Short Communication

Direct Oxidative Cyanation of Dibenzofuran[#]

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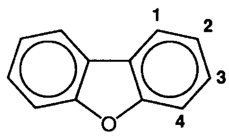
The photochemical nitration of 1-methoxynaphthalene by tetranitromethane in dichloromethane is accompanied by the formation of 1–5 % of 4-methoxy-1-naphthalenecarbonitrile.[1] This type of side-product was also present in the thermal decomposition (GLC) of the pure *cis*-1,4-nitro/trinitromethyl adduct between tetranitromethane and naphthalene (*cis*-1,4-dihydro-1-nitro-4-trinitromethylnaphthalene, produced photochemically in either dichloromethane or acetonitrile).[2]

Thus nitrile formation via thermal decomposition of nitro/trinitromethyl adducts and/or trinitromethyl substitution products seems to be a general side-reaction and was therefore the subject of a separate study, using dibenzofuran (**1**) as the substrate.[3] This compound has a unique



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reactivity in electrophilic aromatic substitution reactions, in that nitration,[4] as distinct from all other electrophilic substitution processes tried, occurs predominantly in the 3-position.

As a prelude to these studies, authentic dibenzofurancarbonitriles were required. In this context, **1** was subjected to a battery of direct cyanation methods,[5–9] which provided new insights into the reactivity of this compound and its radical cation. The results are shown in Table 1.

The first entry is an electrophilic cyanation,[5] yielding predominantly the 2-isomer, as expected from studies of other electrophilic substititions of **1**.[4] Entries 2–4, proceeding via the cyano radical,[7,9a] show an almost statistical distribution of cyano isomers and low absolute yields, again in line with previous studies. The anodic oxidation of **1** in methanol/sodium cyanide (entry 5), occurring by direct oxidation of the substrate to the radical cation,[7] gives predominantly the 3-isomer, as does radical-cation-mediated photocyanation[8] in methanol (entry 6). Thus the reactivities of **1** and its radical cation differ in one important respect, the favoured point of attack by electrophile and nucleophile, respectively. The implications of these findings will be discussed in a future publication.[3]

Finally, the last entry (7) demonstrates that the nitrile mixture obtained in low yield from the photonitration of **1** by tetranitromethane in dichloromethane shows evidence of being initially dependent on the reactivity of the radical cation. If the cyano group is derived from the trinitromethyl group, as is very likely, the reaction would show the regioselectivity of an $ArH^{\bullet +}$/trinitromethanide step. This is consistent with the general picture of the mechanism of photonitration by tetranitromethane.[1,10]

The identity of the various dibenzofurancarbonitriles was established by comparison with authentic samples, prepared by the following procedures. 1- and 2-dibenzofurancarbonitrile were obtained by Pd(II)-promoted cyclization[11] of 3- and 4-cyanodiphenyl ether, respectively. 3-Dibenzofurancarbonitrile was prepared from 3-nitrodibenzofuran[4] via reduction and the Sandmeyer reaction. 4-Dibenzofurancarbonitrile was obtained by carbonation[12] of 4-lithiodibenzofuran, followed by conversion of the carboxylic acid into the nitrile.

Experimental

Materials. Dibenzofuran (Aldrich, 99+ %) and 3- and 4-bromobenzonitrile (Merck, 98+ %) were used without further purification. 3-Nitrodibenzofuran[4] and 3- and 4-cyanodiphenyl ether[13] were prepared according to known methods. All other reagents were of highest commercial quality available.

Instrumentation. GLC analyses were performed on an HP 5890 Ser. II gas chromatograph, equipped with an HP 3396 Ser. II integrator, using a fused silica column (25 m, OV-1701). GLC/MS analyses were performed on a Finnegan 4021 mass spectrometer. NMR spectra were recorded on a Varian 300 MHz instrument, chemical shifts being given vs. tetramethylsilane. Electrolyses were run at constant current (0.5 A) in a non-divided cell (Pt anode and cathode, physically separated by a polypropene gauze).

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[#] Part II in a series on photonitration by tetranitromethane. For Part I, see Ref. 1.

Table 1. Direct cyanation of **1** (for the numbering, see the text) under different conditions. All reactions were run at ambient temperature, unless otherwise stated.

Reaction conditions (entry No.)	Absolute yield (%)	Isomer distribution of dibenzofurancarbonitriles (%)				Occurs via
		1–	2–	3–	4–	
$BrCN/AlCl_3/CS_2$ (1)[a]	90	4	80	15	1	CN^+
ICN/MeOH/*hν* (2)	25	32	23	24	21	$CN^•$
$NH_2CN/NOBF_4/CH_2Cl_2$ (3)	4	19	28	31	22	$CN^•$
$NH_2CN/C_5H_{11}ONO/HOAc$ (4)	2	24	26	28	22	$CN^•$
NaCN/MeOH/anodic oxidation (5)	40	8	17	71	3	$CN^- + ArH^{•+}$
NaCN/MeOH/*hν* (6)	2	9	27	64	<0.5	$CN^- + ArH^{•+}$
$C(NO_2)_4$/2,6-di-*t*-butylpyridine/CH_2Cl_2/*hν* (7)	1	7	15	71	6	$(NO_2)_3C^- + ArH^{•+}$

[a] At reflux temperature.

Photolyses were performed using a DEMA HPK 125 UV lamp immersed in a water-jacketed photochemical vessel (H. Mangels, Germany). Column chromatography was performed on silica gel 60 (Merck) using pentane/dichloromethane as the eluent.

