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The Ozone-Mediated Reaction of Nonactivated Arenes with Nitrogen Oxides(1)

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In the presence of ozone and appropriate catalyst, nitrogen oxides (NO, N_2O_3,and NO_2) exhibit strong nitrating ability, converting nonactivated arenes into the corresponding nitro derivatives in good to moderate yields.

Lower nitrogen oxides are quite inactive toward nonactivated arenes at room temperature or below. Under forced conditions they form a complicated mixture of products in low yields arising from substitution, addition, oxidation and coupling. However, we wish to report herein that nitrogen oxides such as NO, N_2O_3,and NO_2 act as a powerful nitrating agent for aromatic systems in the presence of ozone and appropriate catalyst.

When a stream of ozonized oxygen or air was passed into a solution of an arene and NO_2 in dry inert solvent in the presence or absence of an appropriate catalyst (such as silver oxide, molecular sieves or dimethyl disulfide) under ice-salt cooling, the substrate was rapidly nitrated to afford the corresponding mononitro derivatives in 24-99% yields (Table 1). In contrast to ordinary reactions of nitrogen oxides with arenes, neither side-chain substitution nor addition was observed. The reaction is clean and appears to be electrophilic in nature, as judged from the isomer distribution of products.(1)

$$\mathrm{ArH} \xrightarrow[\mathrm{CH_2Cl_2,\ acid\ catalyst,\ below\ 0\ ^{\circ}C}]{\mathrm{NO_2/O_3}} \mathrm{ArNO_2}$$

The reaction was better carried out in the presence of excess nitrogen oxides, where the efficiency of the nitration considerably depended on a combination of substrate, solvent and acid catalyst employed. Dichloromethane and tetrachloroethylene were the solvent of choice. In chloroform the reaction was often very slow. When the reaction time was extended further, polynitro compounds were formed. Thus toluene was first converted into a mixture of three isomeric nitrotoluenes (*o:m:p*=50-57:3-6:40-44)(2) which, on further reaction, gave a mixture of dinitrotoluenes mainly composed of 2,4- and 2,6-dinitro isomers,(3) the former being predominant.

Reaction of naphthalene went rapidly to completion at - 10 °C, giving a mixture of 1- and 2-nitronaphthalenes and isomeric dinitronaphthalenes in a ratio of 84:2:14.(4) A similar treatment of 1-nitronaphthalene gave 1,5- and 1,8-dinitronaphthalenes and trinitronaphthalenes in a ratio of 22:60:18.(5)

The reaction between NO_2 and ozone is known to produce N_2O_5 and NO_3.(6,7) However, the comparative experiment revealed that the active species in situ generated from a combination of NO_2 and ozone under our conditions was more reactive toward nonactivated arenes than N_2O_5 itself. Thus the mechanism of this attractive nitration is not clear at present.

Recently, the interactions between nitrogen oxides and ozone have been of wide concern because of their relation to environmental problems such as ozone depletion and air pollution. However, no attempts have hitherto been made to apply them for organic synthesis. We would like to emphasize here a potential of the present non-acid methodology as a promising substitute in future for the classical, yet currently ongoing nitration process based on nitric acid/sulfuric acid.

Table 1. Nitration of arenes with NO_2/O_3[a]

Arene	Yield/%	Percent isomer			*ortho/para*
		ortho	*meta*	*para*	
Benzene	3.2	—	—	—	—
	24[b]	—	—	—	—
Toluene	51 (85)[c,d]	57	2	41	1.39
	76[b]	57	3	40	1.43
	99[e]	55	3	42	1.31
Ethylbenzene	79 (96)[c]	44	3	53	0.83
Isopropylbenzene	95	23	4	73	0.32
t-Butylbenzene	99	13	6	81	0.16
Chlorobenzene	61 (97)[c]	46	1	53	0.87
Benzoic acid	62 (91)[c]	7	91	2	3.5

a) All reactions were carried out in dichloromethane at - 10 °C for 3 h using an ozone generator (Nippon Ozone, type ON-1-2) and products were analyzed by LC and GC-MS. Yields based on arenes are not optimized.
b) Molecular Sieves 4 A (40 w/w%) was used as a catalyst.
c) Numerals in parentheses refer to yields based on unrecovered substrates.
d) Dinitro derivatives were obtained in 5% yield.
e) Silver oxide (9 mol%) was used as a catalyst.

References

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