

# Photochemical Nitration by Tetranitromethane. Part XXXIX.† The Photolysis of Tetranitromethane with 2,8-Dimethyl- and 1,3,7,9-Tetramethyl-dibenzofuran

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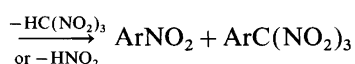
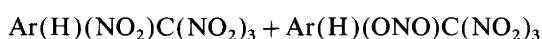
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The photolysis of the charge transfer complex of 2,8-dimethyldibenzofuran in dichloromethane gives 2,8-dimethyl-3-trinitromethyldibenzofuran (11) and 2,8-dimethyl-3-nitrodibenzofuran (12) as the major products, with minor amounts of 2,8-dimethyl-4-nitrodibenzofuran (13) and the 4-hydroxy-3-trinitromethyl adduct 14. In 1,1,1,3,3,3-hexafluoropropan-2-ol the yield of the 3-trinitromethyl compound 11 is much reduced, and the adduct 14 is not detected.

Similar photolysis of 1,3,7,9-tetramethyldibenzofuran gives predominantly 1,3,7,9-tetramethyl-2-nitrodibenzofuran (15) accompanied by the epimeric 1,3,7,9-tetramethyl-1-nitro-4-trinitromethyl-1,4-dihydrodibenzofurans 16 and 17. For reactions in dichloromethane containing trifluoroacetic acid (0.8 M), or in 1,1,1,3,3,3-hexafluoropropan-2-ol, adducts 16 and 17 are not seen among the products and the 2-nitroarene 15 is close to the exclusive reaction product.

The photochemical addition of tetranitromethane to aromatic compounds ArH has been shown to occur predominantly by *addition* of the elements of tetranitromethane,  $-\text{NO}_2$  or  $-\text{ONO}$  (most often ending up as  $-\text{OH}$  under the conditions employed) and  $-\text{C}(\text{NO}_2)_3$ , across the aromatic ring.<sup>2</sup> After the photoelectron transfer step, the product forming reaction sequence is initiated by attack of trinitromethanide ion upon the radical cation  $\text{ArH}^{\cdot+}$ .<sup>3,4</sup> The nitro- and/or nitrito-trinitromethyl adducts are either stable enough to permit isolation or undergo more or less facile elimination of nitroform and/or nitrous acid to give *substitution* products  $\text{ArNO}_2$  and/or  $\text{ArC}(\text{NO}_2)_3$  [eqn. (1)].



For the radical cations of methylated naphthalenes, the regiochemistry of the first ionic coupling of  $\text{ArH}^{\cdot+}$  with trinitromethanide ion appears to be determined by the

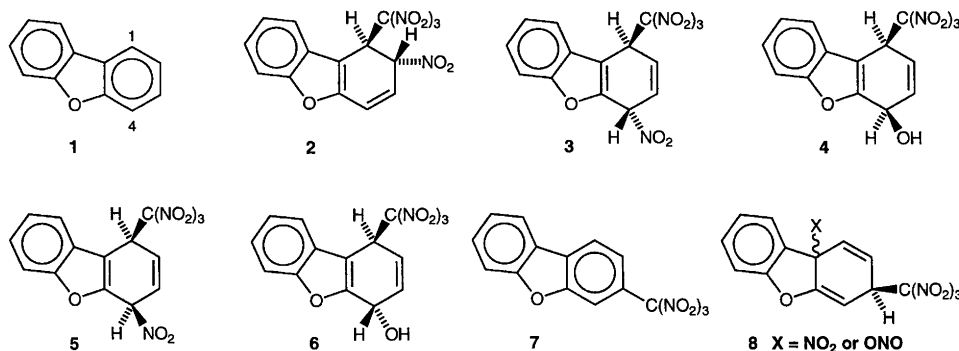
relative stabilities of the various resultant delocalized carbon radicals;<sup>5</sup> subsequent radical coupling of the favoured radicals with nitrogen dioxide yields the predominant nitro-trinitromethyl adducts.

In the photolysis of the charge transfer (CT) complex of dibenzofuran (1) with tetranitromethane, adducts 2–6 and 3-trinitromethyldibenzofuran (7) are formed by attack of trinitromethanide ion at C1 and C3, respectively,<sup>6</sup> in keeping with theoretical predictions for this non-alternant system.<sup>7</sup> The 3-trinitromethyldibenzofuran 7 was envisaged as being formed by photochemically induced loss of nitrous acid from adduct 8 ( $\text{X}=\text{NO}_2$  or  $\text{ONO}$ ).<sup>6</sup>

In the light of the regiochemistry of trinitromethanide ion attack on the radical cation of dibenzofuran we have examined the photolyses of 2,8-dimethyldibenzofuran (9) (Ref. 8) and 1,3,7,9-tetramethyldibenzofuran (10) (Ref. 8) with tetranitromethane to explore the effects of introducing methyl groups into the 2(8)- and 1(9),3(7)-positions on the dibenzofuran ring system. For each substrate the yield(s) of adduct(s) was/were lower than had been found earlier for the parent system 1;<sup>6</sup> to the extent that the regiochemistry of trinitromethanide ion on each radical cation could be determined, such attack occurred at C3 in  $9^{\cdot+}$ , but at C4 in  $10^{\cdot+}$ . We now report the results of this study.

