The formation of 4,4′-difluorobenzophenone from 4,4′-dinitrodiphenylmethane

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Abstract

The novel one pot oxidation/fluorodenitration of 4,4′-dinitrodiphenylmethane to form 4,4′-difluorobenzophenone has been achieved using tetramethylammonium fluoride in *N,N*-dimethylacetamide. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

PEEK (poly(etheretherketone)) is a high temperature thermoplastic which can be compression moulded and extracted [1] and has many uses, with applications in the automotive, oil and aerospace industries [2]. PEEK is usually prepared via a high temperature condensation of 4,4′-difluorobenzophenone (BDF) with hydroquinone [3]. While hydroquinone is readily available, BDF is expensive and contributes greatly to the overall cost of PEEK. Numerous methods exist in the literature for the formation of BDF [4,5]. However, these routes tend to involve hazardous reagents and result in the formation of toxic by-products.

The basic properties of fluoride ion are well-known [6]. The base-catalysed oxidation of diphenylmethanes is also well-documented [7,8] and there are reports in the literature of the use of fluoride ion for such reactions [9]. Fluorodenitration has also been used to form a fluorinated benzophenone [10].

We have found that it is possible to make use of both the basic and nucleophilic properties of fluoride ion in one pot for the novel synthesis of BDF from 4,4′-dinitrodiphenylmethane (DNDPM), Scheme 1.

2. Results and discussion

Reaction of excess dried tetramethylammonium fluoride (TMAF) with DNDPM in DMSO at 100°C resulted in a low yield (20%) of BDF being obtained after 60 min. Traces of

4-nitro-4′-fluorobenzophenone were also detected. Inclusion of an oxygen feed increased the yield of BDF to a modest 28%. Many by-products could be detected, including the expected ethers (formed via hydrolysis of the fluoroaromatic or by reattack of the displaced nitrite ion [11]) and tetra(4-nitrophenyl)ethene, previously identified in the attempted oxidation of DNDPM [12]. It is known that DMSO can be deprotonated by strong bases [13] and indications that reactions involving such anions are occurring was given by the detection of DMSO related products in similar systems [14]. An increase in yield was obtained when the reaction was carried out in *N,N*-dimethylacetamide (DMAc), Table 1.

Quantitative oxidation of DNDPM to 4,4′-dinitrobenzophenone (DNB) was found to be possible at room temperature in DMAc in the presence of small quantities of fluoride. In the absence of fluoride, no reaction occurs. After reaction, the only detectable tetramethylammonium salt is TMAF, indicating that the oxidation is catalytic.

In line with the above results, the fluorodenitration of DNB was found to be solvent dependent. A 70% yield of BDF was obtained after 1 h in DMAc at 100°C. A comparable yield was obtained in sulfolane, but the reaction was slower, taking 2 h to reach completion. In both cases, the only detectable by-products were oligomeric ethers. A low yield of 28% of BDF was obtained in DMSO after 20 min, but, in refluxing acetonitrile, complete conversion to non-volatile products was obtained in this time. Both DMSO and acetonitrile contain relatively abstractable hydrogens, and Christe et al. [15] have reported that it is possible to deprotonate acetonitrile with anhydrous TMAF. In our reaction, IR analysis of the product mixture formed in

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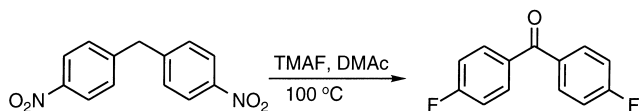
Scheme 1. The formation of BDF from DNDPM.

Table 1
Reaction of DNDPM with TMAF to give BDF

Solvent	Reaction time (min)	Yield (%)[a]
DMSO	60	28
DMAc	60	45
DMAc[b]	60	71(59)

[a]Yields calculated by GC area, corrected by the presence of an internal standard. The figure in parentheses indicates the isolated yield (unoptimised).
[b]Room temperature oxidation (10 mol% TMAF), followed by fluoro-denitration at 100°C after further addition of TMAF (290 mol%).

acetonitrile revealed $C\equiv N$ stretching bands, even after exhaustive drying under vacuum.

Surprisingly, water was found to have very little effect on the reaction. Oxidation at room temperature followed by fluorodenitration resulted in a 71% conversion to BDF. This system contains the added mole equivalent of water formed during oxidation. While added water is expected to lead to side products via the hydrolysis of the fluorinated product, this yield is comparable with that obtained from the fluoro-denitration of pre-formed DNB (72%). The use of anhydrous TMAF (formed via the method of Christe et al. [15]) resulted in a slightly lower yield of BDF (67%), again indicating that the success of the fluorodenitration reaction is not particularly sensitive to the water content.

We also attempted to extend this oxidation/fluorination to another class of compounds, the substituted ethylbenzenes, Table 2. However, only in one case was the desired fluoro-acetophenone formed in measurable quantities. Many side products were formed, with aldol products being identified in the reaction mixture, indicating that the fluoride might be attacking the $-CH_3$ moiety.

In conclusion, we have managed to make use of both the basic and nucleophilic properties of fluoride as a means of forming BDF from DNDPM in one pot.

