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Photochemical Nitration by Tetranitromethane. Part XXXVII.† Adduct Formation and the Regiochemistry of Attack of Trinitromethanide Ion on Radical Cations in the Photochemical Reactions of 2-Methyl-, 2,3-Dimethyl- and 2,4-Dimethylanisoles

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The photolysis of the charge transfer (CT) complex of tetranitromethane and 2-methylanisole **2** in dichloromethane at 20 °C gives the epimeric 1-methoxy-6-methyl-6-nitro-3-trinitromethylcyclohexa-1,4-dienes **8** and **9** in addition to 2-methyl-4-trinitromethylanisole (**3**) and 2-methyl-4-nitroanisole (**4**). In acetonitrile the yields of compound **4** and adducts **8** and **9** are significantly higher. Similar reaction of 2,3-dimethylanisole (**6**) in dichloromethane gave nitro–trinitromethyl adducts **10** and **11**, hydroxy–trinitromethyl adducts **12** and **13**, 2,3-dimethyl-5-trinitromethylanisole (**14**), 4-methoxy-2,3-dimethylbenzonitrile *N*-oxide (**15**), 2,3-dimethyl-4-trinitromethylanisole (**16**), 2,3-dimethyl-4-nitroanisole (**17**), 2,3-dimethyl-4,6-dinitrophenol (**18**), 3-methoxy-4,5-dimethylbenzoic acid (**19**) and the hydroxy dinitro compound (**20**).

The photolysis of the CT complex of 2,4-dimethylanisole (**7**) with tetranitromethane in dichloromethane gave the epimeric 1-methoxy-4,6-dimethyl-6-nitro-3-trinitromethylcyclohexa-1,4-dienes **21** and **22**, together with 4,6-dimethyl-3-trinitromethylanisole (**23**), 4,6-dimethyl-2-nitrophenol (**24**), 4,6-dimethyl-2-trinitromethylanisole (**25**), 4,6-dimethyl-3-nitroanisole (**26**), 4,6-dimethyl-2-nitroanisole (**27**) and 4,6-dimethyl-4-nitrocyclohexa-2,5-dienone (**28**).

The modes of formation of the above products are discussed, including the effects of the reaction solvent on those processes. The X-ray crystal structure of 1-methoxy-2-methyl-*c*-6-nitro-*r*-3-trinitromethylcyclohexa-1,4-diene (**9**) is reported.

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.

$$\underset{\text{CT complex}}{ArH\cdots C(NO_2)_4} \rightarrow \underset{\text{triad}}{ArH^{\cdot+}\ (O_2N)_3C^-\ NO_2} \quad (1)$$

The first chemical step which occurs from the components of the triad, is reaction between $ArH^{\cdot+}$ and trinitromethanide ion [eqn. (2)] to give a carbon radical which then reacts with nitrogen dioxide to give adducts [eqn. (3)].[2]

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

$$Ar(H)C(NO_2)_3^{\cdot} + NO_2 \rightarrow \text{adducts} \quad (3)$$

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

† Part XXXVI, see Ref. 1.
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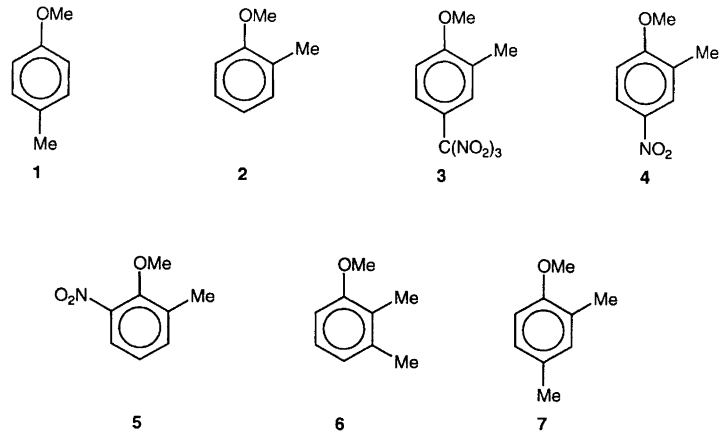


4-methylanisole.[3] The same conclusion was valid for the reaction between 4-fluoroanisole and tetranitromethane.[1]

In 1986 Kochi *et al.* reported the photolysis of the CT complex of 2-methylanisole (**2**) with tetranitromethane in dichloromethane to give mainly the 4-trinitromethyl derivative **3** (60%) accompanied by the two nitro compounds **4** (10%) and **5** (6%).[4] Subsequently this study was extended by reaction in acetonitrile solution, and the latter nitro compounds **4** (68%) and **5** (32%) were reported as the exclusive reaction products.[5] As part of our continuing study of solvent effects in the photolysis reactions of CT complexes of methoxy aromatic compounds with tetranitromethane,[1,3] we have re-examined these reactions for 2-methylanisole (**2**) and extended our study to 2,3-dimethylanisole (**6**) and 2,4-dimethylanisole (**7**). In the event, for each methoxy aromatic substrate, **2**, **6** and **7**, nitro–trinitromethyl adducts are formed, and an analysis of the variation in reaction products with the reaction solvent employed (dichloromethane or acetonitrile) documents further the mechanistic origin of the solvent effects. 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 before,[6] 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 $\leq 0\,^{\circ}C$. The crude product mixtures were stored at $-78\,^{\circ}C$ and were analysed (^1H NMR spectroscopy, see Experimental section; Tables 1, 2 and 5–9) as soon as possible.

Photochemistry of 2-methylanisole (**2**) *in dichloromethane at 20 °C and the identification of products* **3**, **4**, **8** *and* **9**. A solution of 2-methylanisole (**2**) (0.51 mol dm^{-3}) and tetranitromethane (1.02 mol dm^{-3}) in dichloromethane was irradiated at 20 °C. The composition of the mixture was monitored by withdrawing samples for NMR spectral analysis (Table 1). The final solution (after 4 h conversion ca. 50%) after work-up contained the 4-trinitromethyl compound **3** (65%), 2-methyl-4-nitroanisole (**4**) (25%), unidentified aromatic compounds (total 4%), and the nitro–trinitromethyl adducts **8** (4%) and **9** (2%). The aromatic products **3** and **4** were separated by chromatography on a silica gel Chromatotron plate and identified from literature data.[4,7] The two nitro–trinitromethyl adducts **8** and **9** were separated partially by HPLC on a cyanopropyl column using hexane–dichloromethane mixtures as eluting

Table 1. Overview of yields of products from the photolysis of 2-methylanisole (**2**) (0.51 mol dm^{-3}) and tetranitromethane (1.02 mol dm^{-3}) in dichloromethane.