† To Part XXXVIII, see Ref. 1.

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## Results

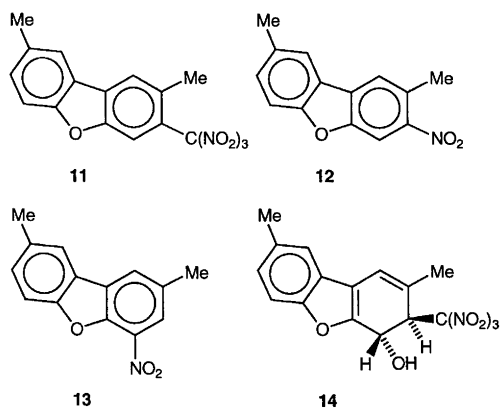
**General.** The photochemical experiments were performed with filtered light (cut-off at 435 nm, 5 cm water IR filter, with a 300 W incandescent lamp) as described before,<sup>9</sup> and small samples were withdrawn for analysis at suitable intervals. The work-up procedure, involving evaporation of solvent and excess tetranitromethane, was conducted at a temperature of  $<0^{\circ}\text{C}$ . The crude product mixtures were stored at  $-78^{\circ}\text{C}$  and were analysed ( $^1\text{H}$  NMR spectroscopy, see Experimental section) as soon as possible.

**Photochemistry of 2,8-dimethyldibenzofuran (9) in dichloromethane at  $20^{\circ}\text{C}$  and the identification of 2,8-dimethyl-3-trinitromethyl dibenzofuran (11), nitro compounds 12 and 13, and adduct 14.** A solution of 9 and tetranitromethane in dichloromethane was irradiated at  $20^{\circ}\text{C}$  and the composition of the mixture was monitored as above (Table 1). The final solution (after 8 h) contained the 3-trinitromethyl compound 11 (37%), nitroarenes 12 (41%) and 13 (5%), the 4-hydroxy-3-trinitromethyl adduct 14 (1%), and unidentified compounds (total 16%).

Two of the components, 11 and 12, of this mixture were separated by chromatography on a silica gel Chromatotron plate. The first material eluted was identified as 2,8-dimethyl-3-trinitromethyl dibenzofuran (11). Although insufficient material was obtained for elemental analysis, the crystal quality was inadequate for single-crystal X-ray analysis, and no parent ion was detectable in the mass spectrum, the molecular formula of 11 was determined by measurement of the  $\text{MH}^+ - \text{NO}_2$  ion, a known fragmentation pattern for such trinitromethylarenes.<sup>10</sup> The point of attachment of the trinitromethyl group on the 2,8-dimethyldibenzofuran skeleton followed from a consideration of the observed H,H-coupling constants and the results of nuclear Overhauser experi-

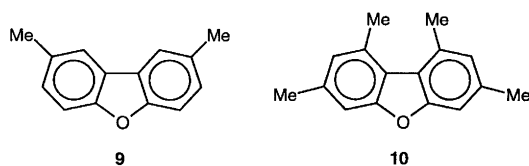
ments. The second material eluted was identified as the 3-nitroarene 12 from its mass spectrum and a consideration of its spectroscopic data (Experimental section).

The 4-nitroarene 13 and the 4-hydroxy-3-trinitromethyl adduct 14 were isolated by HPLC from a similar product mixture to the above. Given the  $^1\text{H}$  NMR



spectrum of the 4-nitroarene 13, and the identification of the 3-nitroarene 12 above, the structure of 13 was established by exclusion. The 4-hydroxy-3-trinitromethyl adduct 14 could not be induced to crystallize, and its structural assignment is based on a consideration of its spectroscopic data. The connectivity 14 was established from the results of nuclear Overhauser experiments coupled with reverse detected heteronuclear correlation spectra (HMQC). In particular, the 4-hydroxy-3-trinitromethyl structural feature was indicated by the relevant  $^{13}\text{C}$  NMR resonances,  $\delta$  50.4 [C3-C(NO<sub>2</sub>)<sub>3</sub>] and  $\delta$  66.2 [C4-OH]. The *t*-4-hydroxy-*r*-3-trinitromethyl stereochemistry of 14 was assigned on the basis of its probable mode of formation. Given that the initially bonded bulky trinitromethyl group would shield the *syn*-face of the molecule from attack by nitrogen dioxide, the radical coupling with nitrogen dioxide will occur at the unhindered face of the delocalized carbon radical and apparently with C-O bond formation, the nitrite ester so formed being hydrolysed either in the reaction medium or during the isolation procedures.

**Photochemistry of 2,8-dimethyldibenzofuran (9) in dichloromethane at  $-20^{\circ}\text{C}$ .** The photolysis of the 9-tetra-



nitromethane CT complex at  $-20^{\circ}\text{C}$  gave similar product mixtures to the reaction at  $20^{\circ}\text{C}$  above. The only feature of note was the increased yield of the 3-nitroarene **12** at the expense of a lower yield of the 3-trinitromethyl compound **11** (Table 1).

