Photochemical nitration by tetranitromethane. Part 36.[1] Adduct formation in the photochemical reactions of 4-fluoroanisole and 4-fluoro-3-methylanisole

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The photolysis of the charge transfer (CT) complex of tetranitromethane and 4-fluoroanisole 2 in dichloromethane at − 20 °C gives the epimeric 1-fluoro-4-methoxy-5-nitro-6-trinitromethylcyclohexa-1,3-dienes 8 and 9, the epimeric 1-fluoro-4-methoxy-3-nitro-6-trinitromethylcyclohexa-1,4-dienes 10 and 12, the epimeric 1-fluoro-4-methoxy-6-nitro-3-trinitromethylcyclohexa-1,4-dienes 11 and 13, a 1-fluoro-6-hydroxy-4-methoxy-3-trinitromethylcyclohexa-1,4-diene 14, together with 4-fluoro-2-trinitromethylanisole 3, 4-fluoro-2-nitroanisole 4 and 3-fluoro-6-hydroxy-5-nitrobenzoic acid 15. In acetonitrile at 20 or − 20 °C, only minor amounts of adducts 13 and 14 are formed, together with aromatic compounds 3, 4 and 16.

The photolysis of the CT complex of tetranitromethane and 4-fluoro-3-methylanisole 7 in dichloromethane at − 20 °C gives the epimeric 1-fluoro-4-methoxy-6-methyl-6-nitro-3-trinitromethyl-cyclo-hexa-1,4-dienes 23 and 24, 1-fluoro-4-methoxy-2-methyl-*r*-5-nitro-*c*-6-trinitromethylcyclohexa-1,3-diene 25 and predominantly 4-fluoro-5-methyl-2-trinitromethylanisole 19. In acetonitrile a similar reaction of 4-fluoro-3-methylanisole 7 gives only adduct 25, lesser amounts of the trinitromethyl compound 19 and increased amounts of 4-fluoro-5-methyl-2-nitroanisole 22. Photolysis reactions with tetranitromethane of either 2 or 7 in 1,1,1,3,3,3-hexafluoropropan-2-ol are slow and yield the nitroanisoles 4, or 20 and 22, respectively. X-Ray crystal structures are reported for 4-fluoro-5-methyl-2-trinitromethylanisole 19 and 4-fluoro-5-methyl-2-nitroanisole 22.

The photochemical addition of tetranitromethane (TNM) to aromatic compounds (ArH) by excitation of the ArH–TNM charge transfer (CT) complex by light matching the wavelength of the CT band has been shown[2] to occur by recombination of a triad consisting of $ArH^{\cdot +}$, trinitromethanide ion, and nitrogen dioxide, eqn. (1). The first chemical step which occurs, leading

$$\underset{\text{CT complex}}{ArH \cdots C(NO_2)_4} \longrightarrow \underset{\text{Triad}}{ArH^{\cdot +}\ (O_2N)_3C^-\ NO_2} \qquad (1)$$

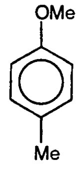
to the formation of adducts, is reaction between $ArH^{\cdot +}$ and trinitromethanide ion [eqn. (2)] to give a carbon radical which

$$ArH^{\cdot +} + (O_2N)_3C^- \longrightarrow Ar(H)C(NO_2)_3^{\cdot} \qquad (2)$$

then reacts with nitrogen dioxide to give adducts [eqn. (3)].[2]

$$Ar(H)C(NO_2)_3^{\cdot} + NO_2 \longrightarrow \text{Adducts} \qquad (3)$$

Recently we demonstrated that the solvent-dependent products, including nitro–trinitromethyl adducts, from the photochemical reaction of 4-methylanisole 1 and tetranitromethane arise as a consequence of solvent-induced variation in the regiochemistry of trinitromethanide ion attack on the radical cation of 4-methylanisole.[3] In dichloromethane solution, particularly at ambient temperatures, the attack of trinitromethanide ion occurs predominantly at C-2 in the radical cation of 4-methylanisole. At lower temperatures, and more dramatically, either on the addition of $Bu_4N^+ClO_4^-$ (0.2 mol dm^{-3}) to the dichloromethane reaction medium, or on changing to the more polar acetonitrile as the reaction solvent, the lowered reactivity of the trinitromethanide ion resulted in extensive, if not exclusive, reaction *ipso* to the methoxy group.[3]



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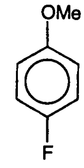

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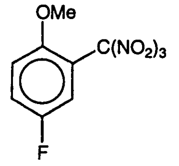

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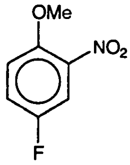

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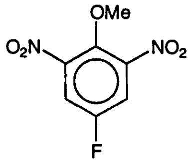

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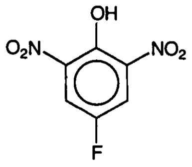

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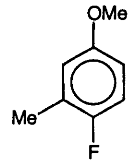

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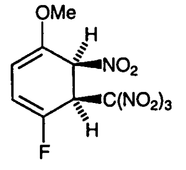
In 1987 Kochi *et al.* reported[4] the photochemical reaction of the CT complex of 4-fluoroanisole 2 and TNM in dichloromethane solution to give substantially 4-fluoro-2-trinitromethylanisole 3 (72%) together with 4-fluoro-2-nitroanisole 4 (9%) and 4-fluoro-2,6-dinitroanisole 5 (6%) as minor products. In contrast, in acetonitrile solution photolysis of the CT complex was reported to yield mainly 4-fluoro-2-nitroanisole 4 (83%) in addition to 4-fluoro-2,6-dinitrophenol 6 (14%). This pattern of product formation is broadly parallel to that found for the reactions of 4-methylanisole 1.[3] Although the presence of transient olefinic products was detected, these were not isolated.[4]

As part of our continuing study of the photolysis reactions of CT complexes of aromatic compounds with tetranitromethane,[5] we have re-examined these reactions of 4-fluoroanisole 2, and extended the study to similar reactions of 4-fluoro-3-methylanisole 7. In the event, six nitro–trinitromethyl adducts 8–13 and a hydroxy–trinitromethyl adduct 14 were isolated from reactions of 4-fluoroanisole 2, and three labile nitro–trinitro-

Table 1 Overview of yields of products from the photolysis of 4-fluoroanisole **2** (0.5 mol dm^{-3}) and tetranitromethane (1.0 mol dm^{-3}) in dichloromethane

	Yield (%)												
t/h	**8**	**9**	**10**	**11**	**12**	**13**	**14**	Unknown adducts	**3**	**4**	**15**	**16**	Unknown aromatics
at 20 °C													
1	1.3	—	5.9	20.0	1.5	17.2	10.0	11.8	22.6	1.6	3.3	—	4.6
2	1.3	—	4.7	17.5	1.3	15.8	9.0	13.4	26.0	1.8	3.5	—	6.0
3	0.6	—	6.4	17.7	2.0	15.3	6.8	7.7	33.8	2.0	2.9	—	4.8
at −20 °C													
1	1.4	—	5.8	17.4	1.9	19.1	9.2	16.9	18.6	2.6	1.8	—	5.4
2	1.5	Trace	6.0	16.6	1.5	20.3	8.7	19.5	17.0	2.3	1.5	—	4.9
3	1.2	Trace	6.1	19.0	1.2	19.0	7.6	19.2	16.5	2.3	1.5	—	6.4
at −78 °C													
1	4.3	—	2.7	17.4	2.9	17.9	8.7	9.6	25.1	5.8	—	—	5.6
2	4.5	Trace	4.2	16.7	3.1	19.2	8.6	7.9	24.7	4.2	1.1	—	5.8
4	5.7	Trace	4.2	15.9	3.2	20.2	6.9	7.4	24.8	3.2	1.3	—	7.2



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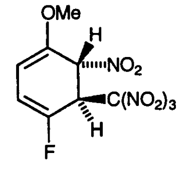

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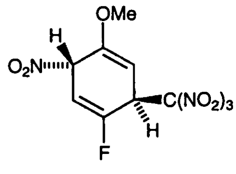

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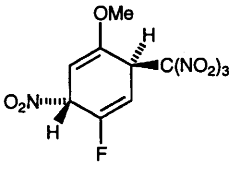

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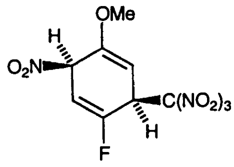

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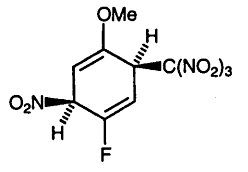

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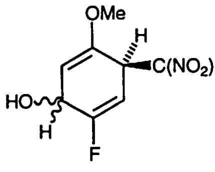

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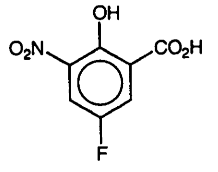

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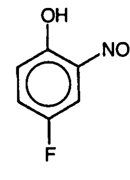

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methyl adducts were identified from their spectroscopic data in product mixtures from reactions of 4-fluoro-3-methylanisole **7**. We now report the results of this study.

Results

General

The photochemical experiments were performed with filtered light (cut-off 435 nm, 5 cm water IR-filter, from a 300 W incandescent lamp) as described previously,[6] and small samples were withdrawn for analysis at suitable intervals. The work-up procedure, involving evaporation of solvent and excess TNM, was conducted at ⩽0 °C. The crude product mixtures were stored at −78 °C and were analysed (^{1}H NMR spectroscopy, see Experimental section; Tables 1–4) as soon as possible.

Photochemistry of 4-fluoroanisole 2 in dichloromethane at −20 °C and the identification of adducts 8–14 and aromatic compounds 3, 4 and 15

A solution of 4-fluoroanisole **2** (0.5 mol dm^{-3}) and tetranitromethane (1.0 mol dm^{-3}) in dichloromethane was irradiated at −20 °C. The composition of the mixture was monitored as above (Table 1). The final solution (after 3 h) after work-up contained the nitro–trinitromethyl adducts **8** (1%), **9** (trace), **10** (6%), **11** (19%), **12** (1%) and **13** (19%), hydroxy–trinitromethyl adduct **14** (8%), unidentified adducts (total 19%), aromatic compounds **3** (17%), **4** (2%) and **15** (1.5%) and unidentified aromatic compounds (total 6%). These products were separated partially by HPLC on a cyanopropyl column using hexane–dichloromethane mixtures as the eluting solvents. The order of elution of materials from the HPLC column is given in the Experimental section, but here for simplicity the evidence for structural assignments will be presented for groups of products.

Epimeric 1-fluoro-4-methoxy-5-nitro-6-trinitromethyl-cyclohexa-1,3-dienes 8 and 9. These adducts **8** and **9** were isolated only in low yield and always in admixture with other minor compounds, and their structures were assigned on the basis of their NMR spectra. The connectivity in each adduct was established from a consideration of the results of nuclear Overhauser experiments coupled with reverse detected heteronuclear correlation spectra (HMQC). For adduct **8** a satisfactory partial ^{13}C NMR spectrum could be obtained, but for **9** the ^{13}C NMR resonances of the protonated carbon atoms C-3, C-5 and C-6 were determined indirectly *via* the HMQC heteronuclear correlation spectrum. The relative stereochemistry of **8** and **9** was assigned on the basis of the coupling constants, $J_{H5,H6}$. For the *cis*-isomer **8** this coupling constant was 5.4 Hz consistent with a H–C–C–H torsional angle of *ca.* 50°, while the *trans*-isomer **9** exhibited a small coupling constant (probably 0–1 Hz) corresponding to a torsional angle approaching 80°. These torsional angles are consistent with the results of an inspection of Dreiding models for the two adducts.