	Yield (%)					
t/h	3	4	Total aromatics (%)[a]	8	9	Total adducts (%)[b]
At 20 °C						
0.5	78.2	9.8	93.5	4.6	1.9	6.5
1	75.4	11.7	92.9	4.7	2.4	7.1
2	70.7	17.4	93.3	4.5	2.2	6.7
4	65.2	25.0	94.2	4.1	1.7	5.8
At −20 °C						
0.5	78.8	10.3	91.8	5.9	1.3	8.2
1	77.6	9.7	91.3	5.8	2.1	8.7
4	68.4	15.5	90.9	6.3	1.8	9.1
At −50 °C						
0.5	75.6	11.9	91.5	6.0	2.0	8.5
1	74.2	11.3	89.4	7.4	2.7	10.6
2	72.6	11.8	90.9	6.4	2.3	9.1
4	70.3	12.5	90.1	7.0	2.3	9.9
At −78 °C						
0.5	71.4	12.7	88.6	8.0	2.9	11.4
1	72.6	11.8	88.9	7.2	3.6	11.1
2	70.5	12.6	89.5	7.1	2.9	10.5
4	70.3	11.8	89.0	7.4	3.0	11.0

[a] Including unidentified aromatics. [b] Including unidentified adducts.

Table 2. Overview of yields of products from the photolysis of 2-methylanisole (**2**) (0.51 mol dm^{-3}) and tetranitromethane (1.02 mol dm^{-3}) in acetonitrile.

	Yield (%)					
t/h	3	4	Total aromatics (%)[a]	8	9	Total adducts (%)[b]
At 20 °C						
0.5	35.2	37.9	74.9	16.1	4.3	23.1
1	30.7	40.8	76.2	17.5	4.2	23.8
2	26.0	43.3	75.0	18.3	4.3	25.0
4	23.9	44.8	73.2	19.5	4.1	26.8
At −20 °C						
1	39.1	34.6	77.5	15.9	4.4	22.5
2	33.7	37.6	76.8	17.7	4.6	23.2
4	29.9	39.2	77.0	17.7	4.2	23.0
At −45 °C						
1	41.4	28.5	74.7	19.2	5.8	23.4
2	39.2	30.8	76.8	18.7	3.9	23.2
4	38.7	31.9	78.8	16.4	4.1	21.3

[a] Including unidentified aromatics. [b] Including unidentified adducts.

Table 3. Fractional coordinates for atoms in 1-methoxy-6-methyl-*c*-6-nitro-*r*-3-trinitromethylcyclohexa-1,4-diene (**9**).

Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	$10^3U(Å^2)$[a]
O(1)	1790(3)	−71(2)	1508(2)	32(1)
O(11)	4674(4)	5055(2)	3291(3)	60(1)
O(12)	1182(4)	5465(2)	3658(2)	56(1)
O(21)	2796(5)	2995(3)	5673(2)	66(1)
O(22)	4419(5)	1414(2)	4960(2)	56(1)
O(31)	−694(4)	2266(3)	4380(2)	61(1)
O(32)	−888(3)	3822(3)	2623(2)	53(1)
O(41)	−1855(4)	2002(3)	1070(2)	58(1)
O(42)	−1357(3)	2999(2)	−875(2)	41(1)
N(1)	2799(5)	4760(2)	3481(2)	40(1)
N(2)	3328(4)	2482(2)	4847(2)	34(1)
N(3)	73(4)	3126(2)	3535(2)	35(1)
N(4)	−664(4)	2408(2)	158(2)	31(1)
C(1)	2333(4)	1167(2)	1539(2)	24(1)
C(2)	3205(4)	1420(2)	2498(2)	25(1)
C(3)	3760(4)	2816(2)	2476(2)	24(1)
C(4)	3341(4)	3858(3)	1238(2)	27(1)
C(5)	2526(4)	3582(3)	282(2)	28(1)
C(6)	1876(4)	2206(3)	308(2)	25(1)
C(7)	1786(7)	−1106(3)	2684(3)	48(1)
C(8)	2515(4)	3279(3)	3540(2)	27(1)
C(9)	2916(5)	1748(3)	−793(2)	36(1)

[a] The equivalent isotropic temperature factor is defined as one-third of orthogonalized U_{ij} tensor ($Å^2$)[a]

solvents. The structure of the minor nitro–trinitromethyl adduct **9** was determined by single-crystal X-ray analysis. A perspective drawing of 1-methoxy-6-methyl-*c*-6-nitro-*r*-3-trinitromethylcyclohexa-1,4-diene (**9**, $C_9H_{10}N_4O_9$), is presented in Fig. 1, and the corresponding atomic coordinates are given in Table 3. In the solid state the alicyclic ring is close to planar (Fig. 2) with the methoxy group close to that plane. The substituents at C(6) are close to being perfectly staggered with the respect to the adjacent methoxy group, and the orientations of the C–NO_2 bonds in the trinitromethyl group relative to the alicyclic ring are such as to minimize

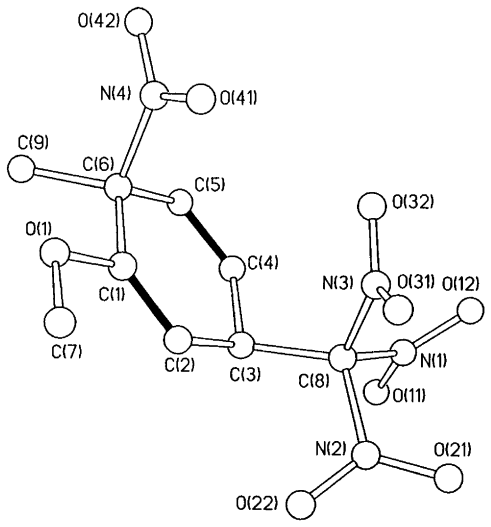


Fig. 1. Perspective drawing of compound **9**.

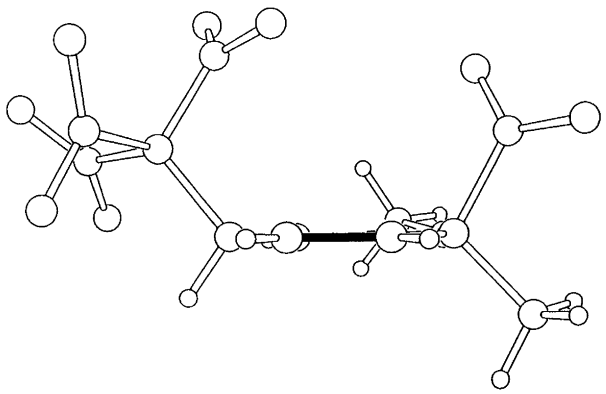
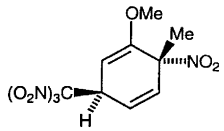


Fig. 2. Side view of the alicyclic ring in compound **9**.

steric interactions. The spectroscopic data for adduct **9** were consistent with the established structure.

The structure of the epimeric adduct **8**, which could not be induced to crystallize, was established from a consideration of its NMR spectra and comparison with corresponding data for adduct **9**. For both adducts **8**



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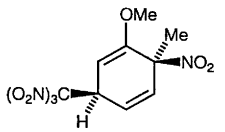

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and **9** the results of nuclear Overhauser experiments and reverse detected heteronuclear correlation spectra allowed the assignment of the ^1H and ^{13}C NMR spectra. The two ^{13}C NMR spectra were closely similar, and the

^{1}H NMR spectra were as might be expected for such epimers.