Synthesis of authentic dibenzofurancarbonitriles. 1-Dibenzofurancarbonitrile was prepared by Pd(II) acetate mediated (twofold excess) intramolecular coupling of 3-cyanodiphenyl ether (387 mg, 2.0 mmol) in 20 ml of HOAc at 80 °C. After dilution with dichloromethane, filtration, washing with water and drying ($MgSO_4$), evaporation and column chromatography (pentane/dichloromethane 9:1) 40 mg of 1-dibenzofurancarbonitrile (0.23 mmol, 11 %) were isolated, m.p. 105–106 °C (cyclohexane). ^1H NMR ($CDCl_3$): 8.40 (H8, dq), 7.80 (H2, dd), 7.66 (H4, dd), 7.64 (H5 dq), 7.59 (H7, dt) 7.53 (H3, t), 7.46 (H6, dt); J_{23} 8.26, J_{24} 0.95, J_{34} 7.66, J_{56} 8.43, J_{57} 1.43, J_{58} 0.75, J_{67} 7.26, J_{68} 1.38, J_{78} 7.88. In the crude product mixture the ratio of the 1- to 3-cyano isomer was 11:1. *2-Dibenzofurancarbonitrile* was prepared analogously from 4-cyanodiphenyl ether, yield 12%, m.p. 144–145 °C (cyclohexane), lit.[14] 140 °C. NMR ($CDCl_3$): 8.27 (H1, dd), 7.98 (H3, dd), 7.74 (H4, dd), 7.65 (H8, dd), 7.62 (H5, dd), 7.56 (H6, dt), 7.43 (H7, dt); J_{13} 1.64, J_{14} 0.61, J_{34} 7.65. *3-Dibenzofurancarbonitrile* was prepared from 3-nitrodibenzofuran via reduction to the amine and a subsequent Sandmeyer reaction,[15] m.p. 125–126 °C (ethanol), lit.[15] 127 °C. ^1H NMR ($CDCl_3$): 8.04 (H1, dd), 8.01 (H2, dd), 7.88 (H4, q), 7.64 (H5 + H8, dd + dd), 7.58 (H6, dt), 7.43 (H7, dt); J_{12} 8.26, J_{14} 0.64, J_{24} 1.29. *4-Dibenzofurancarbonitrile* was prepared by lithiation of **1**, followed by carbonation[12] and subsequent conversion of the acid via the amide into the nitrile,[14] m.p. 114–116 °C (cyclohexane), lit.[14] 122 °C. ^1H NMR ($CDCl_3$): 8.40 (H1, dd), 8.28 (H3, dd), 8.05 (H5, dd), 7.54 (H2, dt), 7.51 (H8, dd), 7.43 (H6, dt), 7.41 (H7, dt); J_{12} 7.82, J_{13} 1.32, J_{23} 7.64.

Direct cyanation reactions. With $BrCN/AlCl_3$.[5] $AlCl_3$ (25 g, 0.18 mol) was added in portions to a mixture of **1** (3.3 g, 0.020 mol) and BrCN (5.0 g, 0.047 mol) in carbon disulfide (250 ml). After reflux for 48 h, the mixture was poured into water/dichloromethane, washed with water and dried ($MgSO_4$). The product composition was determined by GLC (Table 1, 80 % 2-cyano isomer) and after evaporation (crude yield 3.5 g, 90 %) column chromatography afforded 2-dibenzofurancarbonitrile in ca. 60 % yield. *With ICN/hν.* Iodine cyanide (2.0 g, 13 mmol) and **1** (2.0 g, 12 mmol) were photolysed in methanol (210 ml) for 8.5 h. Most of the solvent was evaporated and the residue dissolved in dichloromethane, washed with water, and dried ($MgSO_4$) to give a mixture of dibenzofurancarbonitriles of nearly statistical isomer distribution (Table 1). Owing to its fast elution, the 1-cyano isomer could be readily separated from the others by column chromatography, the first fractions providing a combined yield of 5 % of pure (99+ %) 1-dibenzofurancarbonitrile. *With NaCN/hν.* Replacement of ICN by NaCN (1.0 g, 20 mmol) in the above procedure (irradiation for 12 h) gave a low yield of dibenzofurancarbonitriles, the 3-isomer being the major product (GLC, Table 1). *Anodic cyanation.* Dibenzofuran (1.0 g, 6 mmol) and sodium cyanide (2.0 g, 40 mmol) in methanol (250 ml) was electrolysed (see above) for 6 h, when ca. 50 % of the starting material had been consumed. After work-up (crude yield ca. 40 %) the isomer distribution was determined (GLC, Table 1). Column chromatography gave reasonably pure 3-dibenzofurancarbonitrile. *Cyanation by diazotation of cyanamide.* Following published procedures,[9] **1** was treated with diazotized cyanamide, using isoamyl nitrite[9a] or nitrosonium tetrafluoroborate[9b] as diazotizing reagents. After work-up, the isomer distributions were determined by GLC (Table 1).

Detection of nitriles formed in the photolysis of dibenzofuran and tetranitromethane. GLC analysis of the product mixture resulting from the irradiation (filtered light with cut-off at < 430 nm) of **1**, tetranitromethane and 2,6-di-*t*-butylpyridine in dichloromethane[3] showed the presence of a small amount (ca. 1 %) of dibenzofurancarbonitriles (Table 1). These are presumably formed during work-up and/or in the injection port of the GLC instrument by decomposition of the corresponding trinitromethyldibenzofurans.[1–3]

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