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Polyhalogenonitrobenzenes and derived compounds
Part 4. Attempted fluorination of 1,2,3,4-tetrachloro-5,6-dinitrobenzene [1]

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Abstract

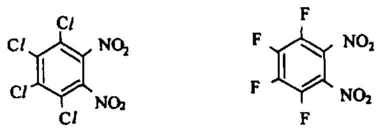
Attempted fluorination of 1,2,3,4-tetrachloro-5,6-dinitrobenzene with potassium fluoride to give 1,2,3,4-tetrafluoro-5,6-dinitrobenzene in DMF or sulpholane, or under solid/liquid phase transfer conditions in toluene using Aliquat 336, TBAI or 18-Crown-6 failed to yield any products resulting from displacement of Cl by F.

Rather surprisingly, the two products obtained were pentachloronitrobenzene and pentachlorofluorobenzene.

Keywords: Fluorination; Polyhalogenonitrobenzenes; Pentachloronitrobenzene; Pentachlorobenzene

1. Introduction

As part of our interest in polyhalogenonitrobenzenes and derived compounds we have carried out an extensive, and systematic, study of the reactions of 1,2,3,4-tetrachloro-5,6-dinitrobenzene (TCDNB) (**1**) (Scheme 1) with amines. The preferences for primary amines in replacing a nitro-group whilst acyclic secondary amines replace a chlorine ortho to a nitro-group have been accounted for [2]. It was therefore of interest to us to compare the reactions of its fluorine analogue, 1,2,3,4-tetrafluoro-5,6-dinitrobenzene (TFDNB) (**2**), with TCDNB to see whether or not the same pattern of substitution is observed. Since some of the products of the reactions of TCDNB with amines showed pesticidal activity we also wished to ascertain if this would be the case with those derived from the reactions of TFDNB. If so, the latter should also be more environmentally acceptable.



TCDNB
(1)

TFDNB
(2)

Scheme 1.

Two methods of preparation of 1,2,3,4-tetrafluoro-5,6-dinitrobenzene (TFDNB) have been reported. One [3] starts from 1,2,3,4-tetrafluorobenzene (TFB) but requires six stages to give TFDNB since it is not possible to dinitrate TFB. The other [4] involves reaction of pentafluoronitrobenzene with ammonia and then separation of the required 2,3,4,5-tetrafluoro-6-nitroaniline from the other three products by column chromatography. Oxidation of this with peroxytrifluoroacetic acid gives TFDNB. We have made a number of improvements to this method and full details are given in the next paper [5]. Note however that both of these methods start from relatively expensive polyfluorobenzenes, and are far from ideal for producing reasonable quantities of TFDNB.

We therefore sought a better method for the preparation of TFDNB and since we had TCDNB available we decided to firstly investigate if it could be fluorinated to give TFDNB. Note that TCDNB is obtained in one step, and in virtually quantitative yield, by the dinitration of the cheap, readily available, 1,2,3,4-tetrachlorobenzene. This approach seemed attractive because halogen exchange is a standard method of making polyfluorobenzenes. However, with TCDNB loss of a nitro-group is a possibility since pentachloronitrobenzene reacts with fluoride ion in DMF to give a 10% yield of pentachlorofluorobenzene [6]. A further relevant example of nitro-group replacement was the reaction of an isomer of TCDNB — 1,2,4,5-tetrachloro-3,6-dinitrobenzene — with

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potassium fluoride in DMF which gave 1,2,4,5-tetrachloro-3-fluoro-6-nitrobenzene. Nevertheless, the reaction between TCDNB and potassium fluoride appeared, if successful, to be an easy and cheap route to TFDNB.

Our first attempt was to react TCDNB with dried potassium fluoride in DMF at 130° for 1 h. During this time brown fumes were evolved and glc analysis of the product showed that it consisted of pentachloronitrobenzene (44%) and pentachlorofluorobenzene (51%).

Replacing DMF by sulpholane gave the same products in 41% and 20% yield respectively, together with 27% of unreacted TCDNB.

We then attempted the fluorination under phase transfer conditions in a solid–liquid system consisting of solid KF [6], and a solution of TCDNB in an organic solvent, toluene. Using Aliquat 336 as the phase transfer catalyst, and heating under reflux conditions for 82 h, gave the same products as before, but the yields were increased to pentachloronitrobenzene (86%) and pentachlorofluorobenzene (11%). Replacing Aliquat 336 by tetra-n-butylammonium iodide (TBAI), and using a reaction time of 64 h, showed that this was a less reactive system since the above two products were obtained in only 12% and 22% yields respectively. There was also a large amount of unreacted TCDNB (57%).