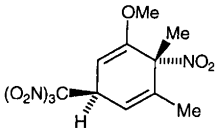
Photochemistry of 2-methylanisole (**2**) *in dichloromethane at −20, −50 and −78 °C and in acetonitrile at 20, −20 and −45 °C.* Similar reactions were performed to the above, except for the reaction temperature for reactions in dichloromethane, and for acetonitrile solution at 20, −20 and −45 °C. The results are summarized in Tables 1 and 2.

Photochemistry of 2-methylanisole (**2**) *in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) at 20 °C.* Photolysis of the CT complex of 2-methylanisole (**2**) and tetranitromethane in HFP at 20 °C for 2 h resulted in a low conversion into products (ca. 8%; cf. ca. 21% in dichloromethane under comparable conditions) and the formation of compounds **3** (35%), **4** (30%), unidentified aromatic compounds (total 15%), adducts **8** (8%) and **9** (4%), and unidentified adducts (total 8%).

Photochemistry of 2,3-dimethylanisole (**6**) *in dichloromethane at 20 °C and the identification of products* **10–20**. A solution of 2,3-dimethylanisole (**6**) (0.46 mol dm^{-3}) and tetranitromethane (0.92 mol dm^{-3}) in dichloromethane was irradiated at 20 °C. After a few min, the solution became deep red. The composition of the mixture was monitored by NMR spectral analysis (Table 4). The final solution (after 8 h, conversion ca. 100%) after work-up contained the nitro–trinitromethyl adducts **10** (15%) and **11** (9%), hydroxy–trinitromethyl adducts **12** (3%) and **13** (1%), and aromatic compounds **14** (10%), **15** (1%), **16** (7%), **17** (42%), **18** (5%), **19** (1%), and hydroxy dinitro compound **20** (1%). These products were separated partially by HPLC, and in the elution order given in the Experimental section. For convenience of the discussion which follows the proof of structure will be presented for groups of compounds.

(A) The epimeric nitro–trinitromethyl adducts **10** *and* **11**, *the epimeric hydroxy–trinitromethyl adducts* **12** *and* **13**, *and the hydroxy dinitro compound* **20**. Neither of the epimeric nitro–trinitromethyl adducts **10** and **11** could be induced to crystallize and consequently their structural assignments are based on a consideration of their spectroscopic data and their order of elution from the HPLC column, *r*-3-nitro-*t*-6-trinitromethylcyclohexa-1,4-dienes (e.g. **10**) being characteristically eluted before the *r*-3-nitro-*c*-6-trinitromethylcyclohexa-1,4-dienes (e.g. **11**).[8,9] The connectivity in each adduct was established from the results of nuclear Overhauser experiments coupled with reverse detected heteronuclear correlation spectra. The ^{1}H and ^{13}C NMR spectra of nitro–trinitromethyl adducts **10** and **11** were closely similar, as might be expected for epimeric structures. However, some relatively minor features of the ^{1}H NMR spectra of adducts **10** and **11** appear to arise as a consequence of the stereochemistry at the Me–C–NO_2 epimeric centre and involve the chemical shifts of H2 ($\Delta\delta -0.04$), H3 ($\Delta\delta -0.10$) and H4 ($\Delta\delta -0.09$) (Fig. 3). A similar pattern is seen for the hydroxy–trinitromethyl adducts **12** and **13**, below, where changes at the Me–C–OH epimeric centre lead to chemical shift differences for H2 ($\Delta\delta -0.05$), H3 ($\Delta\delta -0.10$), and H4 ($\Delta\delta -0.05$). Although the origin(s) of this effect is/are not known, it nonetheless forms the basis of the tentative stereochemical assignments, below, to the epimeric hydroxy–trinitromethyl adducts **12** and **13**.

Neither of the epimeric hydroxy–trinitromethyl adducts **12** and **13** could be isolated either in a pure state or induced to crystallize. The connectivity in each case was established from the results of nuclear Overhauser



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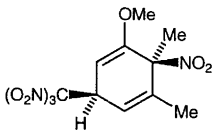

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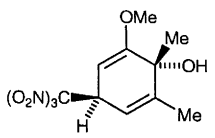

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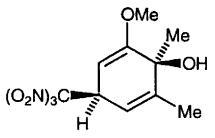

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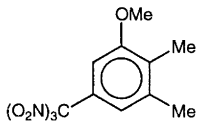

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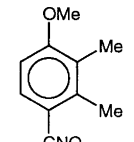

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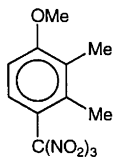

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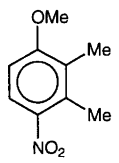

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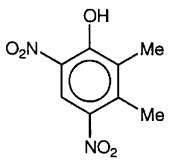

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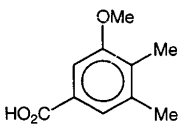

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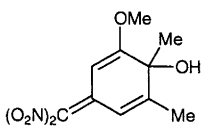

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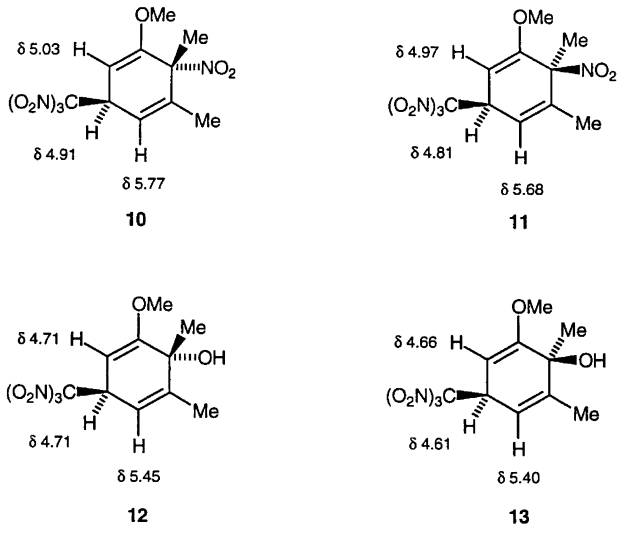
Table 4. Overview of yields of products from the photolysis of 2,3-dimethylanisole (**6**) (0.46 mol dm^{-3}) and tetranitromethane (0.92 mol dm^{-3}) in dichloromethane.