*Photochemistry of 2,8-dimethyldibenzofuran **9** in acetonitrile at  $20^{\circ}\text{C}$ .* In acetonitrile at  $20^{\circ}\text{C}$  the photolysis of **9** with tetranitromethane gave substantially the 3-nitroarene **12** (83%), only small amounts of **11** being detected among the reaction products (Table 1).

*Photochemistry of 2,8-dimethyldibenzofuran **9** in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) at  $20^{\circ}\text{C}$ .* The photolysis of **9**-tetranitromethane at  $20^{\circ}\text{C}$  in HFP gave a product mixture after 8 h (ca. 78% conversion) consisting mainly of 3-nitroarene **12** (91%), with minor amounts of **11** and **13** (Table 1).

*Photochemistry of 1,3,7,9-tetramethyldibenzofuran (**10**) in dichloromethane at  $20^{\circ}\text{C}$  and the identification of 1,3,7,9-tetramethyl-2-nitrodibenzofuran (**15**) and the nitro-trinitromethyl adducts **16** and **17**.* A solution of **10** and tetranitromethane in dichloromethane was irradiated at  $20^{\circ}\text{C}$  for 3 h, and the composition of the mixture was monitored (Table 2). The final solution contained a mixture of the 2-nitroarene **15** (84%), the epimeric nitro-trinitromethyl adducts **16** (10.5%) and **17** (1%), and unidentified aromatic compounds (total 4%). The products **15**–**17** were separated partially by HPLC.

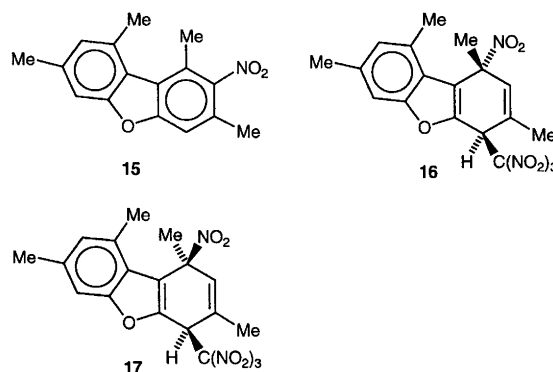
The first compound eluted, 1,3,7,9-tetramethyl-2-nitrodibenzofuran (**15**), was isolated in the presence of a minor (5%) impurity. Nonetheless, on the basis of GCMS and its  $^1\text{H}$  NMR spectroscopic data (Experimental section), the structural assignment to this compound appears secure.

*Table 1.* Overview of yields of products from the photolysis of 2,8-dimethyldibenzofuran (**9**) ( $0.32\text{ mol dm}^{-3}$ ) and tetranitromethane ( $0.64\text{ mol dm}^{-3}$ ) in dichloromethane or in acetonitrile.

t/h	Conversion (%)	Yield (%)				Unidentified adducts
		(11)	(12)	(13)	(14)	
In dichloromethane at $20^{\circ}\text{C}$						
1	21	44.1	13.9	7.7	8.4	25.9
2	40	49.8	18.7	4.8	2.0	24.7
4	66	44.7	29.7	3.5	0.8	21.3
8	95	37.4	40.5	5.3	1.2	15.5
In dichloromethane at $-20^{\circ}\text{C}$						
1	31	14.0	63.0	5.6	0.4	17.1
2	48	13.2	64.1	4.2	0.5	17.9
In acetonitrile at $20^{\circ}\text{C}$						
1	18	—	76.4	10.1	—	13.5
2	30	1.5	83.2	6.4	—	8.8
In 1,1,1,3,3,3-hexafluoropropan-2-ol at $20^{\circ}\text{C}$						
1	17	—	91.7	5.6	—	2.7
2	32	0.8	93.4	4.7	—	1.1
4	51	1.0	94.6	3.5	—	0.9
8	78	2.0	91.4	4.8	—	1.8

*Table 2.* Overview of yields of products from the photolysis of 1,3,8,9-tetramethyldibenzofuran (**10**) ( $0.28\text{ mol dm}^{-3}$ ) and tetranitromethane ( $0.56\text{ mol dm}^{-3}$ ) in dichloromethane, and in dichloromethane containing trifluoroacetic acid (0.8 M), or in acetonitrile.

t/h	Conversion (%)	Yield (%)			
		(15)	Unknown aromatics	(16)	(17)
In dichloromethane at $20^{\circ}\text{C}$					
1	51	80.0	5.1	13.1	1.8
2	92	81.7	5.0	11.8	1.5
3	100	84.4	3.8	10.5	1.3
In dichloromethane at $-20^{\circ}\text{C}$					
1	54	71.2	5.1	21.2	2.5
2	92	73.8	2.9	21.2	2.1
3	100	62.7	4.5	29.5	3.2
In dichloromethane containing trifluoroacetic acid (0.8 M) at $20^{\circ}\text{C}$					
1	17	89.9	10.1	—	—
2	27	89.8	10.2	—	—
3	39	92.2	7.8	—	—
5	56	94.6	5.4	—	—
In acetonitrile at $20^{\circ}\text{C}$					
1	17	83.5	4.7	9.7	2.1
2	63	73.5	4.2	17.9	4.5