Finally we turned to a crown ether, 18-crown-6, with a reaction time of 18 h. This had some similarities to the TBAI reaction in that there was a lot of unreacted TCDNB (40%) and the same two products were formed. However, at 8% for pentachloronitrobenzene and 51% for pentachlorofluorobenzene, the proportions were quite different.

These results, summarised in Table 1, show quite clearly that in none of these reactions did the expected nucleophilic displacement of chlorine by fluoride ion occur. We interpret our results in terms of TCDNB initially reacting with chloride ion (see below) to replace a nitro-group to form pentachloronitrobenzene, and then this reacting with the fluoride ion to yield pentachlorofluorobenzene. A similar explanation was proposed for the formation of significant amounts of hexachlorobenzene during the reaction of pentachloronitrobenzene with nucleophiles such as methoxide ion and piperidine, although in that case the expected nucleophilic displacement of chloride also occurred [7]. As discussed earlier, pentachloronitrobenzene also suffers nitro-group displacement in the reaction with potassium fluoride in DMF. Gore et al. [8] have shown that a nitro-group in 1,3,5-trichloro-2,4,6-trinitrobenzene is replaced by chloride ion from lithium chloride in acetone to give 1,2,3,5-tetrachloro-4,6-dinitrobenzene.

Our results show interesting differences in both reactivity and product distribution, as well as the unexpected lack of nucleophilic displacement of chlorine. Thus all the TCDNB reacted in DMF but only 73% in sulpholane. In the phase transfer reactions Aliquat 336 was much more effective than TBAI or 18-crown-6.

However, since the products of the reaction — pentachloronitrobenzene and pentachlorofluorobenzene — both contain more chlorine than the starting material, TCDNB, and the only other reactant present is potassium fluoride, the key question is where does this chlorine come from? Not from the potassium fluoride since this was Analar grade and the specified limit for chloride ion was 0.005%. The most likely source of chloride ion would be the degradation of the TCDNB itself since product plus unreacted TCDNB were less than 100%, although we were unable to detect any breakdown products. This is all rather intriguing.

Finally, the exceptionally high yield of products using Aliquat 336 — namely 86% pentachloronitrobenzene and 11% pentachlorofluorobenzene — is understandable because the counterbalancing anion to the quaternary ammonium cation in this phase transfer catalyst is chloride ion. Not surprisingly TBAI, with its iodide ion, gave a much lower yield of products.

An alternative strategy which we tried was to attempt reaction of 1,2,3,4-tetrachlorobenzene (TCB) with KF to produce 1,2,3,4-tetrafluorobenzene (TFB), since such reactions of slightly activated aryl halides, under phase transfer conditions have been reported [9,10]. Although, as discussed earlier in this paper, dinitration of TFB using conventional nitrating agents was reportedly unsuccessful [11], we wished to investigate this nitration using new nitrating agents such as the nitronium tetrafluoroborate — crown ether complex [12]. However, only unreacted TCB starting material was

Table 1
Reactions of TCDNB with potassium fluoride

Run No.	Solvent	Phase transfer catalyst	Temp. (°C) or reflux (R)	Reaction time (h)	Products [†]		
					Pentachloronitrobenzene (%)	Pentachlorofluorobenzene (%)	Unreacted TCDNB (%)
1	DMF	–	130	1	44	51	–
2	Sulpholane	–	130	1	41	20	27
3	Toluene	Aliquat 336	R	82	86	11	–
4	Toluene	TBAI	R	64	12	22	57
5	Toluene	18-Crown-6	R	18	8	51	40

[†] Analysis by g.l.c. of material isolated.

recovered on heating it with KF in toluene with either Aliquat 336 at 90 °C for 64 h or 18-crown-6 under reflux for 18 h.

We therefore finally turned our attention to improving the reported route from pentafluoronitrobenzene for obtaining TFDNB. Our success in this is reported in the following paper.

2. Experimental

Gas liquid chromatography was carried out using a Pye 104 instrument equipped with a flame ionisation detector. Typical conditions were: a 5′ glass column packed with 3% OV17 on chromosorb GAW-DMCS (80–100 mesh): a column temperature of 200 °C: and a nitrogen carrier gas flow rate of 40 cm^3 min^{-1}.

The products from the reactions were quantitatively analysed by the method of ''internal normalisation'', using authentic samples of the products.

Thin layer chromatography was carried out using Polygram plastic sheets precoated with 0.25 mm silica gel (impregnated with a fluorescent indicator UV_{254}). The plates were eluted with a variety of solvents, e.g. toluene, 60–80 petrol, etc., and were visualised using an iodine tank and/or a portable ultraviolet lamp.

2.1. Preparation of solvents and reagents

Potassium fluoride: Analar grade, purchased from BDH Chemicals Limited, Poole. The solid was dried in an oven at 120 °C for 24 h before use.