	Yield (%)												
t/h	10	11	12	13	Total adducts[a]	14	15	16	17	18	19	20	Total aromatics[b]
At 20 °C													
1	12.7	14.2	7.1	2.8	39.6	14.6	0.9	11.7	21.1	6.6	—	1.1	60.4
2	13.8	12.5	5.2	2.3	34.5	8.8	0.4	8.4	33.7	6.8	—	2.0	65.5
4	14.0	10.8	4.1	1.8	31.0	9.7	0.4	7.0	39.5	5.7	Trace	1.3	69.0
8	15.1	8.8	3.4	1.4	29.0	9.6	1.4	6.9	41.7	5.1	0.6	0.7	71.0
At −20 °C													
1	9.7	7.0	3.1	1.9	23.6	21.4	5.2	15.7	21.3	5.0	—	—	76.4
2	11.6	7.3	2.7	1.2	24.6	18.5	3.2	13.5	26.7	5.1	—	0.2	75.4
4	11.2	5.8	2.9	1.2	22.4	20.3	3.0	13.2	28.8	4.3	Trace	0.5	77.6
8	13.7	5.5	1.5	0.7	22.7	19.5	1.2	10.5	33.8	2.4	0.4	0.4	77.3

[a] Including unidentified adducts. [b] Including unidentified aromatics.



10 **11** **12** **13**

Fig. 3. ^1H NMR spectroscopic data for nitro–trinitromethyl adducts **10–13**.

experiments and of reverse detected heteronuclear correlation experiments. Although the stereochemical assignments must be regarded as tentative only, they are made on the basis outlined above.

The hydroxydinitro compound **20** was isolated only in low yield as an oil. With a molecular formula, $C_{10}H_{12}N_2O_6$ (mass spectrum), its connectivity was established by a combination of nuclear Overhauser experiments and reverse detected heteronuclear correlation spectra (Experimental section). Consistent with the assigned structure were the infrared (ν_{max} 3427, 1657, 1541 cm^{-1}) and ultraviolet [λ_{max} 386 nm (ε 32 400)] spectra. It appears likely that this compound arises during the photolysis reaction by the loss of nitrous acid from one or both of the hydroxy–trinitromethyl adducts **12** and **13**.

(B) The aromatic products **14–19**. 2,3-Dimethyl-4-nitroanisole (**17**)[10] and 5,6-dimethyl-2,4-dinitrophenol (**18**)[11] were identified by comparison with literature data.

The structures of the trinitromethyl anisoles **14** and **16** were determined from their spectroscopic data, the regiochemistry of each being established decisively by the results of nuclear Overhauser experiments. Although no parent ion was visible in the mass spectrum of compound **16**, the ready loss of nitrogen dioxide from this molecule was typical of such structures,[12] and the identification of this compound appears secure.

The structure of 4-methoxy-2,3-dimethylbenzonitrile *N*-oxide (**15**) was consistent with the molecular formula, $C_{10}H_{11}NO_2$, determined from its mass spectrum, and infrared bands at 2280 and 1263 cm^{-1}.[13] The regiochemistry was determined from the results of nuclear Overhauser experiments, and the ^{13}C NMR spectrum (Experimental section) was in accord with the structure assigned.

Finally, the structure of 3-methoxy-4,5-dimethylbenzoic acid (**19**) was consistent with its spectroscopic data.

Photochemistry of 2,3-dimethylanisole (**6**) *in dichloromethane at −20 °C and in acetonitrile at 20, −20 °C.* Similar reactions were performed to the above, except for the reaction temperature for reactions in dichloromethane, and for acetonitrile solution at 20 and −20 °C. The results are summarized in Tables 4 and 5.

Photochemistry of 2,3-dimethylanisole (**6**) *in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) at 20 °C.* Photolysis of the CT complex of 2,3-dimethylanisole (**6**) and tetranitromethane in HFP at 20 °C for 24 h resulted in complete conversion into nitro–trinitromethyl adducts **10** (1%) and **11** (2%), hydroxy–trinitromethyl adducts **12** (0.3%) and **13** (trace), and aromatic compounds **14** (19%), **16** (4%), **17** (61%), **18** (0.3%), and unidentified

Table 5. Overview of yields of products from the photolysis of 2,3-dimethylanisole (**6**) (0.46 mol dm^{-3}) and tetranitromethane (0.92 mol dm^{-3}) in acetonitrile.

	Yield (%)												
t/h	10	11	12	13	Total adducts[a]	14	15	16	17	18	19	20	Total aromatics[b]
At 20 °C													
1	22.8	4.4	—	—	27.2	1.7	0.4	0.4	53.1	9.1	—	—	72.8
2	21.6	4.3	—	—	25.9	2.6	1.0	0.4	53.0	7.7	—	—	74.1
4	20.9	4.9	—	—	25.8	2.4	1.7	0.4	53.1	6.6	1.4	—	74.2
8	24.1	5.7	—	—	29.8	2.6	1.5	0.4	53.8	3.3	1.0	—	70.2
At −20 °C													
1	15.2	2.8	—	—	18.0	8.1	17.5	—	34.6	6.0	—	—	82.0
2	20.1	3.3	—	—	23.4	4.4	9.4	—	46.5	6.0	—	—	76.6
4	22.6	3.8	—	—	26.4	7.0	4.6	—	48.5	5.7	—	—	73.6
8	24.1	4.0	—	—	28.1	6.9	2.2	—	52.4	2.9	—	—	71.9

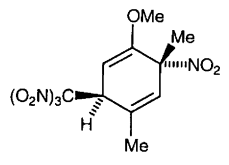
[a] Including unidentified adducts. [b] Including unidentified aromatics.

aromatic compounds (12%) (Table 6). In HFP the conversion of 2,3-dimethylanisole (**6**) into products after a reaction time of 8 h was lower (ca. 30%) compared with essentially complete conversion in dichloromethane at 20 °C.

Photochemistry of 2,3-dimethylanisole (**6**) *at 20 °C in dichloromethane containing trifluoroacetic acid (0.7 mol dm^{-3}).* Photolysis of the CT complex of 2,3-dimethylanisole–tetranitromethane in dichloromethane containing trifluoroacetic acid (0.7 M) for 8 h at 20 °C, as above, resulted in a low conversion (ca. 20%) into a mixture of nitro–trinitromethyl adducts **10** (3%) and **11** (0.5%), aromatic compounds **14** (42%), **15** (7%), **16** (8%), **17** (23%), **18** (2%), and unidentified aromatic compounds (15%) (Table 7).

Photochemistry of 2,4-dimethylanisole (**7**) *in dichloromethane at 20 °C and the identification of adducts* **21** *and* **22.** A solution of 2,3-dimethylanisole (**7**) (0.46 mol dm^{-3}) and tetranitromethane (0.92 mol dm^{-3}) in dichloromethane was irradiated for at 20 °C. The composition of the mixture was monitored by withdrawing samples for NMR spectral analysis (Table 8). The final solution (after 3 h, conversion ca. 81%) after work-up contained the nitro–trinitromethyl adducts **21** (15%) and **22** (2%), unidentified adducts (total 8%), 4,6-dimethyl-3-trinitromethylanisole (**23**) (30%), 4,6-dimethyl-2-nitrophenol (**24**) (9%), 4,6-dimethyl-2-trinitromethylanisole (**25**) (5%), 4,6-dimethyl-3-nitroanisole (**26**) (1.5%), 4,6-dimethyl-2-nitroanisole (**27**) (11%), 2,4-dimethyl-4-nitrocyclohexa-2,5-dienone (**28**) (14%), and unidentified aromatic compounds (total 5%) (Table 8). The nitro–trinitromethyl adducts **21** and **22** were separated partially by HPLC and gave in elution order a mixture of aromatic compounds **23–27**, and the two adducts **21** and **22**. The mixture of aromatic compounds **23–27** were separated subsequently by chromatography on a silica gel Chromatotron plate.