The epimeric nitro-trinitromethyl adducts **16** and **17** were eluted later from the HPLC column. Neither compound could be induced to give crystals of adequate quality for single-crystal X-ray analysis, and consequently their structural assignments rest on considerations of their spectroscopic data. For the major epimer **16** the connectivity was established from the results of nuclear Overhauser experiments and reverse detected heteronuclear correlation spectra (HMBC, HMQC). In particular, C4 ( $\delta$  45.1) was identified as the point of attachment of the trinitromethyl group, C2 ( $\delta$  134.4) and C3 ( $\delta$  128.1) as olefinic carbon atoms, and C1 ( $\delta$  86.6) as the point of attachment of the nitro group; the identity of the nitro substituent ( $\nu_{\text{max}}$   $1529\text{ cm}^{-1}$ ) *ipso* to the 1-Me group follows from the  $^1\text{H}$  NMR chemical shift of the 1-Me group ( $\delta$  2.12). Although the NMR data obtainable for the minor adduct **17** are incomplete, the limited data available are consistent with its assignment

as the epimer of the major adduct **16** (Experimental section). The assignment of the stereochemistry of the two adducts **16** and **17** is based on the known elution order of epimeric 1-nitro-4-trinitromethyl-1,4-dihydro aromatic systems from a cyanopropyl HPLC column using hexane–dichloromethane mixtures as the eluting solvent system.<sup>11</sup>

*Photochemistry of 1,3,7,9-tetramethyldibenzofuran (10) in dichloromethane at -20 °C.* In dichloromethane at -20 °C the reaction products were as for the reaction at 20 °C, except that the yields of the nitro–trinitromethyl adducts **16** and **17** were higher and the yield of the 2-nitroarene **15** was correspondingly somewhat reduced (Table 2).

*Photochemistry of 1,3,7,9-tetramethyldibenzofuran (10) at 20 °C in dichloromethane containing trifluoroacetic acid (0.8 M).* In the presence of trifluoroacetic acid (0.8 M) the formation of the nitro–trinitromethyl adducts **16** and **17** was suppressed and the 2-nitroarene **15** (95%) was the only product which could be identified (Table 2).

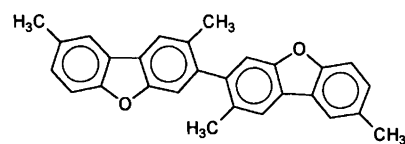
*Photochemistry of 1,3,7,9-tetramethyldibenzofuran (10) in acetonitrile at 20 °C.* The photolysis of **10** with tetranitromethane in acetonitrile at 20 °C gave the 2-nitroarene **15** and the epimeric nitro–trinitromethyl adducts **16** and **17**, the adducts being formed in higher yield than in dichloromethane (Table 2).

*Photochemistry of 1,3,7,9-tetramethyldibenzofuran (10) in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) at 20 °C.* In HFP the photolysis of the CT complex at 20 °C for 5 h gave an essentially quantitative conversion into the 2-nitroarene **15**.

*EPR spectral study of the reactions between tetranitromethane and 9 or 10.* The redox properties of **9** and **10** are known,<sup>12</sup>  $E_{pa}(9/9^{\cdot+}) = 1.75$  V and  $E_{rev}(10/10^{\cdot+}) = 1.53$  V vs. Ag/AgCl, both measured in dichloromethane. Accordingly  $9^{\cdot+}$  should be a rather reactive species, attested to by the fact that its EPR spectrum could not be obtained by oxidation of **9** in HFP (Tl<sup>III</sup> trifluoroacetate) or trifluoroacetic acid (DDQ-*hν*); instead the spectrum of the radical cation of its 3,3'-connected dehydrodimer,  $18^{\cdot+}$ , was obtained. On the other hand, the EPR spectrum of  $10^{\cdot+}$  was persistent under the same conditions.

Irradiation (light of  $\lambda > 430$  nm) of the CT complex between **9** and tetranitromethane in HFP at 22 °C gave an EPR spectrum identical to the one published earlier for  $18^{\cdot+}$ . In the presence of trifluoroacetic acid (0.4 mol dm<sup>-3</sup>) a weak spectrum of  $18^{\cdot+}$  appeared even without irradiation. A control experiment using NO<sub>2</sub>-trifluoroacetic acid (0.4 mol dm<sup>-3</sup>) as the oxidant also gave the EPR spectrum of  $18^{\cdot+}$ , indicating that traces of NO<sub>2</sub> in tetranitromethane might be responsible for the dark reaction.

Similar irradiation of the CT complex between tetranitromethane and **10** in HFP at 22 °C did not give rise to any paramagnetic activity; only with trifluoroacetic

**18**

acid (0.2 mol dm<sup>-3</sup>) present was the EPR spectrum of  $10^{\cdot+}$  at intermediate resolution obtained [0.27 (6 H) and 0.81 (6 H) mT; the smaller couplings of 0.029 and 0.013 mT were not resolvable].