A notable feature of the results of nuclear Overhauser experiments on adducts **8** and **9** was the marked difference in the signal enhancements observed. For the *r*-5-nitro-*c*-trinitromethyl adduct **8** irradiation of the -OMe signal (δ 3.66) resulted in an enhancement (9.3%) of the signal due to the $CH\text{-}NO_2$ proton (δ 4.68), while similar irradiation of the -OMe signal (δ 3.72) for the *r*-5-nitro-*t*-6-trinitromethyl adduct **9**

Table 2 Overview of yields of products from the photolysis of 4-fluoroanisole **2** (0.5 mol dm^{-3}) and tetranitromethane (1.0 mol dm^{-3}) in acetonitrile

	Yield (%)												
t/h	**8**	**9**	**10**	**11**	**12**	**13**	**14**	Unknown adducts	**3**	**4**	**15**	**16**	Unknown aromatics
at 20 °C													
1	—	—	—	—	—	1.1	—	3.1	8.1	61.3	—	14.5	11.9
2	—	—	—	—	—	—	—	—	4.3	62.2	—	23.0	10.4
at −20 °C													
1	—	—	—	—	—	4.4	3.1	12.3	16.2	33.9	—	24.0	6.1
2	—	—	—	—	—	3.5	2.2	8.7	16.8	39.9	—	20.2	9.7

Table 3 Overview of yields of products from the photolysis of 4-fluoro-3-methylanisole **7** (0.45 mol dm^{-3}) and tetranitromethane (0.9 mol dm^{-3}) in dichloromethane

	Yield (%)										
t/h	**17**	**18**	**19**	**20**	**21**	**22**	Unknown aromatics	**23**	**24**	**25**	Unknown adducts
at 20 °C											
2	2.5	—	61.8	—	0.3	7.6	5.0	13.9	1.3	2.0	5.6
4	2.8	0.5	64.9	3.4	3.4	11.3	2.0	9.1	—	0.2	2.3
6	2.6	1.4	64.0	5.2	5.9	12.3	2.0	4.2	—	—	2.5
at −20 °C											
2	Trace	—	45.3	Trace	Trace	5.4	5.1	18.2	11.8	6.8	7.3
4	0.8	—	53.8	1.0	Trace	5.4	5.4	18.6	8.6	6.2	—
6	1.6	—	61.5	3.0	Trace	6.9	5.2	15.0	1.6	4.8	—
at −78 °C											
2	6.7	—	36.8	5.9	1.9	22.6	2.4	6.1	3.5	11.7	2.4
4	6.5	—	24.3	10.0	1.9	35.3	0.8	4.2	1.2	14.9	0.8
6	6.1	—	23.1	9.8	3.1	39.3	—	3.3	—	12.9	2.3

Table 4 Overview of yields of products from the photolysis of 4-fluoro-3-methylanisole **7** (0.45 mol dm^{-3}) and tetranitromethane (0.9 mol dm^{-3}) in acetonitrile

	Yield (%)										
t/h	**17**	**18**	**19**	**20**	**21**	**22**	Unknown aromatics	**23**	**24**	**25**	Unknown adducts
at 20 °C											
4	9.5	4.0	7.3	19.1	10.9	45.5	—	—	—	3.6	0.2
6	8.3	4.8	6.8	19.7	13.3	44.2	—	—	—	2.0	0.8
at −20 °C											
4	11.6	—	18.4	15.2	5.1	32.4	9.5	—	—	6.2	1.7
6	12.7	—	17.0	13.9	3.0	32.0	9.5	—	—	9.1	1.7
at −50 °C											
4	6.0	Trace	13.3	14.0	3.2	37.6	2.2	—	—	23.7	—
6	7.7	Trace	11.2	13.5	2.9	36.7	1.9	—	—	26.1	—

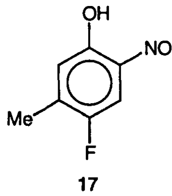
resulted in an enhancement (10.4%) of the signal due to the C(OMe)=C*H* proton (δ 5.17). It appears that this effect reflects the preferential alignment of a doubly-occupied orbital on the methoxy oxygen atom with the C-5–NO_2 bond, coupled with the minimization of non-bonded steric interactions.

On brief storage in [^{2}H]chloroform the *cis*-isomer **8** was partially converted into a mixture of its epimer **9** and 4-fluoro-2-nitroanisole **4**, the latter arising by loss of nitroform. The isomerization mechanism is not known, but in principle it could involve a radical C–NO_2 bond cleavage/re-formation or a heterolytic C–$C(NO_2)_3$ bond cleavage/re-formation—if the latter possibility is operative it would point to the elimination of nitroform occurring *via* an E1 mechanism. The half-lives of **8** and **9** in [^{2}H]chloroform were estimated to be < 1 h at 22 °C.

Epimeric 1-fluoro-4-methoxy-6-nitro-3-trinitromethylcyclohexa-1,4-dienes 11 and 13, and 6-hydroxy-3-trinitromethylcyclohexa-1,4-diene 14. The nitro–trinitromethyl adducts **11** and **13** were the major adducts formed in the photolysis reaction in dichloromethane at −20 °C but proved to be too labile in solution for their crystallization or complete purification by HPLC. The connectivity in each adduct was established from a consideration of the results of nuclear Overhauser experiments coupled with reverse detected heteronuclear correlation spectra (HMQC) and the observed $J_{H,F}$ coupling constants. It was not possible to define the relative stereochemistry of **11** and **13** by spectroscopic means, but this assignment was made on the basis of the known order of elution from a cyanopropyl HPLC column using hexane–dichloromethane mixtures, *i.e.* that *r*-6-nitro-*t*-3-trinitromethylcyclohexa-1,4-diene **11** is eluted before *r*-6-nitro-*c*-3-trinitromethylcyclohexa-1,4-diene **13**.[5,7]

The half-lives of **11** and **13** in [^{2}H]chloroform were estimated to be 2–3 h at 22 °C.

The connectivity of the 6-hydroxy-3-trinitromethyl adduct **14** was also established from a consideration of its spectroscopic data (Experimental section). Adduct **14** also proved to be too labile to allow crystallization to be effective, and consequently the stereochemistry of this adduct could be neither determined nor otherwise assigned.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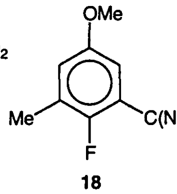
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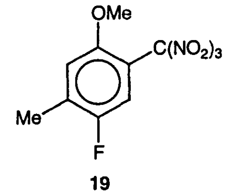
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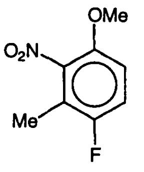
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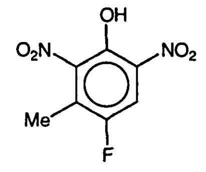
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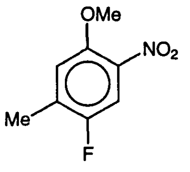
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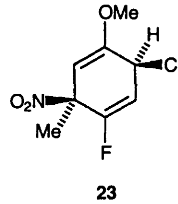
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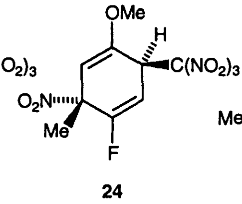
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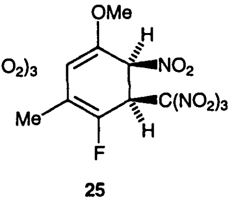
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Epimeric 1-fluoro-4-methoxy-3-nitro-6-trinitromethylcyclohexa-1,4-dienes 10 and 12. The epimeric 3-nitro-6-trinitromethyl adducts **10** and **12** were insufficiently stable to allow complete purification and impure adduct **10** could be obtained only in low yield. Consequently, the obtainable spectroscopic data for adduct **12** were more complete and the connectivity in that compound was established from the results of nuclear Overhauser experiments and reverse detected heteronuclear correlation spectra (HMQC). For the epimeric adduct **10** only ^{1}H NMR spectra and the results of limited nuclear Overhauser experiments could be obtained. However, these data appear sufficient to assign adducts **10** and **12** as epimers. The assignment of stereochemistry to these two adducts **10** and **12** was made, as for the regioisomeric pair of adducts **11** and **13** above, on the basis of the elution order, *i.e.* that *r*-3-nitro-*t*-6-trinitromethylcyclohexa-1,4-diene **10** is eluted before *r*-3-nitro-*c*-6-trinitromethylcyclohexa-1,4-diene **12**.[5,7]

The half-lives of **10** and **12** in [^{2}H]chloroform were estimated to be 2–3 h at 22 °C.

Aromatic compounds 3, 4 and 15. 2-Trinitromethylanisole **3**[4] and 2-nitroanisole **4**[8] were identified by comparison of their ^{1}H NMR spectra with literature data. The assignment of structure to 3-fluoro-6-hydroxy-5-nitrobenzoic acid **15**, recovered only in low yield, was based on its mass spectrum and its ^{1}H NMR spectrum which pointed to a tetrasubstituted benzene structure with the unsubstituted ring positions flanking the fluorine substituent.

Photochemistry of 4-fluoroanisole 2 in acetonitrile at 20 °C and identification of nitrophenol 16

A solution of 4-fluoroanisole **2** (0.5 mol dm^{-3}) and tetranitromethane (1.0 mol dm^{-3}) in acetonitrile was irradiated at 20 °C. The composition of the mixture was monitored by withdrawing samples for NMR spectral analysis (Table 2). The final solution (after 2 h) after work-up contained 4-fluoro-2-trinitromethylanisole **3** (4%), 4-fluoro-2-nitroanisole **4** (62%), 4-fluoro-2-nitrophenol **16** (23%) and unidentified aromatic compounds (total 10%). The 4-fluoro-2-nitrophenol **16** was separated by chromatography on a silica gel Chromatotron plate and identified by comparison of its ^{1}H NMR spectrum with literature data.[9]

Photochemistry of 4-fluoroanisole 2 in dichloromethane at 20 or −78 °C

Photolysis of the CT complex of 4-fluoroanisole–tetranitromethane in dichloromethane at 20 °C (3 h) or at −78 °C (4 h), as above, gave mixtures of products, the composition of which was determined by ^{1}H NMR spectral analysis and is summarized in Table 1.

Photochemistry of 4-fluoroanisole 2 in acetonitrile at −20 °C

Photolysis of the CT complex of 4-fluoroanisole–tetranitromethane in acetonitrile for 2 h at −20 °C, as above, gave mixtures of products, the composition of which was determined by ^{1}H NMR spectral analysis and is summarized in Table 2.