Pentafluoronitrobenzene: This was purchased from Linksfield laboratories Limited, St. Helens and was used without further purification.

Toluene: General purpose grade toluene was redistilled and stored over sodium wire until required.

2.2. Reactions of TCDNB with potassium fluoride

2.2.1. Reaction of TCDNB with potassium fluoride in dimethylformamide (D.M.F.)

Dry potassium fluoride (5.8 g; 0.10 mol) was added to a magnetically stirred solution of TCDNB (3.1 g; 0.010 mol) in D.M.F. (18 cm^3). The mixture was stirred and heated at 130 °C for 1 h. During the reaction brown fumes were evolved. After cooling, the reaction mixture was diluted with water to give a pale yellow precipitate. The product was filtered at the pump and dried to give a pale yellow solid (0.7 g). G.l.c. analysis of the crude product showed that the two major components (accounting for 95% of the total products) were pentachloronitrobenzene (44%) and pentachlorofluorobenzene (51%).

2.2.2. Reaction of TCDNB with potassium fluoride in sulpholane

Dry potassium fluoride (5.8 g; 0.10 mol) was added to a magnetically stirred solution of TCDNB (3.1 g; 0.010 mol) in sulpholane (15 cm^3). The mixture was stirred and heated at 130 °C for 1 h. During the reaction dense brown fumes were evolved. After cooling, the reaction mixture was diluted with water to give a pale yellow precipitate. The product was filtered at the pump and dried to give a pale yellow solid (0.6 g). G.l.c. analysis of the product showed three major components identified as unreacted TCDNB (27%) pentachloronitrobenzene (41%) and pentachlorofluorobenzene (20%).

2.2.3. Reaction of TCDNB with potassium fluoride in the presence of Aliquat 336

Dry potassium fluoride (5.62 g; 0.0968 mol) was added to a magnetically stirred solution of TCDNB (6.73 g; 0.022 mol) and Aliquat 336 (3.0 g; 0.0074 mol) in dry toluene (50 cm^3). The mixture was stirred and heated under reflux conditions for 18 h. During the reaction dense brown fumes were evolved. More potassium fluoride (1.12 g; 0.0193 mol) was added and the reflux was continued for a further 64 h. After cooling, the reaction mixture was filtered and the filtrate was washed with distilled water, dried over anhydrous $MgSO_4$ and filtered. Removal of the solvent gave a dark red oil (7.4 g). A sample of the crude product (1.0 g) was purified by column chromatography (silica 35–70 mesh:toluene) to give two fractions.

Removal of the solvent from the first fraction gave a pale yellow solid (0.53 g). G.l.c. analysis of this fraction showed two major components which were identified as pentachloronitrobenzene (86%) and pentachlorofluorobenzene (11%).

The second fraction was washed from the column using ethyl acetate and removal of the solvent under reduced pressure gave a red oil (0.3 g) which was found (t.l.c., g.l.c.) to consist mainly of Aliquat 336.

2.2.4. Reaction of TCDNB with potassium fluoride in the presence of tetra-n-butylammonium iodide (TBAI)

Dry potassium fluoride (7.57 g; 0.13 mol) was added to a magnetically stirred solution of TCDNB (5.0 g; 0.0163 mol) and TBAI (1.1 g: 0.003 mol) in toluene (100 cm^3). The mixture was stirred and heated under reflux conditions for 64 h. During the reaction dense brown fumes were evolved. After cooling, the reaction mixture was filtered and the filtrate was washed with distilled water, dried over anydrous $MgSO_4$ and filtered. Removal of the solvent under reduced pressure gave a red semi-solid (5.9 g). G.l.c. analysis of the crude product mixture showed three major components which were identified as unreacted TCDNB (57%) pentachloronitrobenzene (12%) and pentachlorofluorobenzene (22%).

2.2.5. *Reaction of TCDNB with potassium fluoride in the presence of 18-crown-6*

Dry potassium fluoride (7.57 g; 0.130 mol) was added to a magnetically stirred solution of TCDNB (5.0 g; 0.0163 mol) and 18-crown-6 (0.43 g; 0.00163 mol) in dry toluene (100 cm^3). The mixture was stirred and heated under reflux conditions for 18 h. During the reaction a pale brown gas was given off. After cooling, the reaction mixture was filtered and the filtrate was washed with distilled water, dried over anhydrous $MgSO_4$ and filtered. Removal of the solvent under reduced pressure gave a pale yellow solid (5.0 g). G.l.c. analysis of the crude product showed three products which were identified as unreacted TCDNB (40%), pentachloronitrobenzene (9%) and pentachlorofluorobenzene (51%).

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