## Discussion

*The photochemistry of 2,8-dimethyldibenzofuran (9) with tetranitromethane.* The EPR spectral examination of the **9**-tetranitromethane-*hν* reaction in HFP with or without trifluoroacetic acid present failed to give any direct indication of the formation of  $9^{\cdot+}$ , as found earlier for other methods of generation. Only a secondary radical cation,  $18^{\cdot+}$ , formed by dimerization of  $9^{\cdot+}$  via its reactive 3-position, was detectable; this behaviour is similar to that found for 1-methoxynaphthalene, where only the radical cation of the 4,4'-connected dehydrodimer was detectable.<sup>13</sup> However, there is a large difference between the two systems from the preparative point of view, in that **9**-tetranitromethane-*hν* gave almost exclusively the nitroarenes **12** and **13** in HFP, whereas 1-methoxynaphthalene gave >70% yield of the dehydrodimer.

In dichloromethane at 20 °C the major products after reaction for 8 h were the 3-trinitromethyl compound **11** (37%) and the 3-nitroarene **12** (41%). At shorter reaction times, e.g. 1 h, the yield of **11** was higher (44%), but that of the 3-nitroarene **12** was significantly reduced (14%), with unidentified adducts (total 26%) now being appreciable products (Table 1 and Fig. 1). It seems probable that **12** is formed to some extent by elimination from unidentified adducts, in which case the trinitromethanide attack must have occurred at C4, but mainly via coupling of  $9^{\cdot+}$  and NO<sub>2</sub> from the first photochemical step and/or homogeneous nitration of **9** by NO<sub>2</sub> which accumulates during irradiation.<sup>9</sup> This would explain the increase in yield of **12** as the reaction progresses. It is also in line with the results from irradiation of **9** in HFP; here most of the chemistry must be due to NO<sub>2</sub> and thus the 3-nitro compound **12** is the major product (>90%, see below). We do not deem it likely that the photo-induced decomposition of **11** can be responsible for the increase of the yield of **12**, since none of the intermediate carboxylic acid was detected.<sup>9,14,15</sup> In terms of the final point of attachment of the trinitromethyl group in compounds **11** and **14** it appears that attack of trinitromethanide ion occurs substantially (52%) at C3(7) in the radical cation of 2,8-dimethyldibenzofuran (**9**). This is the position of highest spin density of dibenzofuran radical cation. However, given the uncertainty about the genesis of the

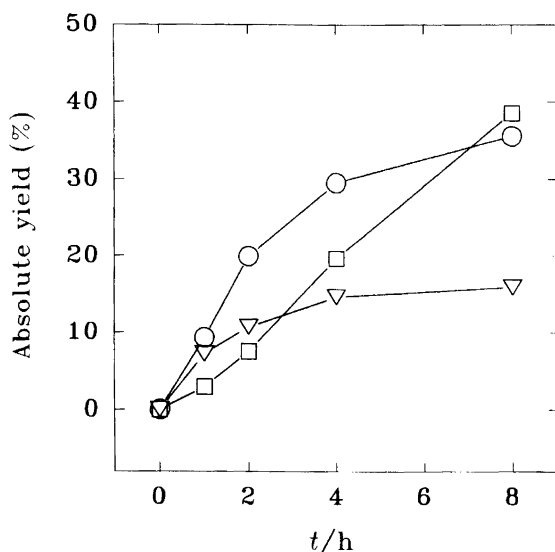


Fig. 1. Time development of the yield of **11** (circles), **12** (squares) and (**14** + unidentified adducts) (triangles) from the photolysis of 2,8-dimethyldibenzofuran and tetranitromethane in dichloromethane at 20 °C.

3-trinitromethyl compound **11** and the incidence of allylic rearrangements of labile nitro-trinitromethyl adducts,<sup>16</sup> this conclusion must remain tentative.

In 1,1,1,3,3,3-hexafluoropropan-2-ol, in which the nucleophilicity of trinitromethanide ion is markedly attenuated,<sup>17</sup> the yields of the 3-trinitromethyl compound **11** and the unidentified adducts were much reduced and the 4-hydroxy-3-trinitromethyl adduct **14** was not detected among the products. The 3-nitro compound **12** was formed in >90% yield, the expected result of NO<sub>2</sub> mediated chemistry.

*The photochemistry of 1,3,7,9-tetramethyldibenzofuran (10) with tetranitromethane.* The EPR spectral examination of the 10-tetranitromethane-*hν* reaction in HFP did not produce 10<sup>•+</sup> in high enough a concentration for its EPR spectrum to be detectable. Thus even in HFP 10<sup>•+</sup> is highly reactive against trinitromethanide ion; only with trifluoroacetic acid present, leading to protonation of trinitromethanide ion, was 10<sup>•+</sup> detectable by EPR spectroscopy.

The 2-nitroarene **15** was the major product in the photolysis of **10** with tetranitromethane in dichloromethane or acetonitrile, but the epimeric nitro-trinitromethyl adducts **16** and **17** were also formed. In dichloromethane containing trifluoroacetic acid (0.8 M) and in 1,1,1,3,3,3-hexafluoropropan-2-ol, where trinitromethanide ion is either protonated (DCM/TFA) or strongly solvated (HFP), no nitro-trinitromethyl adducts were detected and the 2-nitroarene **15** was the exclusive or nearly exclusive product. The probable mode of formation of the nitro-trinitromethyl adducts **16** and **17** is via initial attack of trinitromethanide ion at C4(6) on the radical cation of 1,3,7,9-tetramethyldibenzofuran (**10**) to give the delocalized carbon radical **19** (Scheme 1).