Photochemistry of 4-fluoroanisole 2 in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) at 20 °C

Photolysis of the CT complex of 4-fluoroanisole–tetranitromethane in HFP for 5 h at 20 °C, as above, resulted in an 18% conversion exclusively into 4-fluoro-2-nitroanisole **4**. A control experiment established that the thermal reaction between **2** (0.5 mol dm^{-3}) and NO_2 (*ca.* 0.4 mol dm^{-3}) in HFP at 20 °C gave a 55% conversion into exclusively **4** in 1 h.

Photochemistry of 4-fluoroanisole 2 at 20 °C in dichloromethane containing trifluoroacetic acid (0.7 mol dm^{-3})

Photolysis of the CT complex of 4-fluoroanisole–tetranitromethane in dichloromethane containing trifluoroacetic acid (0.7 mol dm^{-3}) for 2 h at 20 °C, as above, resulted in a 29% conversion into predominantly 4-fluoro-2-trinitromethylanisole **3** (25%) and 4-fluoro-2-nitroanisole **4** (48%), together with lesser amounts of adducts **8** (5%), **10** (2%), **11** (2%), **12** (1%) and **13** (8%), aromatic compounds **15** (trace) and **16** (2%) and unidentified aromatic compounds (total 7%).

Photochemistry of 4-fluoro-3-methylanisole 7 in dichloromethane at 20 °C and identification of aromatic compounds 17–22

Photolysis of the CT complex of 4-fluoro-3-methylanisole–tetranitromethane in dichloromethane at 20 °C, as above, for 6 h resulted in a partial conversion (*ca.* 75%) into a mixture of 4-fluoro-5-methyl-2-nitrophenol **17** (3%), 4-fluoro-5-methyl-3-trinitromethylanisole **18** (1%), 4-fluoro-5-methyl-2-trinitromethylanisole **19** (64%), 4-fluoro-3-methyl-2-nitroanisole **20** (5%), 4-fluoro-3-methyl-2,6-dinitrophenol **21** (6%), 4-fluoro-5-methyl-2-nitroanisole **22** (12%), nitro–trinitromethyl adduct **23** (4%) and unidentified adducts (total 2%). The aromatic compounds were separated by chromatography on a silica gel Chromatotron plate. Compounds **17**, **18**, **20** and **21** were isolated only in low yield and characterized from their mass spectra and ^{1}H NMR spectra. The structures of compounds **19** and **22** were determined by single crystal X-ray analysis. For each compound, **19** and **22**, the spectroscopic data were in accord with the established structure.

In the solid state the conformations of the methoxy group and trinitromethyl group for trinitromethyl compound **19** are defined by the torsional angles, C(3)–C(4)–O(4)–C(8), 18.8(3)° and C(6)–C(5)–C(9)–N(2), −169.6(2)°. The conformation of the trinitromethyl group is presumably largely determined by steric interactions with the adjacent methoxy group.

For 4-fluoro-5-methyl-2-nitroanisole **22** the structure consists of two crystallographically independent molecules. The differences between the two molecules lie in the conformations of the nitro and methoxy functions [molecule 1: C(4)–C(3)–N(1)–O(12), −21.8(6)°, C(5)–C(4)–O(4)–C(7), −2.1(6)°; corresponding data for molecule 2: −38.6(6)° and 2.5(6)°]. These differences are not chemically significant.

Photochemistry of 4-fluoro-3-methylanisole 7 in dichloromethane at −20 °C and identification of nitro–trinitromethyl adducts 23 and 24

Photolysis of the CT complex of 4-fluoro-3-methylanisole–

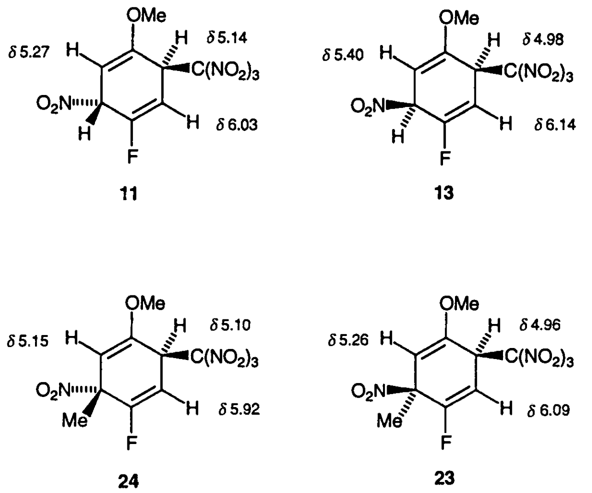


Fig. 1 ^{1}H NMR spectroscopic data for nitro–trinitromethyl adducts **11**, **13**, **23** and **24**

tetranitromethane in dichloromethane at −20 °C, as above, for 6 h resulted in a partial conversion (*ca.* 73%) into a mixture of 4-fluoro-5-methyl-2-nitrophenol **17** (2%), 4-fluoro-5-methyl-2-trinitromethylanisole **19** (62%), 4-fluoro-3-methyl-2-nitroanisole **20** (3%), 4-fluoro-5-methyl-2-nitroanisole **22** (7%) and nitro–trinitromethyl adducts **23** (15%), **24** (5%) and **25** (2%). None of the adducts could be isolated by HPLC on a cyanopropyl column even at −20 °C and consequently the nitro–trinitromethyl adducts **23**–**25** were identified by spectroscopic studies on mixtures of products. The spectroscopic data for the major nitro–trinitromethyl adduct, 1-fluoro-4-methoxy-6-methyl-*c*-6-nitro-*r*-3-trinitromethylcyclohexa-1,4-diene **23**, are more complete and are consistent with the assigned connectivity. The connectivity in the epimeric nitro–trinitromethyl adduct **24**, and the stereochemistry of the pair of adducts **23** and **24**, were established by comparison of the ^{1}H NMR spectra for the epimeric nitro–trinitromethyl adducts **11** and **13**, and the data for adducts **23** and **24** (Fig. 1). In such structures, the steric requirements of the trinitromethyl group will be dominant,[7] and it is therefore a reasonable expectation that the introduction of the methyl substituent in adducts **23** and **24** will have only a limited effect on the conformations of these molecules. This underlying assumption is apparently validated by the systematic ^{1}H NMR chemical shift differences between the methylated and non-methylated pairs of compounds. In particular, for the *c*-6-nitro-*r*-3-trinitromethyl adducts **13** and **23** the signal due to H-2 appears downfield (Δδ 0.11–0.17), the signal due to H3 appears upfield (Δδ 0.14–0.16), and the signal due to H-5 appears downfield (Δδ 0.11–0.13) of the corresponding signals for the *t*-6-nitro-*r*-3-trinitromethyl adducts **11** and **24**. If the stereochemical assignments of the non-methylated adducts **11** and **13** (see above) are accepted, it appears that the stereochemical assignments of the epimeric 6-methyl derivatives **23** and **24** follow.

The half-life of **23** was 2–3 h in [^{2}H]chloroform at 22 °C; adducts **24** and **25** were present in so small amounts that no estimate of their half-lives could be made.

Photochemistry of 4-fluoro-3-methylanisole 7 in acetonitrile at −20 °C and identification of nitro–trinitromethyl adduct 25

Photolysis of the CT complex of 4-fluoro-3-methylanisole–tetranitromethane in acetonitrile at −20 °C, as above, for 6 h resulted in a partial conversion (*ca.* 72%) into a mixture of 4-fluoro-5-methyl-2-nitrophenol **17** (13%), 4-fluoro-5-methyl-2-trinitromethylanisole **19** (17%), 4-fluoro-3-methyl-2-nitroanisole **20** (14%), 4-fluoro-3-methyl-2,6-dinitrophenol **21** (3%), 4-fluoro-5-methyl-2-nitroanisole **22** (32%), unidentified aromatic compounds (total 9%), nitro–trinitromethyl adduct **25** (9%) and unidentified adducts (total 2%).

The connectivity in the nitro–trinitromethyl adduct **25** was established by a consideration of the results of nuclear Overhauser experiments and reverse detected heteronuclear correlation spectra, the latter which allowed the identification of the ^{13}C NMR resonances to the protonated carbons, C-3, C-5 and C-6. The *r*-5-nitro-*c*-6-trinitromethyl stereochemistry was assigned to adduct **25** on the basis of the result of the nuclear Overhauser experiment involving the irradiation of the methoxy ^{1}H NMR signal. For adduct **25** irradiation at δ 3.61 (OMe signal) resulted in an enhancement (12.0%) of the signal due to H-5 (δ 4.66), as for the non-methylated *r*-5-nitro-*c*-6-trinitromethyl adduct **8** above; in contrast, the non-methylated *r*-5-nitro-*t*-6-trinitromethyl adduct **9** gave an enhancement of the signal due to H-3 [δ 5.17 (10.4 %)] on irradiation at the frequency of the OMe signal (δ 3.72).

Photochemistry of 4-fluoro-3-methylanisole 7 in dichloromethane at −78 °C

Photolysis of the CT complex of 4-fluoro-3-methylanisole–tetranitromethane in dichloromethane for 6 h at −78 °C, as above, gave mixtures of products, the composition of which was determined by ^{1}H NMR spectral analysis and is summarized in Table 3.

Photochemistry of 4-fluoro-3-methylanisole 7 in acetonitrile at 20 or −50 °C

Photolysis of the CT complex of 4-fluoro-3-methylanisole–tetranitromethane in acetonitrile for 6 h at 20 or −50 °C, as above, gave mixtures of products, the composition of which was determined by ^{1}H NMR spectral analysis and is summarized in Table 4.

Photochemistry of 4-fluoro-3-methylanisole 7 in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) at 20 °C

Photolysis of the CT complex of 4-fluoro-3-methylanisole–tetranitromethane in HFP for 4 h at 20 °C, as above, resulted in a low conversion (*ca.* 18%) exclusively into 4-fluoro-3-methyl-2-nitroanisole **20** (26%) and 4-fluoro-5-methyl-2-nitroanisole **22** (74%). A control experiment established that the thermal reaction between **7** (0.45 mol dm^{-3}) and NO_2 (*ca.* 0.4 mol dm^{-3}) in HFP at 20 °C gave a 70% conversion into **20** (20%) and **22** (80%) after 1 h.

Photochemistry of 4-fluoro-3-methylanisole 7 at 20 °C in dichloromethane containing trifluoroacetic acid (0.7 mol dm^{-3})

Photolysis of the CT complex of 4-fluoro-3-methylanisole–tetranitromethane in dichloromethane containing trifluoroacetic acid (0.7 mol dm^{-3}) for 4 h at 20 °C, as above, resulted in a 47% conversion into predominantly 4-fluoro-3-methyl-2-nitroanisole **20** (18%) and 4-fluoro-5-methyl-2-nitroanisole **22** (60%), together with lesser amounts of aromatic compounds **17** (9%), **19** (6%), **21** (3%), and unidentified aromatic compounds (total 3%).

Redox properties of 4-fluoroanisole

Cyclic voltammetry of 4-fluoroanisole in dichloromethane–Bu_4NPF_6 showed an irreversible redox couple (at sweep rates, v, up to 50 V s^{-1}) with E_{pa} = 1.86 V (*vs.* Ag/AgCl). In HFP–Bu_4NPF_6, a solvent capable of stabilizing radical cations to an unprecedented degree (see below), reversibility ensued at $v > 2$ V s^{-1}, E_{rev} being 1.45 V *vs.* Ag/AgCl, ΔE_{pp} = 94 mV.

