; a yellow solid was deposited which crystallised from alcohol as very pale yellow crystals (67%), m. p. 126°, of *p*-bromonitrobenzene (Found: C, 35.6; H, 2.4; N, 7.0. Calc. for $C_6H_4O_2NBr$: C, 35.6; H, 2.0; N, 6.9%). In addition a trace of solid, m. p. 40°, probably *o*-bromonitrobenzene was recovered.

Phenol: despite its being dissolved in carbon disulphide there was a tendency for the material to form tar and even to catch fire. The yellow product was separated by steam-distillation into two fractions which gave qualitative evidence of *o*- and *p*-nitrophenol, severally.

m-Cresol, anisole, diphenyl ether, and aniline: with all these substances there was a great chance of inflammation and, even when moderated by dilution and cooling, the reaction produced tars.

Salicylic acid: treatment in nitrobenzene gave a reddish-brown liquid and a pale yellow solid, m. p. 230°, was deposited which qualitative tests showed to be 5-nitrosalicylic acid.

Benzoic acid: treated in carbon disulphide, this showed no evidence of reaction.

Nitrobenzene: there was no reaction in the cold, but evidently some on warming since, on cooling, a few white flakes appeared which were probably *m*-dinitrobenzene.

Benzaldehyde: there was no nitration, but a little oxidation to benzoic acid.

Pyridine: except with very good cooling, the reaction was violently exothermic. A yellow solid (material A) condensed in the second trap and a reddish-brown viscous liquid which did not smell of pyridine remained in the reaction vessel (material B). Material A was 3-nitropyridine (10%), m. p. 40° (lit., 41°) (Found: C, 47.6; H, 4.0; N, 21.8. Calc. for $C_5H_4O_2N_2$: C, 48.4; H, 3.2; N, 22.6%).

Material B was a polymer which frothed badly when warmed in a vacuum and could not be distilled. In a desiccator it set to an orange-brown solid, on the surface of which a small growth of white crystals appeared. Both the polymer and the crystals contained fluorine and the three analyses, (i) and (ii) of the polymer and (iii) of the crystals, show a relationship [Found: (i) C, 41.3; H, 4.35; N, 11.0; (ii) C, 41.5; H, 4.1; N, 13.2; (iii) C, 39.1; H, 3.85; N, 11.3%] but are not readily fitted to any recognisable compound though not far from a hydro-fluoride of 3-nitropyridine (Calc. for $C_5H_5O_2NF$: C, 46.2; H, 3.9; N, 10.8%). When added to water, both the polymer and the crystals yield an orange-brown solid and a colourless solution. The solid, washed with water, light petroleum, and ether, and dried in a vacuum, was a pale orange-brown powder which melted with decomposition at 300°, and was soluble in acetone and in alkali to a yellow solution. The analysis left little doubt that it was 2:6-dihydroxy-3-nitropyridine (Found: C, 38.3; H, 2.5; N, 18.2. Calc. for $C_5H_4O_4N_2$: C, 38.5; H, 2.6; N, 18.0%).

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