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AROMATIC FLUORO DERIVATIVES XXI*)

REACTION OF TETRAHALOGENOPHTHALIC ANHYDRIDES WITH FLUORIDES OF ALKALI METALS

G.G. Yakobson, V.N. Odinokov, N.N. Vorozhtsov, Jr.

Institute of Organic Chemistry,

USSR Academy of Sciences,

Siberian Division, Novosibirsk, U.S.S.R.

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It has been demonstrated recently that tetrachlorophthalic acid dichloride when heated with anhydrous potassium fluoride in the absence of solvent readily affords tetrafluorophthalic acid difluoride (1).

Christe and Pavlath (2) failed to obtain tetrafluorophthalic anhydride by heating the corresponding chloro derivative with potassium fluoride in dimethylformamide (DMF). The only product isolated from the reaction mixture was identified as octafluoroanthraquinone (yield 2%).

Now we report that tetrachlorophthalic anhydride when treated with potassium fluoride in the absence of solvent (300°, 2 hr.) affords octafluoroanthraquinone in a 40-45% yield. (M.p. 342-343°. Found: C,47.3; F,42.8. $C_{14}F_8O_2$ requires

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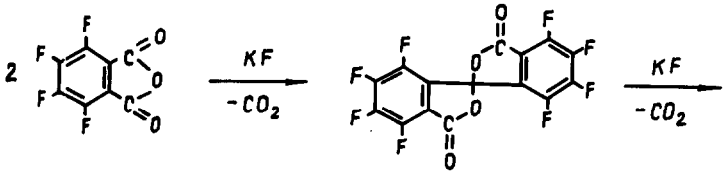
*) Part XX, J.Gen.Chem.USSR, in the press.

C,47.7; F,43.2%). The latter can be obtained in a similar yield also by treating tetrafluorophthalic anhydride with potassium fluoride under analogous conditions. The U.V. spectra of octafluoroanthraquinone, of 1,2,3,4-tetrafluoroanthraquinone and of anthraquinone are quite similar.

Under milder conditions (230°, 2 hr.) α,α-dihydroxyoctafluorodiphenylmethane-2,2'-dicarboxylic acid dilactone I (yield 45-50%) is formed, probably, as intermediate product of the former reaction. (M.p. 177-178°, ν_{max} 1832 cm^{-1} (C=O). Found: C,46.0; F,39.0; Mol.wt. 403. $C_{15}F_8O_4$ requires C,45.5; F,38.4%; M,396). When heated with potassium fluoride (300°, 1 hr.), I produces a high yield of octafluoroanthraquinone.



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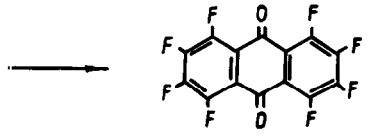

Caesium fluoride is more active in this reaction. Dilactone I (yield about 45%) is formed from tetrafluorophthalic anhydride in the presence of caesium fluoride under milder conditions (120°, 2 hr.). The same yield of I is obtained also when the reaction is carried out in anhydrous DMF (110°, 4 hr.).

This reaction does not take place in the absence of potassium fluoride (or caesium fluoride) both in the absence of solvent and in DMF. Sodium fluoride is inactive in this reaction.

In the presence of potassium fluoride, unsubstituted phthalic anhydride (300°, 3 hr.) forms a small yield of α,α-dihydroxydiphenylmethane-2,2'-dicarboxylic acid dilactone identical with that obtained previously by heating phthalic anhydride at 180-190° with CuO - Cr_2O_3 (3).

The reaction of dilactone I with potassium fluoride in aqueous DMF (70°, 6 hr.) leads to octafluorobenzophenone-2,2'-dicarboxylic acid (yield 85%). (Found: F,36.8. $C_{15}H_2F_8O_5$ requires F,36.8%). Heating of the acid to 170° results in the formation of dilactone I.

Octafluorobenzophenone-2,2'-dicarboxylic acid produces a 85% yield of octafluoroanthraquinone when heated in anhydrous DMF (135°, 15 min.).

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