Attempts to monitor the formation of $2^{\cdot +}$ by EPR spectroscopy were made under the following conditions: photolysis with light of $\lambda > 430$ nm of a solution of **2** (0.17 mol dm^{-3}), tetranitromethane (0.55 mol dm^{-3}) and TFA (0.8 mol dm^{-3}) in dichloromethane at −60 and −70 °C; photolysis with light of $\lambda > 430$ nm of a solution of **2** (0.17 mol dm^{-3}) and tetranitromethane (0.55 mol dm^{-3}) in TFA at −15 °C; photolysis with light $\lambda > 430$ nm of a solution of **2** (0.17 mol dm^{-3}) and tetranitromethane (0.55 mol dm^{-3}) in TFA–HFP (3:2

v/v) at −15 °C; photolysis with light of $\lambda > 430$ nm of a solution of **2** (0.17 mol dm^{-3}) and tetranitromethane (0.55 mol dm^{-3}) in HFP at −3 °C. In spite of the use of long irradiation times (20 min) in combination with spectra accumulation (50 per run), no EPR signal was obtained under any of these conditions.

The thermal reaction between **2** (0.17–0.23 mol dm^{-3}) and a deficit of NO_2 (0.003–0.006 mol dm^{-3}) in HFP did not generate any EPR signal, nor was any signal detected upon Tl^{III} trifluoroacetate addition after 2 min from the start of the reaction.

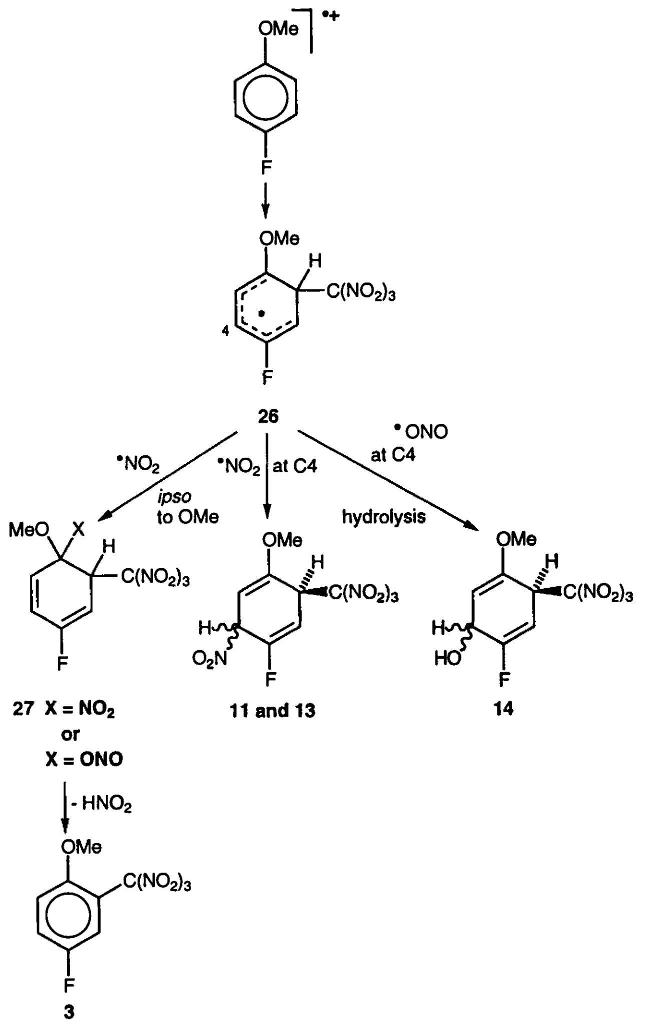
Discussion

Overview of the photolysis products from 4-fluoroanisole 2 in dichloromethane at 20, −20 and −78 °C

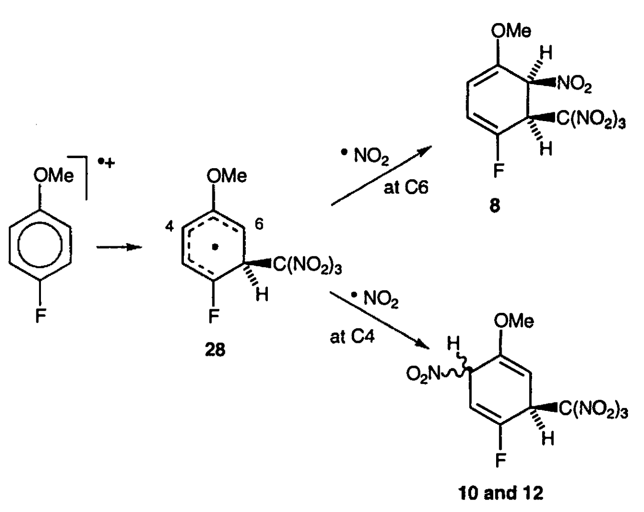
In dichloromethane at 20 °C six adducts, **8** and **10**–**14** were identified as products in addition to significant quantities of 4-fluoro-2-trinitromethylanisole **3** (Table 1). Of the six adducts **8** and **10**–**14**, adducts **11**, **13** and **14** contain a 2-trinitromethyl structural feature and their decomposition by loss of HNO_2 would be expected to augment the yield of 4-fluoro-2-trinitromethylanisole **3**; in the present study the total yields of adducts **11**, **13** and **14**, together with the amount of the 2-trinitromethyl compound **3** isolated, would account for the yield (73%) of compound **3** reported earlier by Kochi *et al.*[4] It is interesting to speculate that the loss of nitroform by decomposition from the three 3-trinitromethyl adducts **8**, **10** and **12** would augment the yield of 4-fluoro-2-nitroanisole **4**, thus accounting for the yield of that compound reported earlier.[4]

Attack of trinitromethanide ion at the 2-position of the 4-fluoroanisole radical cation would give the delocalized carbon radical **26**, the stability of which would be enhanced by the position of the methoxy group (Scheme 1). Attack of nitrogen dioxide at C-4 in this delocalized carbon radical with C–N bond formation would yield adducts **11** and **13**; the alternative C–O mode of bond formation by nitrogen dioxide followed by hydrolysis, either on work-up or in the prevailing reaction conditions, would give the hydroxy–trinitromethyl adduct **14**. Although the possibility of the formation of some 4-fluoro-2-trinitromethylanisole **3** by decomposition of adducts **11**, **13** and **14** cannot be excluded, it appears likely that much of the 4-fluoro-2-trinitromethylanisole **3** isolated in the present study from reactions in dichloromethane arises by decomposition during the photolysis reaction of the sterically compressed diene **27** (where X = NO_2 or ONO). This diene **27** would be formed by attack of nitrogen dioxide on the delocalized carbon radical at C-6 *ipso* to the methoxy group (Scheme 1).

The modes of formation of the 3-trinitromethyl adducts **8**, **10** and **12** are less certain. It is possible that these adducts are formed *via* initial attack of trinitromethanide ion at C-3 in the 4-fluoroanisole radical cation to give the delocalized carbon radical **28**. Subsequent radical coupling of nitrogen dioxide with this delocalized carbon radical at C-4 would give the epimeric adducts **10** and **12**, while coupling at C-6 would give adduct **8** (Scheme 2). However, recently we have reported allylic rearrangements involving the migration of sterically compressed trinitromethyl groups in a series of nitro–trinitromethyl adducts.[5,10] In the present context, allylic rearrangement of the trinitromethyl group in the sterically compressed adduct **29** would yield the 6-nitro-3-trinitromethyl adducts **10** and **12**, while an apparent homoallylic rearrangement would give adduct **8** (Scheme 3). The labile adduct **29** could arise by initial attack of trinitromethanide ion *ipso* to the methoxy group in the 4-fluoroanisole radical cation, followed by radical coupling with nitrogen dioxide at C-2 in the delocalized carbon radical **30**. Recently, we have postulated such a reaction sequence to account for some products formed in the photolysis of the CT complex of 4-methylanisole and tetranitromethane.[3]



Scheme 1

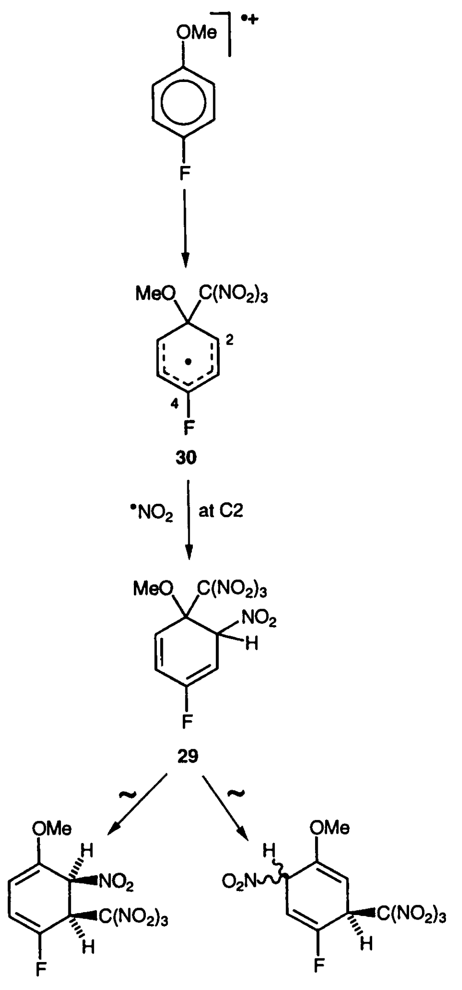


Scheme 2

Overview of the photolysis products from 4-fluoroanisole 2 in acetonitrile at 20 and −20 °C

The trinitromethyl derivatives isolated from photolysis reactions of 4-fluoroanisole **2** in acetonitrile were limited to the 2-trinitromethyl adducts **13** and **14**, and 4-fluoro-2-trinitromethylanisole **3**. The formation of these three compounds implies that trinitromethanide ion is capable of attacking the radical cation of 4-fluoroanisole at C-2 (*cf.* Scheme 1).

As found previously in the analogous photolysis reactions of 4-methylanisole **1** with tetranitromethane,[3] the yields of the 2-

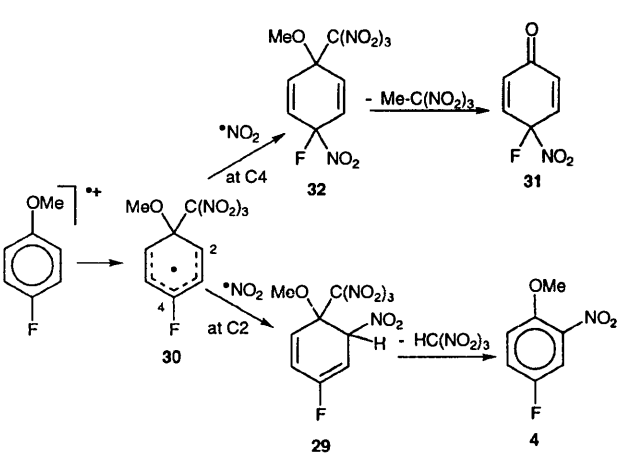


Scheme 3

nitro derivative **4** were considerably higher in acetonitrile than in the corresponding reactions in dichloromethane. Furthermore, the isolation of 4-fluoro-2-nitrophenol **16** supports the detection of 4-fluoro-4-nitrocyclohexa-2,5-dienone **31** in product mixtures. Although the reaction data are less compelling for the reactions in acetonitrile of 4-fluoroanisole **2**, compared with those of 4-methylanisole **1**,[3] it is believed that the nitro dienone **31** (and thence the 4-fluoro-2-nitrophenol **16** by homolytic rearrangement)[11] and much of the 4-fluoro-2-nitroanisole **4** are formed *via* the delocalized carbon radical **30** (Scheme 4). Radical coupling of nitrogen dioxide at C-4 of the delocalized carbon radical **30** would give the diene **32**, which on the loss of the elements of $MeC(NO_2)_3$ would yield the nitro dienone **31**. Analogous radical coupling at C-2 of the delocalized carbon radical **30** with nitrogen dioxide, followed by loss of nitroform from the labile adduct **29** in the polar acetonitrile solvent, would yield 4-fluoro-2-nitroanisole **4** directly; however, the potential intermediacy of nitro–trinitromethyl adducts **8**, **10** and **12** in the transformation **29** ⟶ **4** cannot be excluded.

