Notes

The Formation of Aromatic Ethers from *p*-Nitrofluorobenzene

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In the course of an investigation on the oxidation of alcoholates with *p*-nitrofluorobenzene it was observed[1] that the fluorine atom is remarkably labile and reacts readily with alkaline solution of the alcohols or phenols with nearly quantitative formation of ethers. We now find that this substitution of *p*-nitrofluorobenzene for *p*-nitrochlorobenzene in the older method for the production of aromatic ethers results in a more rapid reaction and usually also a better yield. In addition some of the substituted diphenyl ethers can be obtained easily from phenolic compounds and *p*-nitrofluorobenzene which are produced from *p*-nitrochlorobenzene only with the greatest difficulty. Only rarely is the use of a catalyst necessary. Even with the nitrophenols, where Raiford and Colbert[2] found *p*-nitrochlorobenzene to produce almost no yields of the dinitrodiphenyl ethers, *p*-nitrofluorobenzene gives 70–80% of the theoretical amount.

Holleman and Beekmann[3] reported the ease with which 2,4-dinitrofluorobenzene reacts with sodium methylate to give 2,4-dinitroanisole, but in fluorobenzene itself they found the fluorine atom to be more firmly held to the benzene nucleus than chlorine. In 2-nitro-4-chlorofluorobenzene Swartz found the fluorine atom more easily replaced than chlorine.[4]

Experimental.—The production of ethers from *p*-nitrofluorobenzene is accomplished by three general methods as illustrated in the three following typical experiments.

4-Nitroanisole.—To a cooled solution of 3 g. of potassium hydroxide in 20 cc. of warm methyl alcohol was added 7 g. (0.05 mole) of *p*-nitrofluorobenzene and the mixture shaken. The immediate exothermic reaction was complete in about ten minutes, whereupon the mixture was poured into water and the 4-nitroanisole separated and crystallized from ligroin (b. p. 90–110°); yield 7 g. or 93%.

Ethyl, *n*-propyl, isopropyl, isoamyl, benzyl and phenylethyl alcohols and ethylene glycol behave[5] in the same manner and produce equally good yields of the ethers.

4-Nitrodiphenyl Ether.—To a cooled solution of 3 g. of potassium hydroxide in 15 g. of molten phenol was added 7 g. (0.05 mole) of *p*-nitrofluorobenzene and the mixture heated in an oil-bath at 150–160° for thirty minutes. The mixture was then poured into a dilute sodium hydroxide solution and the solid 4-nitrodiphenyl ether collected on a filter. It was recrystallized from alcohol or ligroin; yield 10 g. or 92%.

By a similar procedure equally good yields of the corresponding substituted diphenyl ethers were obtained by replacing the phenol with one of the three cresols, guiacol, hydroquinone monomethyl ether, *p*-chlorophenol, *o*-iodophenol, *p*-phenylphenol, *p*-*tert*-amylphenol and acetyl-*p*-aminophenol.

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(1) Continuation of the work of Dains, Suter and Kenyon. Dains and Suter, This Journal, **50**, 2733 (1928); Dains and Kenyon, *ibid.*, **53**, 2357 (1931).

(2) Raiford and Colbert, This Journal, **48**, 2660 (1926).

(3) Holleman and Beekmann, *Rec. trav. chim.*, **23**, 249 and 254 (1904).

(4) Swartz, *Rec. trav. chim.*, **35**, 147 (1915).

(5) The ether obtained here is the mono-4-nitrophenyl ether of ethylene glycol.

4,4′-Dinitrodiphenyl Ether.—Nine grams (0.05 mole) of the dry potassium salt of *p*-nitrophenol was heated with 20 g. (13-g. excess) of *p*-nitrofluorobenzene and 0.2 g. of copper powder at 200° for one hour. The excess of *p*-nitrofluorobenzene was recovered by distillation in steam and the crude 4,4′-dinitrodiphenyl ether crystallized from ligroin; yield 11 g. or 85%.

The dry potassium salts of *m*-nitrophenol, salicylic aldehyde, *p*-hydroxybenzaldehyde and *p*-hydroxybenzoic acid, when substituted for the dry potassium salt of *p*-nitrophenol in the above procedure, produce approximately the same yields of the corresponding ethers.

The dry potassium salt of *o*-nitrophenol, however, gives only 30% of the theoretical amount.

Analyses.—Since some of the ethers prepared above are not recorded in the literature, their melting points and analyses are here reported.

ANALYSES

Ether	M. p., °C.	Nitrogen, % Calcd.	Found	
p-Nitrophenyl isopropyl ($C_9H_{11}O_3N$)	B. p. 276–277 at 738 mm.	7.73	7.70	
p-Nitrophenyl phenylethyl ($C_{14}H_{13}O_3N$)	56–57	5.76	5.80	
p-Nitrophenyl *m*-tolyl ($C_{13}H_{11}O_3N$)	63	6.11	6.12	
p-Nitrophenyl *o*-iodophenyl ($C_{12}H_8O_3NI$)	105	4.11	4.20	
p-Nitrophenyl *p*-phenylphenyl ($C_{18}H_{13}O_3N$)	120	4.81	4.85	4.89
p-Nitrophenyl *p*-*tert*-amylphenyl ($C_{17}H_{19}O_3N$)	60	4.92	4.95	4.99
p-Nitrophenyl *p*-acetaminophenyl ($C_{14}H_{12}O_4N_2$)	153	10.30	10.30	
p-Nitrophenyl *m*-nitrophenyl ($C_{12}H_8O_5N_2$)	123	10.77	10.84	10.87
2-(*p*-Nitrophenoxy)-benzaldehyde ($C_{13}H_9O_4N$)	112	5.76	5.83	5.96

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The Preparation of Vinyl Iodide

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Vinyl iodide is the one vinyl halide suitable for study because of its comparatively high boiling point and the absence of any marked polymerizing tendency. An improved method for the preparation of vinyl iodide was used whereby the time of preparation was reduced and the yield increased from 18 to 35%.[1]

Ethylene diiodide was prepared by passing a rapid current of ethylene through a number of flasks in series containing iodine dissolved in 80% alcohol in presence of a large excess of solid iodine. It was found advantageous to carry out this operation in the illumination supplied by a 500-watt lamp; 500 g. of iodine gave approximately 300 g. of product after the customary purification.

Vinyl Iodide.—To 282 g. (1 mole) of ethylene diiodide was added 334 cc. of 3 *N* sodium ethoxide. The distillate was collected at a temperature of

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(1) Baumann, *Ann.*, **163**, 319 (1872).