A New Route to Tetrafluorophthalonitrile and Tetrafluoroterephthalonitrile

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(Received August 1, 1966)

Tetrafluorophthalonitrile and tetrafluoroterephthalonitrile have recently been prepared by, respectively, the reaction of 1, 2- and 1, 4-dibromotetrafluorobenzene with cuprous cyanide in dimethylformamide.[1] Finger and his co-workers[2] have demonstrated an activating effect of the cyano group on the halide-fluoride exchange reaction in the halogenated benzonitriles and cyanopyridines. This report prompted us to investigate the halide-fluoride exchange reaction of tetrachlorophthalonitrile and tetrachloroterephthalonitrile with potassium fluoride; we have found an efficient method for the preparation of the corresponding tetrafluoro nitriles. During the preparation of this paper for publication, a patent reporting essentially the same preparative method as ours appeared.[3] We have independently achieved this synthesis, however, and the results will be described in the present paper.

Tetrachlorophthalonitrile[4] has been prepared by the vapor-phase catalytic chlorination of phthalonitrile in the presence of an activated carbon catalyst. Since no synthetic study of tetrachloroterephthalonitrile has been reported, its preparation followed the general method for the synthesis of nitriles. The treatment of tetrachloroterephthaloyl chloride with ammonia smoothly yielded the corresponding amide, and the subsequent dehydration with phosphorus oxychloride in pyridine afforded tetrachloroterephthalonitrile in an excellent yield.

The replacement of chlorine by fluorine was effected by heating a chloro nitrile in an autoclave with a large excess of anhydrous potassium fluoride without solvents at elevated temperatures for an optional number of hours; the correlation between the yields and the reaction times was then investigated. As is shown in Fig. 1, both the chloro nitriles responded to the complete replacement under certain reaction conditions, thus giving rise to the corresponding fluoro nitriles in satisfactory yields. The structural assignment was made by comparing their infrared spectra and melting points with those reported previously.[1]

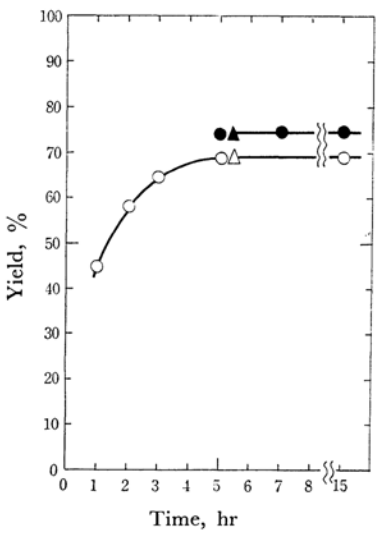

Fig. 1. Effect of reaction time on the yields of tetrafluorophthalonitrile (-○-○- at 250°C, △ at 300°C) and tetrafluoroterephthalonitrile (-●-●- at 300°C, ▲ at 350°C).

1) L. J. Belf, M. W. Buxton and G. Fuller, *J. Chem. Soc.*, **1965**, 3372 (1965).
2) G. C. Finger, D. R. Dickerson, T. Adl and T. Hodgins, *Chem. Commun.*, No. 18, 430 (1965).
3) R. N. Haszeldine, Brit. Pat. 1026290 (1966).
4) S. Saito, *Yuki Gosei Kagaku Kyokai Shi (J. Soc. Org. Syn. Chem., Japan)*, **22**, 834 (1964). Tetrachlorophthalonitrile was supplied by courtesy of Sanko Chemical Industries. Co., Ltd., Ichinomiya, Samukawa-machi, Koza-gun, Kanagawaken.

Thus the halide-fluoride exchange reaction of tetrachlorophthalonitrile and tetrachloroterephthalonitrile with potassium fluoride emphasizes the potent activating effect of the cyano groups toward the nucleophilic ring substitution by the fluoride ion; this effect is more potent than the successful exchange reaction of tetrachloroterephthaloyl chloride and fluoride with only the more powerful fluorinating agent, cesium fluoride.[5] Since the hydrolysis of the tetrafluoro nitriles occurs readily, this route also provides a convenient method for the preparation of the corresponding acids.

Experimental[6]

Tetrachloroterephthalamide. Ammonia gas was passed for 30 min through a solution of 53 g of tetrachloroterephthaloyl chloride in 600 m*l* of dioxane. The resulting precipitate was collected by filtration, and the filtrate was concentrated to give an additional precipitate. The combined product was washed with water and dried to yield 45 g (95%) of a solid which, on recrystallization from dioxane, gave colorless crystals, mp>300°C.