Overview of the photolysis products from 4-fluoro-3- methylanisole 7 in dichloromethane and acetonitrile

Comment on the photolysis products from these reactions must be limited necessarily because of the inherent lability of the nitro–trinitromethyl adducts **23**–**25**. However, some broad trends are evident in the product yield data which follow the pattern found earlier for 4-methylanisole **1**[3] and for 4-fluoro anisole **2**, above. At ambient temperatures in dichloromethane the photolysis of the complex of 4-fluoro-3-methylanisole **7** involves the attack of trinitromethanide ion on the radical cation vicinal to the methoxy group at the less-hindered ring position *para* to the methyl substituent, and leading to high yields of 4-fluoro-5-methyl-2-trinitromethylanisole **19**. At lower temperatures in dichloromethane and acetonitrile the yield of nitro–trinitromethyl adduct **25** increases, indicative of a change in the balance of the regiochemistry of attack of trinitromethanide ion on the radical cation of 4-fluoro-3-methylanisole **7** towards attack *ipso* to the methoxy function.



Scheme 4

Overview of the photolysis products from 4-fluoroanisole 2 and 4-fluoro-3-methylanisole 7 in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP)

HFP has been found to strongly stabilize radical cations, partly by rendering any nucleophilic species present exceedingly unreactive.[12] We therefore anticipated that HFP would inhibit the attack of trinitromethanide ion on the radical cation and by default favour the occurrence of the $ArH^{\cdot +}$–NO_2 coupling process. In the event, this prediction was correct but the conversion of each substrate into products was slow, 4-fluoroanisole **2** (18% after 5 h) and 4-fluoro-3-methylanisole **7** (18% after 4 h); 4-fluoroanisole **2** was converted exclusively into 4-fluoro-2-nitroanisole **4**, while 4-fluoro-3-methylanisole **7** gave the two nitro anisoles **20** (26%) and **22** (74%) as the exclusive products.

These results should be contrasted with those obtained in the thermal reaction between **2** or **7** and NO_2 in HFP: the yields of nitro products were **4** (55%) or **20** (14%) and **22** (56%), respectively, after 1 h.

Overview of the photolysis products from 4-fluoroanisole 2 and 4-fluoro-3-methylanisole 7 in dichloromethane containing trifluoroacetic acid (0.7 mol dm^{-3})

In the presence of trifluoroacetic acid (0.7 mol dm^{-3}) one component of the triad, trinitromethanide ion, formed on photolysis of a ArH–TNM charge transfer complex will be converted into the less nucleophilic nitroform [$HC(NO_2)_3$] by protonation. For 4-fluoroanisole **2** the addition of trifluoroacetic acid (0.7 mol dm^{-3}) only partially suppressed adduct formation (total 18%), and some 4-fluoro-2-trinitromethylanisole **3** (25%) was also formed in addition to 4-fluoro-2-nitroanisole **4** (48%). In contrast, the corresponding reaction of 4-fluoro-3-methylanisole **7** resulted in the formation of mainly the nitro anisoles **20** (18%) and **22** (60%), together with minor amounts of other aromatic products.

Implications of the EPR spectral results

In general, reactive and moderately reactive radical cations $ArH^{\cdot +}$ generated by photolysis of ArH with tetranitromethane [eqn. (1)] form adducts by initial reaction with trinitromethanide ion, followed by NO_2 trapping by the neutral radical formed [eqns. (2) and (3)]. However, a minor, competing pathway might be reaction between $ArH^{\cdot +}$ and NO_2 to give eventually $ArNO_2$ [eqn. (4)].[2] We previously devised two

$$ArH^{\cdot +} + NO_2 \longrightarrow Ar(H)NO_2^{+} \longrightarrow ArNO_2 + H^{+} \qquad (4)$$

methods to remove trinitromethanide ion from the triad of eqn. (1), namely (*i*) by carrying out the photolysis in the presence of trifluoroacetic acid, capable of protonating trinitromethanide ion and thus convert it into a much weaker nucleophile,[13] and (*ii*) by carrying out the photolysis in HFP, a solvent with a very strongly attenuating effect on nucleophile reactivity.[12] In particular, the reactivity of trinitromethanide ion toward tris(4-bromophenylaminium ion) was decreased by a factor of *ca.* 3×10^3 in going from acetonitrile to HFP,[12f] and by a factor of about 10^3 in going from dichloromethane to acetonitrile,[14] *i.e.* by a factor $>10^6$ in going from dichloromethane to HFP.

Thus, it was possible to detect moderately reactive $ArH^{\cdot +}$ by their EPR spectra—or by EPR spectra of secondarily formed radical cations, such as dehydrodimer radical cations $Ar\text{-}Ar^{\cdot +}$ —during photolysis of ArH–tetranitromethane–TFA in dichloromethane at low temperature (−60 °C)[13] or during photolysis of ArH–tetranitromethane in HFP at room temperature.[12a,b] The limit for EPR spectral detection was determined by the reactivity of the radical cation—even if the reactivity of the trinitromethanide ion can be greatly reduced, one nevertheless eventually reaches a point where the reaction of eqn. (4) becomes too fast for $ArH^{\cdot +}$ to accumulate. It may also be that trinitromethane can act as a weak nucleophile when the reactivity of $ArH^{\cdot +}$ is high enough.

The 4-fluoroanisole radical cation $\mathbf{2}^{\cdot +}$ according to its electrochemical characteristics should have similar high reactivity as that of 4-methylanisole (E_{pa} = 1.87 *vs.* 1.86 V).[12d] Accordingly, no EPR spectral activity could be detected during photolysis of **2**-tetranitromethane under the standard conditions usually employed (dichloromethane–TFA at −60 °C; TFA at −12 °C; HFP at −3 or 22 °C). This is similar to the behaviour of 4-methylanisole, except that weak EPR spectra due to the formation of its dehydrodimer were detectable.[3] The high reactivity of $\mathbf{2}^{\cdot +}$ was also obvious (see above) from the fact that added TFA did not completely eliminate the adducts from the photolysis of **2**-tetranitromethane in dichloromethane.

On the other hand, the photolysis of **2**-tetranitromethane in HFP had some characteristics not encountered before. As expected, the reactivity of trinitromethanide ion was completely suppressed and only the nitro product **4** was obtained, in all probability by eqn. (4) totally outcompeting eqn. (2). However, the photochemical reaction was very inefficient, the conversion into **4** being only 18% after 5 h. If this low efficiency would be caused by a slow coupling between $\mathbf{2}^{\cdot +}$ and NO_2, there is no reason why the radical cation should not be observable by EPR spectroscopy. This is normally found for relatively stable radical cations, like that of tetraphenylethylene.[13] We suggest that the low photochemical yield in HFP is caused by competition from the back electron transfer (ET) reaction in the first photochemical step, formation of $\mathbf{2}^{\cdot +}$ and $C(NO_2)_4^{\cdot -}$ [eqn. (5)]. It was previously[15] estimated that the lifetime of

$$\mathbf{2}\cdots C(NO_2)_4 \rightleftharpoons \mathbf{2}^{\cdot +}\, C(NO_2)_4^{\cdot -} \longrightarrow \mathbf{2}^{\cdot +}\, C(NO_2)_3^{-}\, NO_2 \qquad (5)$$

$C(NO_2)_4^{\cdot -}$ is < 3 ps in dichloromethane, but it is likely that the strong anion stabilizing effect of HFP[16] will prolong the lifetime of this species sufficiently for competition by back ET to become effective.

Conclusions

The photochemical reaction between 4-fluoroanisole **2** and tetranitromethane in dichloromethane at 20 °C gave predominantly unstable adducts (*ca.* 50%), 4-fluoro-2-trinitromethylanisole **3** (*ca.* 30%) and some 4-fluoro-2-nitroanisole **4** (2%). In acetonitrile, adduct formation was detectable, but the main products were **4** (62%), 4-fluoro-2-nitrophenol **16** (23%) and **3** (4%). The effect of the solvent on product distribution is suggested to involve differential reactivity of trinitromethanide ion toward $\mathbf{2}^{\cdot +}$ in different solvents, attack *ipso* to the methoxy group being more prominent in the more polar solvent acetonitrile. Adducts formed *via* initial *ipso* attack are unstable and decompose to nitro substitution products.

The above model of the solvent effect contrasts with the previously proposed one,[4] in which direct substitution mechanisms starting from the triad of eqn. (1) and leading to **3** or **4**, were favoured.

Experimental

Methods and materials

Melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR spectrometer; ^1H and ^{13}C NMR spectra were recorded on a Varian Unity 300 spectrometer with $SiMe_4$ 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 by the Upgrade Version ESP 3220-200SH of a Bruker ER-200D spectrometer. Photolyses were performed in the photolysis cavity (ER 4104 OR), using a 50 W high-pressure Hg lamp from Bruker (ER 202). The spectra were recorded with a 100 kHz modulation frequency with an amplitude of 0.001–0.04 mT, microwave effect 0.4–1.6 mW. Cyclic voltammetry was performed by the BAS-100 instrument in dichloromethane- or HFP–Bu_4NPF_6 (0.15 mol dm^{-3}) at a Pt button electrode. The reference electrode was an Ag/AgCl electrode. In HFP, the ferricinium/ferrocene couple had $(E_{pa} + E_{pc})/2 = 0.05$ V *vs.* Ag/AgCl.

Tetranitromethane, 4-fluoroanisole and 4-fluoro-3-methylanisole were purchased from Aldrich. Dichloromethane (AR) and acetonitrile (HiPerSolv) were from BDH and 1,1,1,3,3,3-hexafluoropropan-2-ol from Sigma.

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 molecules.[17]

General procedure for the photolysis of 4-fluoroanisole 2 with tetranitromethane

A solution of 4-fluoroanisole **2** (500 mg, 0.5 mol dm^{-3}) and tetranitromethane (1.0 mol dm^{-3}) in dichloromethane (at 20, −20 or −78 °C) or acetonitrile (20 or −20 °C) was irradiated with filtered light (λ_{cutoff} 435 nm). Aliquots were withdrawn from the reaction mixture at appropriate time intervals, the volatile material removed under reduced pressure at ⩽0 °C, and the product composition determined by NMR spectral analysis (Tables 1 and 2). A similar reaction was carried out in 1,1,1,3,3,3-hexafluoropropan-2-ol.