(A) The epimeric nitro–trinitromethyl adducts **21** *and* **22.** Although the epimeric nitro–trinitromethyl adducts **21** and **22** could be isolated by HPLC, they were too unstable for complete purification and neither could be induced to crystallize. The connectivity in each epimer was established from the results of nuclear Overhauser experiments and reverse detected heteronuclear correlation spectra. The two ^{13}C NMR spectra were closely



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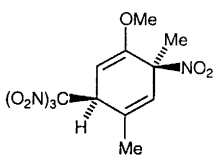

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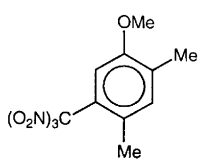

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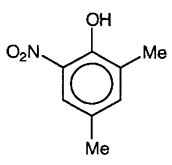

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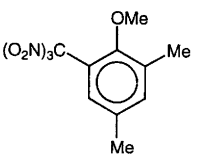

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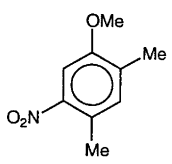

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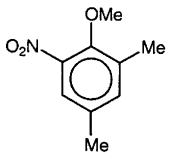

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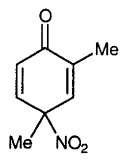

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Table 6. Overview of yields of products from the photolysis of 2,3-dimethylanisole (**6**) (0.46 mol dm^{-3}) and tetranitromethane (0.92 mol dm^{-3}) in 1,1,1,3,3,3-hexafluoropropan-2-ol at 20 °C.

	Yield (%)											
t/h	10	11	12	13	Total adducts[a]	14	15	16	17	18	19	20	Total aromatics[b]
1	14.9	4.2	1.3	0.6	21.0	10.7	8.2	5.0	38.4	3.1	—	—	79.0
2	14.3	5.0	1.6	0.8	21.7	13.7	1.6	4.4	41.9	3.0	—	—	78.3
4	10.6	4.0	2.3	1.1	18.0	25.8	0.8	4.4	40.2	1.2	—	—	82.0
8	7.8	4.0	3.1	1.6	16.5	23.3	0.4	4.1	47.0	0.5	—	—	83.5
24	1.0	2.2	0.3	Trace	3.5	19.2	—	4.0	60.8	0.3	—	—	96.5

[a] Including unidentified adducts. [b] Including unidentified aromatics.

Table 7. Overview of yields of products from the photolysis of 2,3-dimethylanisole (**6**) (0.46 mol dm^{-3}) and tetranitromethane (0.92 mol dm^{-3}) in dichloromethane containing trifluoroacetic acid (0.7 M) at 20 °C.

	Yield (%)											
t/h	10	11	12	13	Total adducts[a]	14	15	16	17	18	19	20	Total aromatics[b]
1	3.3	0.9	—	—	4.2	41.6	8.1	5.3	11.0	—	—	—	95.8
2	3.3	0.9	—	—	4.2	47.1	6.0	8.8	15.3	—	—	—	95.8
4	4.3	1.1	—	—	5.4	45.9	6.0	4.4	17.4	Trace	—	—	94.6
8	3.0	0.5	—	—	3.5	41.7	6.7	8.0	23.3	1.6	—	—	96.5

[a] Including unidentified adducts. [b] Including unidentified aromatics.

similar, and the ^1H NMR spectra were as might be expected for such epimers. The assignment of stereochemistry was made on the basis of the elution order of the two epimers from the HPLC column, the *t*-6-nitro-*r*-3-trinitromethylmethyl compound **21** being eluted before the *c*-6-nitro-*r*-3-trinitromethyl adduct **22**.[8,9]

(B) The aromatic products **23–27** *and nitro dienone* **28**. The aromatic compounds **23–27** were separated by chromatography on a silica gel Chromatotron plate. The structures of the regioisomeric trinitromethyl aromatic compounds **23** and **25** were determined from their spectroscopic data. For the major isomer **23** crystalline material was obtained but of an inadequate quality for single-crystal X-ray analysis. Nonetheless, given the molecular formula ($C_{10}H_{11}N_3O_7$, mass spectrum), its structure was securely established from the observed enhancement of the signal due to H2 (δ 6.66, singlet) on irradiation at the OMe resonance (δ 3.79) in a nuclear Overhauser experiment. The structure of the minor isomer **25** then followed by exclusion, the ^1H NMR signals due to H3 (δ 6.81) and H5 (δ 7.00) appearing as singlets. Similarly, the structures of the 3-nitro- and 2-nitro-4,6-dimethylanisoles **26** and **27** were established from their spectroscopic data (Experimental section).

The structures of the nitrophenol **24** and its precursor, 2,4-dimethyl-4-nitrocyclohexa-2,5-dienone (**28**), were assigned by comparison with literature data.[14] The nitrodienone **28** was not isolated from chromatography on the silica gel Chromatotron plate, and under those conditions it would be expected to undergo isomerization to give the nitrophenol **24**.

Photochemistry of 2,4-dimethylanisole (**7**) *in dichloromethane at −20 °C and in acetonitrile at 20, −20 °C.* Similar reactions were performed to the above, except for the reaction temperature for reactions in dichloromethane, and for acetonitrile solution at 20, and −20 °C. The results are summarized in Tables 8 and 9.

Photochemistry of 2,4-dimethylanisole (**7**) *in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) at 20 °C.* Photolysis of the CT complex of 2,4-dimethylanisole (**7**) and tetranitromethane in HFP at 20 °C for 3 h resulted in a conversion (ca. 46%; cf. 81% in dichloromethane under similar conditions) into nitro–trinitromethyl adducts **21** (1%) and **22** (2%), aromatic compounds **23** (21%), **24** (6%), **25** (2%), **26** (16%), **27** (38%), and unidentified aromatic compounds (total 14%).

Attempts at EPR spectroscopic detection of intermediates. Radical cations $ArH^{\cdot+}$ of moderate reactivity can often be detected by EPR spectroscopic monitoring of continuously photolyzed dichloromethane solutions of ArH, tetranitromethane and trifluoroacetic acid at low temperatures,[15] usually −60 °C. The acid serves to protonate trinitromethanide ion and thus strongly decrease its reactivity toward $ArH^{\cdot+}$. When the substrates studied here were exposed to such treatment ([substrate]= 20–100 mmol dm^{-3}, [tetranitromethane]=0.8 mol dm^{-3}, [TFA]=0.8 mol dm^{-3}, light of $\lambda > 430$ nm) at −60 °C, no EPR spectral activity was detected. However, the solution containing 2,3-dimethylanisole (**6**) developed an EPR spectrum characteristic of radical cations of

Table 8. Overview of yields of products from the photolysis of 2,4-dimethylanisole (**7**) (0.46 mol dm^{-3}) and tetranitromethane (0.92 mol dm^{-3}) in dichloromethane.

