Notes

The Formation of Aromatic Ethers from *p*-Nitrofluorobenzene

By Morgan J. Rarick, R. Q. Brewster and F. B. Dains

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

BY JOHN SPENCE

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).

−30 to −50°. Distillation was continued with heating until no further separation of halide was observed on addition of a saturated solution of sodium chloride. Crude vinyl iodide was thus separated, washed with dilute sodium bisulfite solution, with water and finally dried over calcium chloride. On redistillation practically all the product passed over at a temperature of 56–56.5°. Approximately 50 g. was obtained. The refractivity was determined. Owing to the ease of oxidation of vinyl iodide the observations were made in an atmosphere of nitrogen.

SPECIFIC GRAVITY 2.037 (20°)

Line	Index of refraction	Molecular refraction (found)	Molecular refraction (calcd.)
Hydrogen (α)	1.53232	23.365	23.546
Sodium (D)	1.53845	23.651	23.769
Hydrogen (β)	1.55186	24.153	24.209
Hydrogen (γ)	1.56468	24.495	24.706

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The Mechanism of the Reduction of Sulfonyl Halides by Phosphorus Tribromide

BY A. H. KOHLHASE[1]

In a recent paper, Hunter and Sorenson[2] have stated that "previous work[3] has shown that sulfonyl chlorides are not reduced by phosphorus tribromide." This is in error as Kohlhase showed (Table I and Experiment XI) that 3-nitro-6-methylbenzenesulfonyl chloride was reduced readily and in good yield to the corresponding disulfide. It is true that sulfonyl chlorides were reduced far less *readily* than the corresponding bromides.

Kohlhase had concluded that the thiols formed in two instances of the reduction of sulfonyl derivatives by phosphorus tribromide, resulted as follows

$$\mathrm{RSSR} + \mathrm{PBr_3} \rightleftharpoons \mathrm{(RS)_2{\cdot}PBr_3}$$
$$\mathrm{(RS)_2{\cdot}PBr_3} + 4\mathrm{H_2O} \longrightarrow 2\mathrm{RSH} + 3\mathrm{HBr} + \mathrm{H_3PO_4}$$

Hunter and Sorenson concluded that the mechanism is

$$\mathrm{RSO_2Br} \xrightarrow{\mathrm{PBr_3}} \mathrm{RSBr} \xrightarrow{\mathrm{PBr_3}} \mathrm{RSPBr_4} \xrightarrow{4\mathrm{H_2O}} 2\mathrm{RSH} + 4\mathrm{HBr} + 2\mathrm{H_3PO_4}$$

This interpretation seems rather convincing but Kohlhase[3] showed that phenyl 3,5-dinitrobenzenethiosulfonate, treated with phosphorus tribromide and then with ether and water, gave a very good yield of 3,5-di-

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(1) Present address, Whipple, Arizona.

(2) Hunter and Sorenson, THIS JOURNAL, **54**, 3368 (1932).

(3) Kohlhase, *ibid.*, **54**, 2441 (1932).

nitrothiophenol. Here the intermediate formation of a sulfur bromide is hardly possible and the mechanism originally proposed by Kohlhase seems the only one available. It is quite probable that in these reductions of all RSO_2X derivatives by phosphorus tribromide, *both* mechanisms may be operative, the relative speeds depending on conditions and on the nature of R and X, although the mechanism of Hunter and Sorenson is undoubtedly the chief one in *most* cases where a thiol is produced.

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Notes on the Thompson–Oakdale Method for the Determination of Halogen in Organic Compounds

BY J. J. THOMPSON AND U. O. OAKDALE

The Thompson–Oakdale method[1] for the determination of halogen has been used with excellent results in hundreds of instances in our laboratories. However, the fact is not always recognized that the alkaline solution of the halide contains a considerable amount of sodium sulfite and consequently erroneous results may be obtained in the gravimetric estimation of the halogen due to the fact that the precipitated silver halide is apt to be contaminated, possibly with silver sulfide formed by decomposition of silver sulfite. This difficulty may be obviated in the following manner. The alkaline solution to which sodium arsenite has been added in accordance with the original directions is poured into a beaker, cooled thoroughly and after the addition of about 5 cc. of superoxol or perhydrol, to oxidize the alkaline sulfite to sulfate, the mixture is stirred and boiled for a few minutes. The solution is then cooled, acidified with nitric acid and the halide precipitated in the usual manner.

In view of our observations on the use of this method by students it seems necessary to emphasize the fact that *all* of the halogen, especially in the case of iodine, cannot be driven through the condenser into the alkaline solution unless the mixture in the Kjeldahl flask is boiled in such a manner that a continuous stream of steam passes through the apparatus for a short time.

The potassium persulfate used must always be tested for perchlorate since many commercial brands of persulfate contain this impurity. Potassium persulfate, free from perchlorate, is now available commercially (Mallinckrodt Chemical Works).

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[1] Thompson and Oakdale, THIS JOURNAL, **52**, 1195 (1930).

1-Propyl-2-iodoacetylene

BY THOMAS H. VAUGHN

When the densities and indices of refraction of the alkyl iodoacetylenes are plotted against molecular weight it becomes apparent that the values for these constants reported for propyl iodoacetylene by Grignard and Perrichon [*Ann. chim.*, **5**, 5–36 (1926)] are seriously in error.

This compound has been prepared in this Laboratory in 77% yield by the action of iodine on pentinylmagnesium bromide according to the procedure outlined by Grignard and Perrichon and has been found to possess the following properties: b. p. 67.0–67.5° at 35 mm.; 75–77° at 51 mm.; γ_{25} 34.22 dynes/cm. (maximum bubble pressure method); [P], obs., 283.3; calcd., 281.3; n^{25}_{D} 1.52231, n^{10}_{D} 1.5310; d_{25} 1.6557; MR'_D calcd., 36.54; obs., 35.73. These values for the index of refraction and density lie on their curves as determined from the other members of the series.

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COMMUNICATIONS TO THE EDITOR

HYDROGENOLYSIS OF ALCOHOLS TO HYDROCARBONS

Sir:

Recently we have found a method for the preparation of certain hydrocarbons which were not readily available. The reaction involved is the hydrogenolysis of a primary alcohol according to the equation $RCH_2OH + 2H_2 = RH + CH_4 + H_2O$. The reaction proceeded smoothly with duodecanol-1, tetradecanol-1, octadecanol-1 and 3-cyclohexylpropanol-1, from which were obtained *n*-undecane [b. p. 189–190° (740 mm.), n^{25}_{D} 1.4164], *n*-tridecane [b. p. 84–85° (3 mm.), n^{25}_{D} 1.4250, m. p. −7–8°], *n*-heptadecane [b. p. 290–292° (738 mm.), n^{25}_{D} 1.4360, m. p. 20–21°], and ethylcyclohexane [b. p. 127–128° (738 mm.), n^{25}_{D} 1.4310]. Similarly the diprimary glycol, decanediol-1,10, by the removal of both carbinol groups was converted into *n*-octane [b. p. 121–123° (742 mm.), n^{25}_{D} 1.3975].

Hydrogenolysis was accomplished by subjecting 40 to 50 g. of the alcohol or glycol for about five hours to the action of hydrogen (100 to 200 atmospheres) at 250° over a nickel catalyst. The reaction proceeded almost quantitatively and no product other than the indicated hydrocarbon was found in any case. In some experiments a small amount of the original alcohol or glycol was recovered. [The catalyst and apparatus have