3. Experimental

^{1}H-NMR and ^{19}F-NMR spectra were recorded on a JEOL EX 270 spectrometer operating at 270 MHz for ^{1}H and 254 MHz for ^{19}F. Reactions were carried out in conventional glassware. Analysis by GC–MS used a Finnigan MAT Magnum system fitted with a DB5 capillary column (50 m) and ion trap system. Further mass spectrometry was carried out on a VG Analytical Autospec instrument. All chemicals used except TMAF were purchased from Aldrich and used without further purification. TMAF was purchased from Apollo as the tetrahydrate. This was dried for three days at 60°C on a Schlenk line. Karl Fischer analysis of the dried TMAF gave 19.4 w/w% water.

3.1. 4,4′-Dinitrodiphenylmethane

Diphenylmethane (12.8 g, 76.2 mmol) was placed in a round bottomed flask and cooled in an ice bath. Nitric acid (40 ml) and sulphuric acid (10 ml) were added and the mixture gently heated to 50°C. After 2 h, solid precipitated. Water (150 ml) was added and the solution was stirred for 30 min. The solid was then collected by filtration and washed well with ether. After boiling in ethanol, the solid was recrystallised from toluene to give 4,4′-dinitrodi-phenylmethane (3.95 g 21% yield).

4,4′-Dinitrodiphenylmethane: MS (*m/z*, %) M$^+$ 258: 165 (100), 258 (59), 212 (37), 241 (14), 63 (13), 89 (11), 77 (8); ^{1}H-NMR (CDCl$_3$) δ 8.17 (d), 7.57 (d) ppm, m.p. 182°C.

3.2. Typical simultaneous reaction

DNDPM (0.062 g, 0.24 mmol) was placed in a round bottomed flask under an argon atmosphere, along with biphenyl (0.025 g, 0.16 mmol), the internal standard. The solvent (10 ml) was then added and the reaction heated to the required temperature. After removal of a sample, TMAF (0.086 g, 0.72 mmol) was added and the reaction regularly sampled. Samples were removed, DCM added and washed once with 1 M HCl and twice with water. After drying, the samples were analysed by GC. The identity of the products was confirmed by comparison of GC retention time, GC–MS, ^{1}H- and ^{19}F-NMR spectroscopy with authentic samples.

4,4′-Difluorobenzophenone: MS (*m/z*, %) M$^+$ 218: 123 (100), 95 (62), 75 (43), 218 (37); ^{19}F-NMR (CDCl$_3$) δ -106 ppm.

4-Nitro-4′-fluorobenzophenone: MS (*m/z*, %) M$^+$ 245: 123 (100), 245 (56), 95 (36), 150 (23), 75 (14), 104 (9), 170 (7); ^{19}F-NMR (CDCl$_3$) δ-105 ppm.

Table 2
Reaction of ethylbenzenes with TMAF in DMAc at 100°C

Substrate	Product	Reaction time (min)	Yield (%)[a]
4-Nitroethylbenzene	4-Fluoroacetophenone	60	15
2-Nitroethylbenzene	2-Nitroacetophenone	120	13
4-Chloroethylbenzene	No reaction	180	–

[a]Yield based on GC area, corrected by the presence of an internal standard.

3.3. 4,4′-Dinitrobenzophenone

4,4′-Dinitrodiphenylmethane (0.9852 g, 3.82 mmol) was placed in a round bottomed flask with DMAc (50 ml). TMAF (0.090 g, 0.75 mmol) was then added and the system sealed under a positive pressure of oxygen. After stirring overnight, the solution was poured into cold water (300 ml) and the solid collected by filtration to give 4,4′-Dinitrobenzophenone, which was recrystallised from toluene (0.901 g, 87% yield).

4,4′-Dinitrobenzophenone: MS (*m/z*, %) M$^+$ 272: 150 (100), 272 (77), 104 (32), 92 (21), 76 (20), 84 (7), 120 (6); ^{1}H-NMR (DMSO) δ 8.40 (d), 8.01 (d) ppm, m.p. 186°C.

3.4. Tetra(4-nitrophenyl)ethylene

An authentic sample was prepared by the nitration of tetraphenylethylene with nitric acid at 50°C, MS (*m/z*, %): 512 (100), 408 (6), 326 (12), 313 (9), 300 (6), ^{1}H-NMR (CDCl$_3$) δ 7.19 (8H, d), 8.08 (8H, d) ppm. IR (KBr disc) v max (cm^{-1}) 1598, 1522, 1345; m.p. 304°C. Analysis: Calc. for C$_{26}$H$_{12}$N$_4$O$_8$ requires: C, 60.9%; H, 3.1%; N, 10.9%. Found: C, 61.19%; H, 3.09%; N, 10.9%.

3.5. Reactions of substituted ethylbenzenes

Reactions were carried out as above for DNDPM.

4-Fluoroacetophenone: MS (*m/z*, %) M$^+$ 139: 123(100), 139(18), 76(15), 63(5); ^{19}F-NMR (CDCl$_3$) δ-105 ppm.

Acknowledgements

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