Photochemistry of 4-fluoroanisole 2 in dichloromethane at −20 °C and the identification of adducts 8–14 and aromatic compounds 3, 4 and 15

Reaction of 4-fluoroanisole–tetranitromethane in dichloromethane at −20 °C, as above, for 3 h resulted in partial conversion (*ca.* 50%) into a product which was shown by ^1H NMR spectra to be a mixture of the nitro–trinitromethyl adducts (**8**) (1%), (**9**) (trace), (**10**) (6%), (**11**) (18%), (**12**) (2%), (**13**) (19%), hydroxy-trinitromethyl adduct (**14**) (8%), unidentified adducts (total 19%), aromatic compounds (**3**) (17%), (**4**) (2%), (**15**) (2%), and unidentified aromatic compounds (total 6%). The mixture was

Table 5 NOEs for compounds isolated

Compound	Irradiated at δ	Enhancement(s) (%) at δ
8	3.66	4.68 (9.3)
	4.68	3.66 (1.3); 5.62 (4.4)
	6.41	5.94 (3.0)
9	3.72	5.17 (10.4)
10	3.66	5.25 (9.0)
	5.64	5.97 (2.9)
	5.97	5.64 (2.2)
11	3.66	5.27 (9.2)
	5.14	6.03 (1.3)
	5.27	3.66 (1.0); 5.71 (2.4)
	5.71	5.27 (1.4)
	6.03	5.14 (2.5)
12	3.70	5.28 (6.1); 5.55 (0.5)
	5.11	5.28 (1.5)
	5.28	3.70 (0.6); 5.11 (1.6)
	5.55	3.70 (0.1); 6.06 (1.4)
	6.60	5.55 (1.7)
13	3.68	5.40 (9.4)
	4.98	3.68 (0.1); 6.14 (2.4)
	5.40	3.68 (1.3); 5.59 (3.6)
	5.59	5.40 (1.8);
	6.14	4.98 (2.7)
14	3.60	5.24 (6.5)
	4.74	5.24 (1.6)
	4.81	5.66 (2.0)
	5.24	3.60 (1.1); 4.74 (2.5)
	5.66	4.82 (1.9)
18	2.34	7.09 (3.7)
23	1.89	5.26 (6.7)
	3.63	5.26 (11.5)
	4.96	6.01 (2.8)
	5.26	1.89 (0.3); 3.63 (1.2)
	6.01	4.96 (2.7)
25	1.91	6.07 (5.5)
	3.61	4.66 (12.0)

partially separated into its components by HPLC and gave the following in elution order.

4-Fluoro-2-trinitromethylanisole 3. ^{1}H NMR (CDCl$_3$) δ 3.83 (s, OMe), 7.09 (m, H-3 and H-6), 7.44 (ddd, $J_{H5,H6}$ 9.5 Hz, $J_{H5,F}$ 6.4 Hz, $J_{H5,H3}$ 2.5 Hz, H-5); identical with lit.[4] values.

4-Fluoro-2-nitroanisole 4. Mp 59–60 °C (lit.,[8] 61.5–62 °C). ^{1}H NMR (CDCl$_3$) δ 3.95 (s, OMe), 7.07 (dd, $J_{H6,H5}$ 9.8 Hz, $J_{H6,F}$ 3.9 Hz, H-6), 7.28 (ddd, $J_{H5,H6}$ 9.8 Hz, $J_{H5,F}$ 7.3 Hz, $J_{H5,H3}$ 3.4 Hz, H-5), 7.60 (dd, $J_{H3,F}$ 7.8 Hz, $J_{H3,H5}$ 3.4 Hz, H-3).

1-Fluoro-4-methoxy-*r*-5-nitro-*c*-6-trinitromethylcyclohexa-1,3-diene 8. Isolated only in admixture with aromatic compounds **3** and **4** and its epimer **9** into which it isomerizes in solution. ^{1}H NMR (CDCl$_3$) δ 3.66 (s, OMe), 4.68 (ddd, $J_{H5,H6}$ 5.4 Hz, $J_{H5,F}$ 2.5 Hz, $J_{H5,H3}$ 2.0 Hz, H-5), 5.62 (dd, $J_{H6,F}$ 5.8 Hz, $J_{H6,H5}$ 5.4 Hz, H-6), 5.94 (dd, $J_{H2,F}$ 11.8 Hz, $J_{H2,H3}$ 10.3 Hz, H-2), 6.41 (dd, $J_{H3,H2}$ 10.3 Hz, $J_{H3,H5}$ 2.0 Hz, H-3); assignments confirmed by double irradiation experiments. Nuclear Overhauser experiments, see Table 5. ^{13}C NMR (CDCl$_3$) δ 44.1 (d, $J_{C6,F}$ 13.6 Hz, C-6), 55.3 (OMe), 84.05 (d, $J_{C5,F}$ 2.9 Hz, C-5), 121.2 (d, $J_{C2,F}$ 22.9 Hz, C-2), 132.7 (d, $J_{C3,F}$ 11.4 Hz, C-3), resonances for C-1, C-4 and $C(NO_2)_3$ were not observed; the above assignments were confirmed by reverse detected heteronuclear correlation spectra (HMQC).

1-Fluoro-4-methoxy-*r*-5-nitro-*t*-6-trinitromethylcyclohexa-1,3-diene 9. Isolated only in admixture with the nitro compound **4** and two minor aromatic compounds. ^{1}H NMR (CDCl$_3$) δ 3.72 (s, OMe), 5.17 (dd, $J_{H3,H2}$ 7.3 Hz, $J_{H3,F}$ 3.4 Hz, H-3), 5.27 (br d, $J_{H5,F}$ 4.9 Hz, $J_{H5,H6}$ small, H-5), 5.43 (br d, $J_{H6,F}$ 5.9 Hz, $J_{H6,H5}$ small, H-6), 6.05 (dd, $J_{H2,F}$ 10.7 Hz, $J_{H2,H3}$ 7.3 Hz, H-2); assignments confirmed by double irradiation experiments. Nuclear Overhauser experiment, see Table 5. ^{13}C NMR (CDCl$_3$) δ 41.9 (C-6), 82.5 (C-5), 131.0 (C-3), resonances for C-1, C-2, C-4 and $C(NO_2)_3$ were not observed; the above ^{13}C NMR assignments were made from reverse detected heteronuclear correlation spectra (HMQC).

3-Fluoro-6-hydroxy-5-nitrobenzoic acid 15. A viscous oil (insufficient for elemental analysis. Found: M$^+$, 201.0073. $C_7H_4FNO_5$ requires 201.00735). ^{1}H NMR (CDCl$_3$) δ 7.55 (dd, $J_{H,F}$ 7.8 Hz, $J_{H,H}$ 2.9 Hz), 8.26 (dd, $J_{H,F}$ 7.3 Hz, $J_{H,H}$ 2.9 Hz), 11.29 (br s, OH).

1-Fluoro-4-methoxy-*r*-3-nitro-*t*-6-trinitromethylcyclohexa-1,4-diene 10. Isolated in low yield in admixture with impurities (*ca.* 10%). ^{1}H NMR (CDCl$_3$) δ 3.66 (s, OMe), 5.20 (m, H-6), 5.25 (m, H-5), 5.64 (dd, $J_{H3,F}$ 8.8 Hz, $J_{H3,H2}$ 3.9 Hz, H-3), 5.97 (dd, $J_{H2,F}$ 15.6 Hz, $J_{H2,H3}$ 3.9 Hz, H-2). Nuclear Overhauser experiments, see Table 5.

1-Fluoro-4-methoxy-*t*-6-nitro-*r*-3-trinitromethylcyclohexa-1,4-diene 11. Isolated only in admixture with impurities (*ca.* 10%). ^{1}H NMR (CDCl$_3$) δ 3.66 (s, OMe), 5.14 (br d, $J_{H3,H2}$ 3.9 Hz, $J_{H3,F}$ and $J_{H3,H6}$ small, H-3), 5.27 (dd, $J_{H5,F}$ 5.4 Hz, $J_{H5,H6}$ 4.4 Hz, H-5), 5.71 (m, $J_{H6,H5}$ 4.4 Hz, $J_{H6,F}$ 2.9 Hz, $J_{H6,H5}$ small, H-6), 6.03 (dd, $J_{H2,F}$ 13.2 Hz, $J_{H2,H3}$ 3.9 Hz, H-2); assignments confirmed by double irradiation experiments. Nuclear Overhauser experiments, see Table 5. ^{13}C NMR (CDCl$_3$) δ 44.5 (d, $J_{C3,F}$ 8.4 Hz, C-3), 56.7 (OMe), 80.8 (d, $J_{C6,F}$ 26.9 Hz, C-6), 94.0 (d, $J_{C5,F}$ 7.4 Hz, C-5), 102.5 (d, $J_{C2,F}$ 26.1 Hz, C-2), 150.4 (C-4), resonances for C-1 and $C(NO_2)_3$ were not observed; the above assignments were confirmed by reverse detected heteronuclear correlation spectra (HMBC, HMQC).

1-Fluoro-4-methoxy-*r*-3-nitro-*c*-6-trinitromethylcyclohexa-1,4-diene 12. Isolated only in admixture with impurities (*ca.* 10%). ^{1}H NMR (CDCl$_3$) δ 3.70 (s, OMe), 5.11 (br m, H-6), 5.28 (dd, $J_{H5,F}$ 5.8 Hz, $J_{H5,H6}$ 3.9 Hz, H-5), 5.54 (dd, $J_{H3,F}$ 10.2 Hz, $J_{H3,H2}$ 4.9 Hz, H-3), 6.06 (dd, $J_{H2,F}$ 13.7 Hz, $J_{H2,H3}$ 4.9 Hz, H-2); assignments confirmed by double irradiation experiments. Nuclear Overhauser experiments, see Table 5. ^{13}C NMR (CDCl$_3$) δ 43.7 (d, $J_{C6,F}$ 22.1 Hz, C-6), 56.5 (OMe), 81.3 (C-3), 90.1 (C-5), 105.1 (d, $J_{C2,F}$ 25.2 Hz, C-2), 157.0 (C-4), resonances for C-1 and $C(NO_2)_3$ were not observed; the above ^{13}C NMR assignments were made from reverse detected heteronuclear correlation spectra (HMQC).