	Yield (%)								
t/h	21	22	Total adducts[a]	23	24	25	26	27	28
At 20 °C									
1	11.4	1.8	29.0	14.2	5.3	6.5	1.3	13.6	18.1
2	14.9	1.8	25.8	24.9	4.9	6.0	1.0	9.4	14.0
3	15.2	2.1	22.0	29.7	9.0	4.6	1.5	11.0	13.8
At −20 °C									
1	11.5	1.8	25.1	1.9	1.9	2.4	1.9	12.7	27.9
2	16.9	2.7	28.2	2.0	2.9	3.5	3.9	15.9	29.3
3	21.3	3.2	37.3	2.4	2.0	1.9	5.0	16.8	24.8
At −50 °C									
2	32.8	4.1	44.4	0.4	1.3	1.1	5.6	13.5	21.5
3	36.5	4.3	47.4	1.8	0.7	1.1	7.3	14.5	17.5
4	38.0	4.4	50.0	1.7	0.9	0.8	8.5	15.2	14.8
At −78 °C									
1	30.8	3.2	40.3	6.8	2.6	3.8	0.8	3.2	28.4
2	34.7	4.0	47.2	1.5	1.4	1.5	2.8	6.6	25.0
3	39.0	3.8	50.1	1.9	2.2	1.2	4.4	8.1	21.7

[a] Including unidentified adducts.

Table 9. Overview of yields of products from the photolysis of 2,4-dimethylanisole (**7**) (0.46 mol dm^{-3}) and tetranitromethane (0.92 mol dm^{-3}) in acetonitrile.

	Yield (%)								
t/h	21	22	Total adducts[a]	23	24	25	26	27	28
At 20 °C									
2	47.0	13.4	60.4	0.9	3.0	1.1	6.4	9.6	9.6
3	44.4	16.1	60.5	1.3	3.7	0.9	7.3	11.0	7.3
At −20 °C									
2	49.2	7.2	59.2	0.6	1.4	1.1	2.9	1.6	23.4
3	49.0	7.2	61.6	1.2	1.3	0.9	3.0	1.5	21.5

[a] Including unidentified adducts.

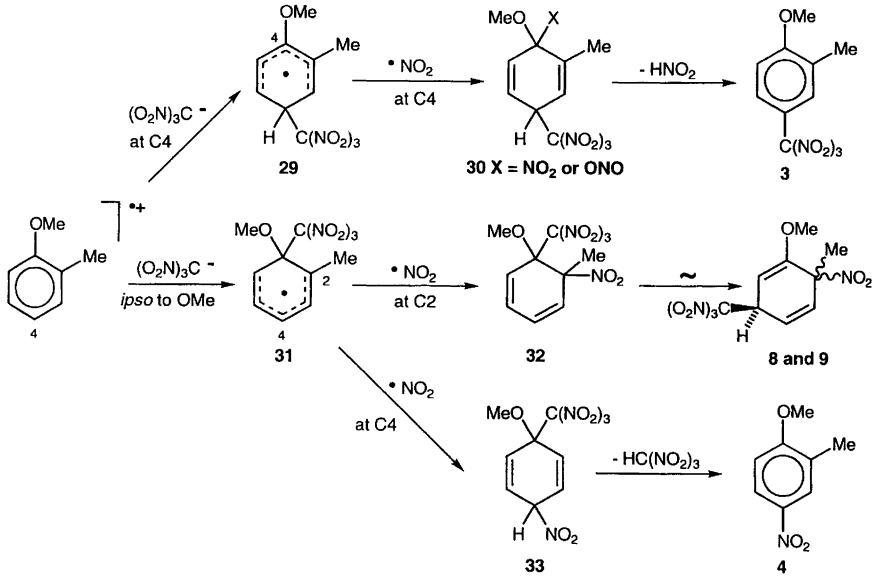
aromatic nitroso compounds (a^N 32–34 G)[16] upon irradiation at temperatures around 0 °C.

Discussion

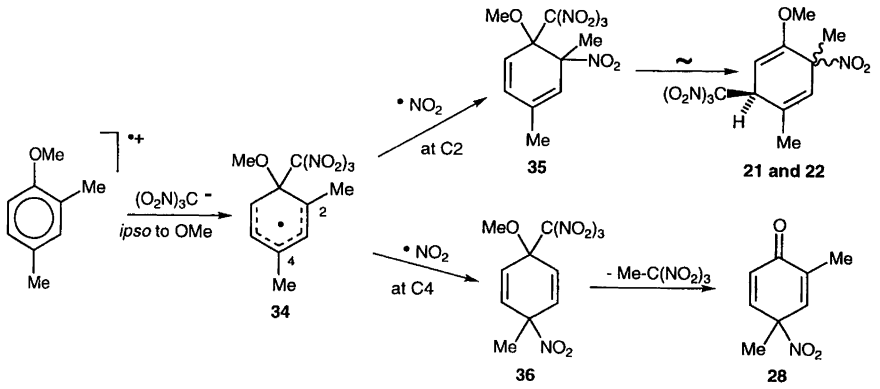
The photolysis of the CT complex of 2-methylanisole (**2**) *with tetranitromethane.* At all reaction temperatures in dichloromethane (from 20 to −78 °C) and in acetonitrile (from 20 to −45 °C) the trinitromethyl compound **3**, nitro compound **4**, and the two epimeric 1-methoxy-6-methyl-6-nitro-3-trinitromethylcyclohexa-1,4-dienes **8** and **9** were formed (Tables 1 and 2). In dichloromethane at 20 °C, and in acetonitrile at 20 and −20 °C, some decomposition of the trinitromethyl compound **3** occurred yielding, in part, the nitro compound **4**. The formation of the trinitromethyl compound **3** is envisaged as occurring via initial attack of trinitromethanide ion at C4 in the radical cation of 2-methylanisole to give the delocalized carbon radical **29**. Radical coupling of this delocalized carbon radical **29** with nitrogen dioxide and loss of nitrous acid from the adduct **30** would give the trinitromethyl compound **3** (Scheme 1).

Notably the change from the less polar dichloromethane to the more polar acetonitrile as solvent results in increased yields of the nitro compound **4** *and* the epimeric adducts **8** and **9**. These observations may be rationalized in terms of some shift in the regiochemistry of attack of trinitromethanide ion on the radical cation of 2-methylanisole towards attack *ipso* to the methoxy group when the trinitromethanide ion is rendered less nucleophilic by the more polar solvent. This mode of attack would give the delocalized carbon radical **31** (Scheme 1). Radical coupling with nitrogen dioxide at C2 would give adducts **32**, which might be expected[1,8] to undergo heterolytic allylic rearrangement to give the epimeric 6-methyl-6-nitro-3-trinitromethyl adducts **8** and **9**. In the radical coupling to form the postulated intermediate adducts **32**, the preferred orientation of bond formation would be *anti* to the adjacent bulky trinitromethyl group. If the heterolytic allylic rearrangement proceeded via a 'tight' ion pair, the observed higher yield of the *t*-6-nitro-*r*-3-trinitromethyl adduct **8** may be rationalized. The alternative radical coupling of nitrogen dioxide with the delocalized carbon radical **31** at C4 would give adducts **33**, from which nitro compound **4** would arise by loss of nitroform.