Subsequent radical coupling at C1 of this delocalized carbon radical **19** with nitrogen dioxide would give the epimeric nitro-trinitromethyl adducts **16** and **17**, with the *r*-1-nitro-*t*-4-trinitromethyl epimer predominant.<sup>18</sup>

## Experimental

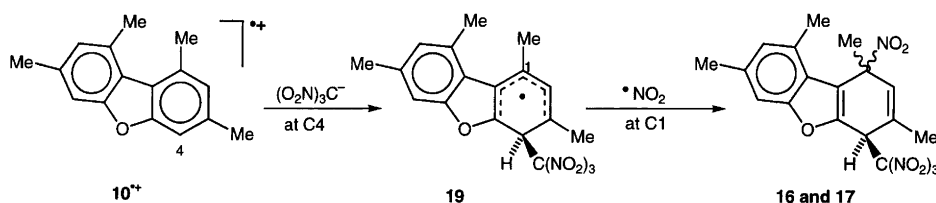
Melting points are uncorrected. Infrared spectra were recorded on a Perkin Elmer 1600 series FTIR spectrometer; <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Unity 300 spectrometer with SiMe<sub>4</sub> as an internal standard. HPLC separations were carried out on a Varian 5000 liquid chromatograph equipped with an Alltech cyanopropyl column, and using a Varian UV-50 ultraviolet spectrometric detector and hexane-dichloromethane as solvent mixtures. EPR spectra were recorded as published. Tetranitromethane was purchased from Aldrich. 2,8-Dimethyldibenzofuran and 1,3,7,9-tetramethyldibenzofuran were available from an earlier study.<sup>8</sup> Dichloromethane (AR) and acetonitrile (HiPerSolv) were from BDH. 1,1,1,3,3,3-Hexafluoropropan-2-ol was purchased from Acros Organics.

**WARNING.** While we did not experience any incidents in working with tetranitromethane, it should be noted that its mixtures with hydrocarbons are detonative within certain concentration limits, and that due care should be taken in handling mixtures of tetranitromethane and organic compounds.<sup>19</sup>

*General procedure for the photonitration of 2,8-dimethyldibenzofuran (9) with tetranitromethane.* A solution of **9** (500 mg, 0.32 mol dm<sup>-3</sup>) and tetranitromethane (0.64 mol dm<sup>-3</sup>) in dichloromethane at 20 or -20 °C, in acetonitrile at 20 °C, or in HFP at 20 °C was irradiated with filtered light (λ<sub>cut-off</sub> 435 nm). Aliquots were withdrawn from each reaction mixture at appropriate time intervals, the volatile material removed under reduced pressure at ≤0 °C, and the product composition of each sample determined by NMR spectral analysis (Table 1).

*Photochemistry of 2,8-dimethyldibenzofuran (9) in dichloromethane at 20 °C and the identification of products (11-14).* Reaction of **9**-tetranitromethane in dichloromethane at 20 °C, as above, for 8 h resulted in substantial conversion (95%) into 3-trinitromethyldibenzofuran (**11**) (37%), 3-nitrodibenzofuran (**12**) (41%), 4-nitrodibenzofuran (**13**) (5%), 4-hydroxy-3-trinitromethyl adduct (**14**) (1%) and unidentified compounds (total 16%). The products (**11-14**) were separated by chromatography on a silica gel Chromatotron plate and gave in elution order:

2,8-Dimethyl-3-trinitromethyldibenzofuran (**11**), m.p. 102-104 °C (decomp.) (Insufficient for elemental analysis. Found: *MH*<sup>+</sup>-NO<sub>2</sub> 300.074 67. C<sub>15</sub>H<sub>12</sub>N<sub>2</sub>O<sub>5</sub> requires 300.074 62). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.34 (s, 2-Me), 2.53 (s, 8-Me), 7.40 (dd, *J*<sub>H7,H6</sub> 8.8 Hz, *J*<sub>H7,H9</sub> 2.5 Hz, H7), 7.50 (d, *J*<sub>H6,H7</sub> 8.8 Hz, H6), 7.56 (s, H4), 7.79 (s, H9), 7.94



Scheme 1.

(s, H1). Nuclear Overhauser experiments gave the following results: irradiation at  $\delta$  2.34 gave an enhancement of  $\delta$  7.94 (7.6%); irradiation at  $\delta$  2.53 gave enhancements at  $\delta$  7.40 (3.4%) and at  $\delta$  7.78 (7.2%); irradiation at  $\delta$  7.94 gave an enhancement at  $\delta$  2.34 (2.1%).