Found: C, 31.32; H, 1.81; Cl, 46.65; N, 9.81%. Calcd for $C_8H_4Cl_4N_2O_2$: C, 31.82; H, 1.34; Cl, 46.97; N, 9.28%.

Tetrachloroterephthalonitrile. A mixture of 21 g of the above amide and 42 m*l* of phosphorus oxychloride in 750 m*l* of pyridine was stirred at 80°C for 1 hr. The solvent was then evaporated at reduced pressure, and the remaining solution was poured onto ice water. The precipitated product was separated by filtration and recrystallized from benzene to yield 16.2 g (88%) of crystals, mp 298°C (in a sealed tube).

Found: C, 36.41; Cl, 53.02; N, 10.33%. Calcd for $C_8Cl_4N_2$: C, 36.14; Cl, 53.33; N, 10.53%.

Tetrafluorophthalonitrile. A mixture of 5 g of finely-ground tetrachlorophthalonitrile and 19 g of anhydrous potassium fluoride was placed in a 100-m*l* autoclave, and the atmosphere in the autoclave was replaced with nitrogen. The mixture was heated at 250°C for 5 hr and then cooled and extracted with ether. The ether extract was washed thoroughly with water and dried over anhydrous sodium sulfate. The removal of the solvent left 2.6 g (68.7%) of a crystalline solid which showed a single peak in vapor-phase chromatography. Recrystallization from aqueous ethanol yielded colorless needles, mp 86—88°C, lit.[1] 88—89°C.

Found: F, 37.71; N, 14.11%. Calcd for $C_8F_4N_2$: F, 37.98; N, 14.00%.

The product was further characterized by a study of its infrared spectrum, which exhibited absorptions at 2250 (C≡N) and 1630, 1521 and 1503 cm^{-1} (fluorinated benzene ring).

The same reaction was also carried out by heating the mixture for 1 hr instead of 5 hr. The product was taken up in ether, and the residue, after the solvent had been removed, was steam-distilled to give 2.4 g of crystals, mp 45—55°C. This wide melting range and its infrared spectrum suggested contamination by partially-fluorinated compounds. A vapor-phase chromatogram of this product showed two peaks, one corresponding to tetrafluorophthalonitrile (as shown by peak enhancement) and the other probably chlorotrifluorophthalonitrile (ratio of peak areas, 4.2 : 1). The elemental analyses (Cl, 7.25; F, 33.80; N, 13.16%) of the total products indicated the presence of an additional compound, probably dichlorodifluorophthalonitrile. From these results, the molar ratio of tetrafluoro, trifluoro, and difluoro components in the product was estimated to be 7.0 : 1.7 : 1, where the vapor-phase chromatographic response of each component was assumed to be the same. Thus, the yield of tetrafluorophthalonitrile was found to be approximately 45%.

Similarly, the yields of tetrafluorophthalonitrile obtained by the exchange reaction at 2-hr and 3-hr reaction times were estimated to be 58% and 65% respectively. Neither reaction periods more prolonged than 5 hr nor temperatures higher than 300°C increased the yield.

Tetrafluoroterephthalonitrile. A mixture of 5 g of tetrachloroterephthalonitrile and 19 g of anhydrous potassium fluoride was heated in an autoclave at 300°C for 5 hr in an atmosphere of nitrogen. After cooling, the contents were then extracted with hot benzene. The solvent was evaporated to yield 2.8 g (74.4%) of a pale yellow solid which, on recrystallization from acetone, yielded colorless crystals, mp 196—198°C, lit.[1] mp 196—198°C.

Found: F, 38.10; N, 14.11%. Calcd for $C_8F_4N_2$: F, 37.98; N, 14.00%.

The infrared spectrum exhibited absorptions at 2242 (C≡N) and 1505 cm^{-1} (fluorinated benzene ring).

At a 3-hr reaction time, the product was shown by its infrared spectrum to be contaminated with a partially-fluorinated compound, probably chlorotrifluoroterephthalonitrile. The reactions at 350°C for 5 hr and at 300°C for 15 hr afforded tetrafluoroterephthalonitrile in almost identical yields.

5) G. G. Yakobson, V. N. Odinokov, T. D. Petrova and N. N. Vorozhtsov Jr., *Zh. Ohshch. Khim.*, **34**, 2953 (1964).

6) Melting points are uncorrected. Vapor phase chromatographic analyses were performed on a stainless steel column packed with silicone DC 550 on Kieselguhr at 180°C. In all cases helium was used as carrier gas. Samples were provided with the ethereal solutions for vapor phase chromatography. Infrared spectra were measured on a Hitachi infrared spectrophotometer with KBr pellets. Microanalyses were carried out by a member of the analytical section of our laboratories.