The photolysis of the CT complex of 2,4-dimethylanisole (**7**) *with tetranitromethane.* At low temperatures in both dichloromethane and acetonitrile solution the products formed were the epimeric 1-methoxy-4,6-dimethyl-6-nitro-3-trinitromethylcyclohexa-1,4-dienes **21** and **22**, and the 2,4-dimethyl-4-nitrocyclohexa-2,5-dienone **28**. These products are envisaged as being formed via initial attack of trinitromethanide ion *ipso* to the methoxy group in the radical cation of 2,4-dimethylanisole to give the delocalized carbon radical **34** (Scheme 2). As for the reaction sequence (Scheme 1) for 2-methylanisole, radical coupling of this carbon radical **34** at C2 with nitrogen dioxide followed by allylic rearrangement of adducts **35** would yield the epimeric 1-methoxy-4,6-dimethyl-6-nitro-3-trinitromethylcyclohexa-1,4-dienes **21** and **22**, with the *t*-6-nitro-*r*-3-trinitromethyl epimer predominant (Tables 8 and 9). Alternatively, radical coupling of nitrogen dioxide at C4 of the delocalized carbon radical **34** would give the adducts **36**, which on the loss of the elements of $Me\text{-}C(NO_2)_3$ would lead to the formation of the nitrodienone **28**; an analogous process was postulated to account for nitrodienone formation in the photolysis of the charge-transfer complex of 4-methylanisole (**1**) with tetranitromethane.[3]



Scheme 1.



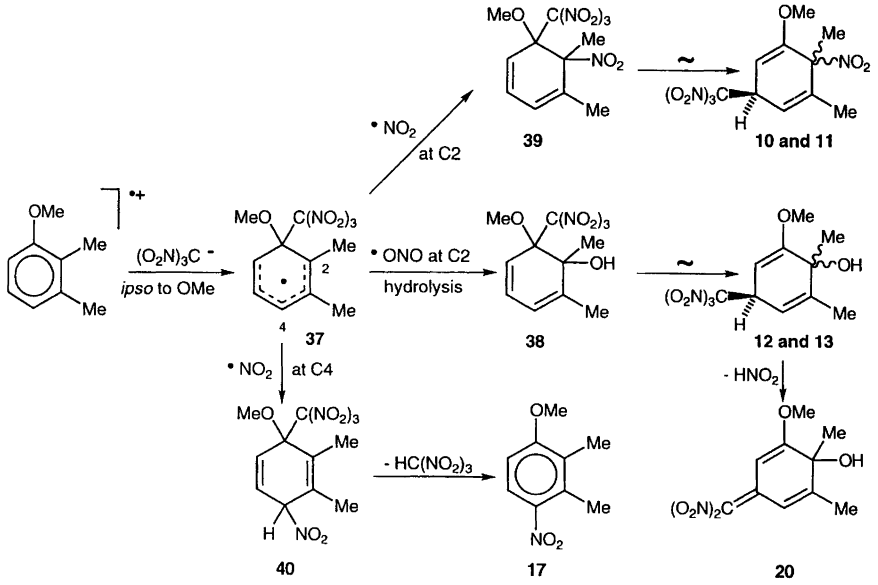
Scheme 2.

The photolysis of the CT complex of 2,3-dimethylanisole (**6**) *with tetranitromethane.* The product mixtures formed in the photolysis reactions of 2,3-dimethylanisole (**6**) were seemingly more complex. However, much of this apparent complexity is readily rationalized. In the radical coupling of nitrogen dioxide with the delocalized carbon radical **37** both C–N and C–O bond formation occurs, the latter being favoured by the steric compression at C2;[17] hydrolysis of the nitrite ester so formed then yields the hydroxy adducts **38** counterpart of of the nitro adducts **39**. Loss of nitrous acid from the rearranged hydroxy–trinitromethyl adducts **12** and **13** provides a mode of genesis of the hydroxy dinitro compound **20**.

While it appears likely that much of the nitro compound **17** arises by loss of nitroform from adduct **40** (Scheme 3), some nitro compound **17** is probably formed by a series of reaction steps beginning with 2,3-dimethyl-4-trinitromethylanisole (**16**). Such compounds are known to yield the corresponding nitro derivative by nitrodecarboxylation of the carboxylic acid formed by decomposition of the trinitromethyl group.[18] In the present study the nitrile *N*-oxide **15** was isolated and it is attractive to place this compound on a reaction pathway to nitro compound **17**, given its clear conversion into that compound for the photolysis reaction in acetonitrile at −20 °C (Table 5).

Photolysis reactions of 2-methylanisole (**2**)*, 2,3-dimethylanisole* (**6**) *and 2,4-dimethylanisole* (**7**) *in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP).* HFP has been found to strongly stabilize radical cations, largely by rendering any nucleophilic species present exceedingly unreactive.[19] In the present work we therefore anticipated that reaction of each radical cation with trinitromethanide ion would be slow and allow competition from the $ArH^{\cdot+}/{}^{\cdot}NO_2$ coupling process. For each substrate, **2**, **6** and **7**, the conversion into products was somewhat slowed but product formation involving attack by trinitromethanide ion remained significant reaction pathways.

Implications of the EPR spectral results. The failure to observe any EPR spectral activity upon irradiation of **2**,



Scheme 3.

6 or **7** together with tetranitromethane and trifluoroacetic acid in dichloromethane at −60 °C shows that the radical cations of the compounds react fast under these conditions, either with trinitromethanide ion which has escaped protonation, nitroform or NO_2 [eqn. (4)].[15] The triad of eqn. (1) is initially formed as a kinetically unique entity, and with a highly reactive $ArH^{\cdot +}$ reaction with trinitromethanide ion can take place at least partially before protonation has occurred. This phenomenon has been found for naphthalene radical cation–trinitromethanide ion, a minor part of the latter (ca. 15%) not being accessible for protonation even at higher [TFA].[15]

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

In the preparative experiments involving **6** the irradiated solution rapidly attained a deep-red colour, signifying that a better electron acceptor had been formed. After workup, a sample of the crude product mixture upon treatment with thallium(III) trifluoroacetate in HFP gave a strong EPR spectrum of the radical cation of an aromatic nitroso compound.[19b] This spectrum was the same as that obtained in dichloromethane around 0 °C. Efficient nitrosation of many aromatic compounds has been achieved by NO_2 in dichloromethane,[20] and it is therefore not surprising that a nitroso compound ArNO can be detected in tetranitromethane photolyses with ArH.[19a,b] Generally, ArNO are easier to oxidize than their parent ArH,[16,20] and thus the drastic colour change is explicable, as well as the EPR spectral behaviour.