**2,8-Dimethyl-3-nitrodibenzofuran (12)**, m.p. 162–164 °C (Insufficient for elemental analysis. Found:  $M^+$  241.073 86. C<sub>14</sub>H<sub>11</sub>NO<sub>2</sub> requires 241.073 89). IR:  $\nu_{\max}$  (CHCl<sub>3</sub>) 1524 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.52 (s, 8-Me), 2.74 (s, 2-Me), 7.36 (dd,  $J_{H7,H6}$  8.3 Hz,  $J_{H7,H9}$  2.0 Hz, H7), 7.48 (s,  $J_{H6,H7}$  8.3 Hz, H6), 7.76 (br s, H9), 7.81 (s, H1), 8.21 (s, H4). Nuclear Overhauser experiments gave the following results: irradiation at  $\delta$  2.74 gave an enhancement at  $\delta$  7.81 (6.1%); irradiation at  $\delta$  7.81 gave an enhancement at  $\delta$  2.74 (1.3%).

The products 13 and 14 were isolated from a similar product mixture to the above by HPLC and gave in elution order:

**2,8-Dimethyl-4-nitrodibenzofuran (13)**, m.p. 161–164 °C (Insufficient for elemental analysis. Found:  $M^+$  241.073 45. C<sub>14</sub>H<sub>11</sub>NO<sub>3</sub> 241.073 89). IR:  $\nu_{\max}$  (CHCl<sub>3</sub>) 1531 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.53, 2.59 (each s, 2-, 8-Me), 7.36 (dd,  $J_{H7,H6}$  8.8 Hz,  $J_{H7,H9}$  1.5 Hz, H7), 7.60 (d,  $J_{H6,H7}$  8.8 Hz, H6), 7.74 (br s, H3), 8.01 (br s, H1), 8.08 (d,  $J_{H9,H7}$  1.5 Hz, H9).

**t-4-Hydroxy-2,8-dimethyl-r-3-trinitromethyl-3,4-dihydrodibenzofuran (14)**, as an oil containing traces of hexane. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.78 (br s, 2-Me), 2.36 (s, 8-Me), 4.06 (br s, OH), 4.75 (br s, H3), 5.44 (br s, H4), 6.06 (br s, H1), 6.83 (d,  $J_{H6,H7}$  8.3 Hz, H6), 7.16 (m, H7 and H9). Nuclear Overhauser experiments gave the following results: irradiation at  $\delta$  2.36 gave an enhancement at  $\delta$  7.16 (4.7%); irradiation at  $\delta$  4.75 gave enhancements at  $\delta$  1.78 (0.5%) and at  $\delta$  5.44 (2.5%); irradiation at  $\delta$  5.44 gave an enhancement at  $\delta$  4.75 (3.7%); irradiation at  $\delta$  6.06 gave enhancements at  $\delta$  1.78 (1.4%) and at  $\delta$  7.16 (1.3%). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  50.4 (C3), 66.2 (C4), 110.6 (C6), 131.4 (C1), the remainder of the signals being obscured in a weak spectrum; these assignments were confirmed by reverse detected heteronuclear correlation spectra (HMQC).

**Photochemistry of 2,8-dimethyldibenzofuran (9) in dichloromethane at -20 °C.** Reaction of 9-tetranitromethane in dichloromethane at 20 °C, as above, for 2 h resulted in partial conversion (48%) into 3-trinitromethyldibenzofuran (11) (13%), 3-nitro-

dibenzofuran (12) (64%), 4-nitrodibenzofuran (13) (4%), 4-hydroxy-3-trinitromethyl adduct (14) (0.5%) and unidentified compounds (total 18%) (Table 1).

**Photochemistry of 2,8-dimethyldibenzofuran (9) in acetonitrile at 20 °C.** Reaction of 9-tetranitromethane in acetonitrile at 20 °C, as above, for 2 h resulted in partial conversion (ca. 30%) (<sup>1</sup>H NMR spectra) into trinitromethyldibenzofuran (11) (2%), 3-nitrodibenzofuran (12) (83%), 4-nitrodibenzofuran (13) (6%) and unidentified compounds (total 9%) (Table 1).

**Photochemistry of 2,8-dimethyldibenzofuran (9) in HFP at 20 °C.** Reaction of 9-tetranitromethane in HFP at 20 °C, as above, for 8 h resulted in partial conversion (ca. 78%) (<sup>1</sup>H NMR spectra) into 3-trinitromethyldibenzofuran (11) (2%), 3-nitrodibenzofuran (12) (91%), and 4-nitrodibenzofuran (13) (5%) (Table 1).

**General procedure for the photonitration of 1,3,7,9-tetramethyldibenzofuran (10) with tetranitromethane.** A solution of 10 (500 mg, 0.28 mol dm<sup>-3</sup>) and tetranitromethane (0.56 mol dm<sup>-3</sup>) in dichloromethane at 20 or -20 °C, in dichloromethane containing trifluoroacetic acid (0.8 M) at 20 °C, in acetonitrile at 20 °C, or in HFP at 20 °C was irradiated with filtered light ( $\lambda_{\text{cut-off}}$  435 nm). Aliquots were withdrawn from each reaction mixture at appropriate time intervals, the volatile material removed under reduced pressure at  $\leq 0$  °C, and the product composition of each sample determined by NMR spectral analysis (Table 2).