1-Fluoro-4-methoxy-*c*-6-nitro-*r*-3-trinitromethylcyclohexa-1,4-diene 13. Isolated only in admixture with impurities (total 5%). ^{1}H NMR (CDCl$_3$) δ 3.68 (s, OMe), 4.98 (ddd, $J_{H3,H6}$ 5.4 Hz, $J_{H3,F}$ 4.4 Hz, $J_{H3,H2}$ 4.4 Hz, H-3), 5.40 (dd, $J_{H5,F}$ 5.4 Hz, $J_{H5,H6}$ 5.4 Hz, H-5), 5.59 (ddd, $J_{H6,F}$ 5.4 Hz, $J_{H6,H5}$ 5.4 Hz, $J_{H6,H3}$ 5.4 Hz, H-6), 6.14 (br dd, $J_{H2,F}$ 12.7 Hz, $J_{H2,H3}$ 4.4 Hz, H-2); assignments confirmed by double irradiation experiments. Nuclear Overhauser experiments, see Table 5. ^{13}C NMR (CDCl$_3$) δ 44.8 (d, $J_{C3,F}$ 8.3 Hz, C-3), 56.9 (s, OMe), 79.7 (d, $J_{C6,F}$ 28.2 Hz, C-6), 94.3 (d, $J_{C5,F}$ 7.3 Hz, C-5), 102.4 (d, $J_{C2,F}$ 25.9 Hz, C-2), resonances for C-1 and $C(NO_2)_3$ were not observed; the above assignments were confirmed by reverse detected heteronuclear correlation spectra (HMBC, HMQC).

1-Fluoro-6-hydroxy-4-methoxy-3-trinitromethylcyclohexa-1,4-diene 14. Isolated in admixture with impurities (total 10%). ^{1}H NMR (CDCl$_3$) δ 3.60 (s, OMe), 4.74 (m, H-6), 4.81 (m, H-3), 5.24 (dd, $J_{H5,H6}$ 5.4 Hz, $J_{H5,F}$ 5.4 Hz, H-5), 5.66 (dd, $J_{H2,F}$ 12.7 Hz, $J_{H2,H3}$ 3.9 Hz, H-2); assignments confirmed by double irradiation experiments. Nuclear Overhauser experiments, see Table 5. ^{13}C NMR (CDCl$_3$) δ 44.4 (d, $J_{C3,F}$ 8.4 Hz, C-3), 55.6 (OMe), 61.4 (d, $J_{C6,F}$ 28.2 Hz, C-6), 96.2 (d, $J_{C2,F}$ 27.1 Hz, C-2), 100.6 (d, $J_{C5,F}$ 9.4 Hz, C-5), resonances for C-1, C-4 and $C(NO_2)_3$ were not observed; the above assignments were confirmed by reverse detected heteronuclear correlation spectra (HMQC).

Photochemistry of 4-fluoroanisole 2 in acetonitrile at 20 °C and the identification of the nitro phenol 16

Reaction of 4-fluoroanisole–tetranitromethane in acetonitrile at 20 °C, as above, for 2 h resulted in partial conversion (*ca.* 40%) into a product which was shown by ^{1}H NMR spectra to be a mixture of the aromatic compounds **3** (4%), **4** (62%), 4-fluoro-2-nitrophenol **16** (23%) and unidentified aromatic compounds (total 10%). Chromatography of this mixture on a silica gel Chromatotron plate gave:

4-Fluoro-2-nitrophenol 16. ^{1}H NMR (CDCl$_3$) δ 7.16 (dd, $J_{H6,H5}$ 9.8 Hz, $J_{H6,F}$ 4.4 Hz, H-6), 7.37 (ddd, $J_{H5,H6}$ 9.8 Hz, $J_{H5,F}$ 7.3 Hz, $J_{H5,H3}$ 2.9 Hz, H-5), 7.82 (dd, $J_{H3,F}$ 8.3 Hz, $J_{H3,H5}$ 2.9 Hz, H-3), 10.36 (s, OH); identical with lit.[4] values.

Photochemistry of 4-fluoroanisole 2 in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) at 20 °C

A solution of 4-fluoroanisole **2** (250 mg, 0.5 mol dm^{-3}) and tetranitromethane (1.0 mol dm^{-3}) in HFP at 20 °C was irradiated with filtered light (λ_{cutoff} 435 nm) for 5 h. The conversion of 4-fluoroanisole **2** was low (*ca.* 18%) and exclusively into 4-fluoro-2-nitroanisole **4**.

Photochemistry of 4-fluoroanisole 2 at 20 °C in dichloromethane containing trifluoroacetic acid (0.7 mol dm^{-3})

Reaction of 4-fluoroanisole–tetranitromethane in dichloromethane containing trifluoroacetic acid (0.7 mol dm^{-3}) at 20 °C, as above, for 2 h resulted in a relatively low conversion (*ca.* 29%) into a mixture (^{1}H NMR spectra) of adducts **8** (5%), **10** (2%), **11** (2%), **12** (1%) and **13** (8%), aromatic compounds **3** (25%), **4** (48%), **15** (trace) and **16** (2%) and unidentified aromatic compounds (total 7%).

Thermal reaction between 4-fluoroanisole 2 and NO$_2$ in HFP

A solution of 4-fluoroanisole (**2**, 250 mg, 0.5 mol dm^{-3}) in HFP saturated with NO$_2$ (*ca.* 0.4 mol dm^{-3}) was stored in the dark at 20 °C. The degree of conversion was monitored at regular intervals (NMR spectroscopy). After 1 h, 4-fluoro-2-nitroanisole **4** was the only product formed (55% conversion).

General procedure for the photolysis of 4-fluoro-3-methylanisole 7 with tetranitromethane

A solution of 4-fluoro-3-methylanisole **7** (500 mg, 0.45 mol dm^{-3}) and tetranitromethane (0.9 mol dm^{-3}) in dichloromethane (at 20, −20 or −78 °C) or acetonitrile (20, −20 or −50 °C) was irradiated with filtered light (λ_{cutoff} 435 nm). Aliquots were withdrawn from the reaction mixture at appropriate time intervals, the volatile material removed under reduced pressure at $\leqslant$0 °C and the product composition determined by NMR spectral analysis (Tables 3 and 4). A similar reaction was carried out in 1,1,1,3,3,3-hexafluoropropan-2-ol.

Photochemistry of 4-fluoro-3-methylanisole 7 in dichloromethane at 20 °C and the identification of aromatic compounds 17–22

Reaction of 4-fluoro-3-methylanisole–tetranitromethane in dichloromethane at 20 °C, as above, for 6 h resulted in partial conversion (*ca.* 75%) into a product which was shown by ^{1}H NMR spectra to be a mixture of the aromatic compounds **17** (3%), **18** (1%), **19** (64%), **20** (5%), **21** (6%) and **22** (12%), nitro–trinitromethyl adduct **23** (4%) and unidentified adducts (total 2%). The aromatic compounds (**17–22**) were separated by chromatography on a silica gel Chromatotron plate and gave in order of elution.

4-Fluoro-5-methyl-2-nitrophenol 17. Isolated in low yield as an oil (insufficient for elemental analysis. Found: M$^+$, 171.0331. C$_7$H$_6$FNO$_3$ requires 171.0332). ^{1}H NMR (CDCl$_3$) δ 2.34 (d, $J_{Me,F}$ 1.5 Hz, Me), 6.99 (d, $J_{H6,F}$ 6.3 Hz, H-6), 7.74 (d, $J_{H3,F}$ 8.8 Hz, H-3), 10.37 (s, OH).

4-Fluoro-5-methyl-3-trinitromethylanisole 18. Isolated in low yield as an oil (insufficient for elemental analysis. Found: M$^+$, 289.0345. C$_9$H$_8$FN$_3$O$_7$ requires 289.0346). ^{1}H NMR (CDCl$_3$) δ 2.34 (d, $J_{Me,F}$ 1.9 Hz, 5-Me), 3.80 (s, OMe), 6.76 (dd, $J_{H2,F}$ 5.4 Hz, $J_{H2,H6}$ 2.9 Hz, H-2), 7.10 (dd, $J_{H6,F}$ 5.8 Hz, $J_{H6,H2}$ 2.9 Hz, H-6). Nuclear Overhauser experiment, see Table 5.

4-Fluoro-5-methyl-2-trinitromethylanisole 19. Mp 55–59 °C (X-ray crystal structure determined, see below). IR: ν_{max}/cm^{-1} (KBr) 1624, 1593. ^{1}H NMR (CDCl$_3$) δ 2.38 (d, $J_{Me,F}$ 2.0 Hz, 4-Me), 3.80 (s, OMe), 6.93 (d, $J_{H6,F}$ 5.9 Hz, H-6), 7.01 (d, $J_{H3,F}$ 9.3 Hz, H-3).

4-Fluoro-3-methyl-2-nitroanisole 20. Isolated in low yield as an oil (insufficient for elemental analysis. Found: M$^+$, 185.0488. C$_8$H$_8$FNO$_3$ requires 185.0488). ^{1}H NMR (CDCl$_3$) δ 2.21 (d, $J_{Me,F}$ 1.9 Hz, Me), 3.85 (s, OMe), 6.82 (dd, $J_{H6,H5}$ 8.8 Hz, $J_{H6,F}$ 4.4 Hz, H-6), 7.10 (dd, $J_{H5,F}$ 9.2 Hz, $J_{H5,H6}$ 8.8 Hz, H-5).

4-Fluoro-3-methyl-2,6-dinitrophenol 21. Isolated in low yield as an oil (insufficient for elemental analysis. Found: M$^+$, 216.0183. C$_7$H$_5$FN$_2$O$_5$ requires 216.01825). ^{1}H NMR (CDCl$_3$) δ 2.35 (d, $J_{Me,F}$ 1.9 Hz, 3-Me), 7.96 (d, $J_{H5,F}$ 8.8 Hz, H-5), 10.60 (br s, OH).

4-Fluoro-5-methyl-2-nitroanisole 22. Mp 84–85 °C (X-ray crystal structure determined, see below). IR: ν_{max}(KBr) 1526 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 2.35 (d, $J_{Me,F}$ 1.9 Hz, 5-Me), 3.93 (s, OMe), 6.89 (d, $J_{H6,F}$ 6.4 Hz, H-6), 7.62 (d, $J_{H3,F}$ 8.8 Hz, H-3).

The nitro–trinitromethyl adduct **23** was not eluted from the silica gel Chromatotron plate and it also decomposed during an attempted HPLC separation on a cyanopropyl column at −20 °C.

Photochemistry of 4-fluoro-3-methylanisole 7 in dichloromethane at −20 °C and the identification of nitro–trinitromethyl adducts 23 and 24

Reaction of 4-fluoro-3-methylanisole–tetranitromethane in dichloromethane at −20 °C, as above, for 6 h resulted in partial conversion (*ca.* 73%) into a product which was shown by ^{1}H NMR spectra to be a mixture of the aromatic compounds **17** (2%), **19** (62%), **20** (3%) and **22** (7%), and the nitro–trinitromethyl adducts **23** (15%), **24** (5%) and **25** (2%). None of the nitro–trinitromethyl adducts **23–25** could be isolated by HPLC using a cyanopropyl column even at −20 °C. Adducts **23** and **24** were identified therefore by spectroscopic studies on this mixture of products, and adduct **25** by similar studies on a mixture of products from a reaction in acetonitrile at −20 °C (see below).