**Photochemistry of 1,3,7,9-tetramethyldibenzofuran (10) in dichloromethane at 20 °C and the identification of products (15–17).** Reaction of 10-tetranitromethane in dichloromethane at 20 °C, as above, for 3 h resulted in essentially complete conversion (<sup>1</sup>H NMR spectra) into 1,3,7,9-tetramethyl-2-nitrodibenzofuran (15) (84%), unidentified aromatic compounds (total 4%), and the epimeric nitro-trinitromethyl adducts (16) (10.5%) and (17) (1%) (Table 2). The products (15–17) were separated by HPLC and gave in elution order:

**1,3,7,9-Tetramethyl-2-nitro-dibenzofuran (15)**, isolated as a slightly impure (5%) solid. (Found for the major component;  $M^+$  269.105 48. C<sub>16</sub>H<sub>15</sub>NO<sub>3</sub> requires 269.105 19). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.39 (s, 3-Me), 2.45 (s, 7-Me), 2.75 (s, 1-Me), 2.82 (s, 9-Me), 6.94 (br s, H8), 7.18 (br s, H6), 7.20 (s, H4). Nuclear Overhauser experi-

ments gave the following results: irradiation at  $\delta$  2.39 gave an enhancement at 7.20 (8.0%); irradiation at  $\delta$  2.45 gave enhancements at  $\delta$  6.94 (4.6%) and at  $\delta$  7.18 (5.3%); irradiation at  $\delta$  2.82 gave an enhancement at  $\delta$  6.94 (8.5%); no signal enhancements were observed on irradiation at  $\delta$  2.75.

*1,3,7,9-Tetramethyl-r-1-nitro-t-4-trinitromethyl-1,4-dihydrodibenzofuran (16)*, m.p. 180°C (decomp.) (Insufficient for elemental analysis. No parent ion visible in mass spectrum under all operating conditions). IR:  $\nu_{\max}$  (CHCl<sub>3</sub>) 1603, 1529 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.01 (br s, 3-Me), 2.12 (s, 1-Me), 2.31, 2.42 (each s, 7-, 9-Me), 5.72 (br s, H4), 6.17 (dq,  $J_{\text{H2,3-Me}} \approx 1.5$  Hz,  $J_{\text{H2,H4}} \approx 1.5$  Hz, H2), 6.94, 7.17 (each br s, H6, H8). Nuclear Overhauser experiments gave the following results: irradiation at  $\delta$  5.72 gave an enhancement at  $\delta$  2.01 (0.6%); irradiation at  $\delta$  6.17 gave enhancements at  $\delta$  2.01 (1.2%) and at  $\delta$  2.12 (1.1%). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  45.1 (C4), 86.6 (C1), 128.1 (C3) and 134.4 (C2) were assigned by reverse detected heteronuclear correlation spectra (HMBC, HMQC).

*1,3,7,9-Tetramethyl-r-1-nitro-c-4-trinitromethyl-1,4-dihydrodibenzofuran (17)*, isolated only as an impure oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.11 (s, 1-Me), 2.23 (br s, 3-Me), 2.38, 2.42 (each s, 7-, 9-Me), 5.68 (br s, H4), 6.25 (dq,  $J_{\text{H2,3-Me}} \approx 1.5$  Hz,  $J_{\text{H2,H4}} \approx 1.5$  Hz, H2), 7.00, 7.31 (each br s, H6, H8). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  44.5 (C4), 133.8 (C2) were assigned by reverse detected heteronuclear correlation spectra (HMQC).

*Photochemistry of 1,3,7,9-tetramethyldibenzofuran (10) in dichloromethane at -20°C.* Irradiation of 10-tetranitromethane in dichloromethane at -20°C, as above, for 3 h resulted in essentially complete conversion (<sup>1</sup>H NMR spectra) into 1,3,7,9-tetramethyl-2-nitrobenzofuran (**15**) (63%), unidentified aromatic compounds (total 4%), and the epimeric nitro-trinitromethyl adducts (**16**) (29%) and (**17**) (3%) (Table 2).

*Photochemistry of 1,3,7,9-tetramethyldibenzofuran (10) in dichloromethane containing trifluoroacetic acid (0.8 M) at 20°C.* Irradiation of 10-tetranitromethane in dichloromethane containing trifluoroacetic acid (0.8 M) at 20°C, as above, for 5 h resulted in partial conversion (ca. 56%) (<sup>1</sup>H NMR spectra) into 1,3,7,9-tetramethyl-2-nitrodibenzofuran (**15**) (95%), and unidentified aromatic compounds (total 5%) (Table 2).

*Photochemistry of 1,3,7,9-tetramethyldibenzofuran (10) in acetonitrile at 20°C.* Reaction of 10-tetranitromethane in acetonitrile at 20°C, as above, for 2 h resulted in partial conversion (ca. 63%) (<sup>1</sup>H NMR spectra) into 1,3,7,9-tetramethyl-2-nitrodibenzofuran (**15**) (73%), unidentified aromatic compounds (total 4%), and the epimeric nitro-trinitromethyl adducts (**16**) (18%) and (**17**) (4.5%) (Table 2).

*Photochemistry of 1,3,7,9-tetramethyldibenzofuran (10) in HFP at 20°C.* Reaction of 10-tetranitromethane in HFP at 20°C, as above, for 5 h resulted in essentially complete conversion (<sup>1</sup>H NMR spectra) into 1,3,7,9-tetramethyl-2-nitrodibenzofuran (**15**).

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