1-Fluoro-4-methoxy-6-methyl-*c*-6-nitro-*r*-3-trinitromethylcyclohexa-1,4-diene 23. ^{1}H NMR (CDCl$_3$) δ 1.89 (d, $J_{Me,F}$ 1.0 Hz, 6-Me), 3.63 (s, OMe), 4.96 (dd, $J_{H3,F}$ 4.8 Hz, $J_{H3,H2}$ 3.9 Hz, H-3), 5.26 (d, $J_{H5,F}$ 6.4 Hz, H-5), 6.01 (dd, $J_{H2,F}$ 13.6 Hz, $J_{H2,H3}$ 3.9 Hz, H-2). Nuclear Overhauser experiments, see Table 5. ^{13}C NMR (CDCl$_3$) δ 44.7 (C-3), 56.6 (OMe), 85.0 (C-6), 100.2 (C-2), 101.7 (C-5), 150.4 (C-4), 160.7 (C-1), the resonance for C(NO$_2$)$_3$ was not observed; the above ^{13}C NMR assignments were made from reverse detected heteronuclear correlation spectra (HMBC, HMQC).

1-Fluoro-4-methoxy-6-methyl-*t*-6-nitro-*r*-3-trinitromethylcyclohexa-1,4-diene 24. ^{1}H NMR (CDCl$_3$) δ 5.10 (br dd, $J_{H3,F}$ 3.4 Hz, $J_{H3,H2}$ 3.4 Hz, $J_{H3,H5}$ *ca.* 1.0 Hz, H-3), 5.15 (br d, $J_{H5,F}$ 6.3 Hz, $J_{H5,H3}$ *ca.* 1.0 Hz, H-5), 5.92 (dd, $J_{H2,F}$ 14.2 Hz, $J_{H2,H3}$ 3.4 Hz, H-2), resonances for -OMe and 6-Me not assigned. The above assignments were confirmed by double irradiation experiments.

Photochemistry of 4-fluoro-3-methylanisole 7 in acetonitrile at −20 °C and the identification of nitro–trinitromethyl adduct 25

Reaction of 4-fluoro-3-methylanisole–tetranitromethane in acetonitrile at −20 °C, as above, for 6 h resulted in partial conversion (*ca.* 72%) into a product which was shown by ^{1}H NMR spectra to be a mixture of the aromatic compounds **17** (13%), **19** (17%), **20** (14%), **21** (3%), **22** (32%) and unidentified aromatic compounds (9%), nitro–trinitromethyl adduct **25** (9%) and unidentified adducts (total 2%).

1-Fluoro-4-methoxy-2-methyl-*r*-5-nitro-*c*-6-trinitromethylcyclohexa-1,3-diene 25. ^{1}H NMR (CDCl$_3$) δ 1.91 (dd, $J_{Me,F}$ 1.9 Hz, $J_{Me,H3}$ 1.5 Hz, 3-Me), 3.61 (s, OMe), 4.66 (ddd, $J_{H5,F}$ 4.9 Hz, $J_{H5,H6}$ 4.4 Hz, $J_{H5,H3}$ 2.3 Hz, H-5), 5.41 (br d, $J_{H6,H5}$ 4.4 Hz, H-6), 6.07 (ddq, $J_{H3,F}$ 2.7 Hz, $J_{H3,H5}$ 2.3 Hz, $J_{H3,Me}$ 1.5 Hz, H-3). Nuclear Overhauser experiments, see Table 5. ^{13}C NMR (CDCl$_3$) δ 44.4 (C-6), 83.5 (C-5), 128.1 (C-3); these assignments were made from reverse detected heteronuclear correlation spectra (HMQC).

Photochemistry of 4-fluoro-3-methylanisole 7 at 20 °C in dichloromethane containing trifluoroacetic acid (0.7 mol dm^{-3})

Reaction of 4-fluoro-3-methylanisole–tetranitromethane at 20 °C in dichloromethane containing trifluoroacetic acid (0.7 mol dm^{-3}), as above, for 4 h resulted in partial conversion (*ca.* 47%) into a product which was shown by ^{1}H NMR spectra to be a mixture of the aromatic compounds **17** (9%), **19** (6%), **20** (18%), **21** (3%) and **22** (60%) and unidentified aromatic compounds (total 3%).

Photochemistry of 4-fluoro-3-methylanisole 7 in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) at 20 °C

A solution of 4-fluoro-3-methylanisole **7** (250 mg, 0.5 mol dm^{-3}) and tetranitromethane (1.0 mol dm^{-3}) in HFP at 20 °C was irradiated with filtered light (λ_{cutoff} 435 nm) for 4 h. The conversion of 4-fluoro-3-methylanisole **7** was low (*ca.* 18%) and exclusively into 4-fluoro-3-methyl-2-nitroanisole **20** (26%) and 4-fluoro-5-methyl-2-nitroanisole **22** (74%).

Thermal reaction between 4-fluoro-3-methylanisole 7 and NO$_2$ in HFP

A solution of 4-fluoro-3-methylanisole (**7**, 250 mg, 0.45 mol dm^{-3}) in HFP saturated with NO$_2$ (*ca.* 0.4 mol dm^{-3}) was stored in the dark at 20 °C. The degree of conversion was monitored at regular intervals (NMR spectroscopy). After 1 h, a 70% conversion into 4-fluoro-3-methyl-2-nitroanisole **20** (20%) and 4-fluoro-5-methyl-2-nitroanisole (80%) had taken place.

Crystallography

Crystal data, established from precession photographs and measured accurately, by means of a Siemens R3m/V four-circle diffractometer [molybdenum X-radiation, λ(Mo-Kα) 0.710 73 Å from a crystal monochromator] are given below. The space group, in each case, was determined unambiguously as a result of the structure analyses reported below, but indicated initially by conditions limiting possible reflections. ω-Scans were used to collect reflection intensities out to a maximum Bragg angle θ, given below. The cell parameters were determined by least-squares refinements for which the setting angles of accurately centred high-angle reflections were used.

Crystal data

4-Fluoro-5-methyl-2-trinitromethylanisole 19. $C_9H_8FN_3O_7$, *M* 289.18, mono-clinic, space group $P2_1/n$, *a* 7.646(1), *b* 7.272(2), *c* 21.196(9) Å, β 94.28(2)°; *V* 1175.2(6) Å^3, D_c 1.634 g cm^{-3}, *Z* 4, μ(Mo-Kα) 1.52 cm^{-1}. The crystal was yellow in colour and of approximate dimensions 0.7 by 0.6 by 0.3 mm. Data were collected at 158(2) K out to a maximum Bragg angle $\theta = 24.0°$. Number of independent reflections measured 1845, 1389 with $I > 2\sigma(I)$. Absorption corrections were not applied; g_1 0.0463, g_2 0.6000; $R_{(obs)}$ factor 0.041, $wR_{(all\ data)}$ 0.107.

4-Fluoro-5-methyl-2-nitroanisole 22. $C_8H_8FNO_3$, *M* 185.15, monoclinic, $P2_1/n$, *a* 7.979(2), *b* 12.852(3), *c* 15.932(3) Å, β 98.15(2)°; *V* 1617.3(6) Å^3, D_c 1.521 g cm^{-3}, *Z* 8, μ(Mo-Kα) 1.31 cm^{-1}. The crystal was colourless and of approximate dimensions 0.8 × 0.7 × 0.3 mm. Data were collected at 158(2) K out to a maximum Bragg angle $\theta = 22.5°$. Number of independent reflections measured 2105, 1272 with $I > 2\sigma(I)$. Absorption corrections were not applied; g_1 0.0516, g_2 1.3300; $R_{(obs)}$ factor 0.047, $wR_{(all\ data)}$ 0.142.

Structure determination

Full-matrix least-squares refinements (SHELXL-93)[18] were employed. This program is based on intensities and uses all data. The observed threshold $I > 2\sigma(I)$ was used only for calculating $R_{(obs)}$, shown here as a comparison for the refinement based on *F*. Reflection weights $1/[\sigma^2(F_o^2) + (g_1P)^2 + g_2P]$, where $P = [F_o^2 + 2F_c^2]/3$, were used. All non-hydrogen atoms were assigned anisotropic thermal parameters. Methyl hydrogens were included as rigid groups pivoting about their carbon atoms. Final Fourier syntheses show no significant residual electron density, and there were no abnormal discrepancies between observed and calculated structure factors.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 188/13.

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References

1 J. O. Svensson, *Acta Chem. Scand.*, 1996, in the press.
2 L. Eberson, M. P. Hartshorn and F. Radner, *Acta Chem Scand.*, 1994, **48**, 937 and references cited therein.
3 C. P. Butts, L. Eberson, M. P. Hartshorn and W. T. Robinson, *Acta Chem. Scand.*, 1996, **50**, 122.
4 S. Sankararaman, W. A. Haney and J. K. Kochi, *J. Am. Chem. Soc.*, 1987, **109**, 7824.
5 C. P. Butts, L. Eberson, M. P. Hartshorn, and W. T. Robinson, *Aust. J. Chem.*, 1995, **48**, 1989.
6 J. L. Calvert, L. Eberson, M. P. Hartshorn, R. G. A. R. Maclagan and W. T. Robinson, *Aust. J. Chem.*, 1994, **47**, 1211.
7 C. P. Butts, J. L. Calvert, L. Eberson, M. P. Hartshorn, F. Radner and W. T. Robinson, *J. Chem. Soc., Perkin Trans. 2*, 1994, 1485 and references cited therein.
8 R. G. Clewley, A. Fischer and G. N. Henderson, *Can. J. Chem.*, 1989, 1472.
9 R. G. Clewley, G. G. Cross, A. Fischer and G. N. Henderson, *Tetrahedron*, 1989, 1299.
10 L. Eberson, M. P. Hartshorn, W. T. Robinson and D. J. Timmerman-Vaughan, *Acta Chem. Scand.*, 1995, **49**, 571.
11 C. E. Barnes and P. C. Myhre, *J. Am. Chem. Soc.*, 1978, **100**, 973.
12 (*a*) L. Eberson, M. P. Hartshorn and O. Persson, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2268; (*b*) L. Eberson, O. Persson, F. Radner and M. P. Hartshorn, *Res. Chem. Intermed.*, in the press; (*c*) L. Eberson, M. P. Hartshorn and O. Persson, *J. Chem. Soc., Chem. Commun.*, 1995, 1131; (*d*) L. Eberson, M. P. Hartshorn and O. Persson, *J. Chem. Soc., Perkin Trans. 2*, 1995, 1735; (*e*) L. Eberson, M. P. Hartshorn and O. Persson, *Acta Chem. Scand.*, 1995, **49**, 640; (*f*) L. Eberson, M. P. Hartshorn and O. Persson, *J. Chem. Soc., Perkin Trans. 2*, 1996, 141; (*g*) L. Eberson and M. P. Hartshorn, *J. Chem. Soc., Perkin Trans. 2*, 1996, 151.
13 L. Eberson, M. P. Hartshorn, F. Radner and J. O. Svensson, *J. Chem. Soc., Perkin Trans. 2*, 1994, 1719.
14 L. Eberson and F. Radner, *J. Am. Chem. Soc.*, 1991, **113**, 5825.
15 J. K. Kochi, *Adv. Phys. Org. Chem.*, 1994, **29**, 185.
16 Gas-phase studies have demonstrated strong stabilization of anions by HFP; see J. W. Larson and T. B. McMahon, *J. Am. Chem. Soc.*, 1987, **109**, 6230 and references cited therein.
17 J. G. Tschinkel, *Ind. Eng. Chem.*, 1965, **48**, 732.
18 G. M. Sheldrick, *J. Appl. Crystallogr.*, 1996, in preparation.

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