In HFP, a solvent which vastly attenuates the reactivity of nucleophiles and stimulates nitrosation by NO_2, similar EPR spectral behaviour of **6** as in dichloromethane–trifluoroacetic acid is found.[19b] Both the primary radical cation $\mathbf{6}^{\cdot +}$ and the radical cation of an aromatic nitroso compound were detected.

Experimental

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. Tetranitromethane, 2-methylanisole, 2,3-dimethylanisole and 2,4-dimethylanisole were purchased from Aldrich. Dichloromethane (AR) and acetonitrile (HiPerSolv) were from BDH and HFP from Sigma or Aldrich.

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.[21]

General procedure for the photonitration of 2-methylanisole (**2**) *with tetranitromethane.* A solution of 2-methylanisole (**2**) (500 mg, 0.51 mol dm^{-3}) and tetranitromethane (1.02 mol dm^{-3}) in dichloromethane (at 20, −20, −50 or −78 °C), acetonitrile (at 20, −20 or −45 °C), or HFP (20 °C) was irradiated with filtered light ($\lambda_{cut\text{-}off}$ 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 (dichloromethane reactions, Table 1; acetonitrile reactions, Table 2).

Photochemistry of 2-methylanisole (**2**) *in dichloromethane at 20 °C and the identification of products* (**3**, **4**, **8** *and* **9**). Reaction of 2-methylanisole–tetranitromethane in

dichloromethane at 20 °C, as above, for 4 h resulted in partial conversion (ca. 50%) (^{1}H NMR spectra) into 2-methyl-4-trinitromethylanisole (**3**) (65%), 2-methyl-4-nitroanisole (**4**) (25%), unidentified aromatic compounds (total 4%), and nitro–trinitromethyl adducts **8** (4%) and **9** (2%) (Table 1). The aromatic compounds **3** and **4** were separated by chromatography on a silica gel Chromatotron plate and gave in elution order:

2-Methyl-4-trinitromethylanisole (**3**), ^{1}H NMR ($CDCl_3$) δ 2.27 (s, 2-Me), 3.93 (s, OMe), 6.95 (d, $J_{H6,H5}$ 8.8 Hz, H6), 7.36 (dq, $J_{H3,H5}$ 2.9 Hz, $J_{H3,2\text{-Me}}$ 1.0 Hz, H3), 7.45 (dd, $J_{H5,H6}$ 8.8 Hz, $J_{H5,H3}$ 2.9 Hz, H5); essentially identical with literature data.[4]

2-Methyl-4-nitroanisole (**4**), m.p. 62.5–63.5 °C (Lit.[7] m.p. 64 °C), ^{1}H NMR ($CDCl_3$) δ 2.24 (s, 2-Me), 3.92 (s, OMe), 6.85 (d, $J_{H6,H5}$ 8.8 Hz, H6), 7.97 (br s, H3), 8.05 (br d, $J_{H5,H6}$ 8.8 Hz, H5).

The nitro–trinitromethyl adducts **8** and **9** were separated partially by HPLC and gave in elution order:

1-Methoxy-6-methyl-t-*6-nitro*-r-*3-trinitromethylcyclohexa-1,4-diene* (**8**), isolated as an oil containing impurities (ca. 10%). ^{1}H NMR ($CDCl_3$) δ 1.83 (s, 6-Me), 3.66 (s, OMe), 4.95 (m, H3), 5.03 (m, H2), 6.04 (ddd, $J_{H4,H5}$ 9.8 Hz, $J_{H4,H3}$ 3.0 Hz, $J_{H4,H2}$ 2.0 Hz, H4), 6.17 (dd, $J_{H5,H4}$ 9.8 Hz, $J_{H5,H3}$ 2.0 Hz, H5). Nuclear Overhauser experiments, see Table 10. ^{13}C NMR ($CDCl_3$) δ 23.5 (6-Me), 43.7 (C3), 55.7 (OCH_3), 85.7 (C6), 89.3 (C2), 121.8 (C4), 133.9 (C5), 157.5 (C1), resonance for $C(NO_2)_3$ not observed. The above correlations were confirmed by reverse detected heteronuclear correlation spectra (HMQC).

1-Methoxy-6-methyl-c-*6-nitro*-r-*3-trinitromethylcyclohexa-1,4-diene* (**9**), m.p. 75–77 °C (decomp.) (X-ray crystal structure determined, see below). IR: ν_{max} ($CDCl_3$ solution) 1603, 1560, 1556 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.85 (s, 6-Me), 3.71 (s, OMe), 4.86 (m, H3), 5.03 (m, H2), 5.99 (ddd, $J_{H4,H5}$ 9.8 Hz, $J_{H4,H3}$ 3.5 Hz, $J_{H4,H2}$ 2.0 Hz, H4), 6.22 (dd, $J_{H5,H4}$ 9.8 Hz, $J_{H5,H3}$ 1.9 Hz, H5). Nuclear Overhauser experiments, see Table 10. ^{13}C NMR ($CDCl_3$) δ 23.6 (6-Me), 42.6 (C3), 55.8 (OCH_3), 85.5 (C6), 89.5 (C2), 121.8 (C4), 133.6 (C5), 157.1 (C1), resonance for $C(NO_2)_3$ not observed. The above correlations were confirmed by reverse detected heteronuclear correlation spectra (HMQC).

Photochemistry of 2-methylanisole (**2**) *in HFP at 20 °C.* Reaction of 2-methylanisole–tetranitromethane in HFP at 20 °C, as above, for 2 h resulted in a low conversion (ca. 8%; to be compared with ca. 21% in dichloromethane for 2 h at 20 °C) of 2-methylanisole (**2**) into 2-methyl-4-trinitromethylanisole (**3**) (35%), 2-methyl-4-nitroanisole (**4**) (30%), unidentified aromatic compounds (total 15%), 1-methoxy-6-methyl-*t*-6-nitro-*r*-3-trinitromethylcyclohexa-1,4-diene (**8**) (8%), 1-methoxy-6-methyl-*c*-6-nitro-*r*-3-trinitromethylcyclohexa-1,4-diene (**9**) (4%), and unidentified adducts (total 8%).

Table 10. Nuclear Overhauser effects for compounds isolated.

Compound	Irradiated at δ (ppm)	Enhancement(s) (%) at δ(ppm)
8	5.03	3.66 (0.5)
	6.04	4.95 (0.1); 6.17 (3.3)
	6.17	1.83 (0.2); 6.04 (5.9)
9	1.85	6.22 (5.1)
	3.71	5.03 (9.3)
	4.86	5.03 (2.0); 5.99 (1.6)
	5.03	3.71 (0.8); 4.86 (0.8)
	5.99	4.86 (1.3); 6.22 (5.5)
	6.22	1.85 (0.5)
10	1.80	5.77 (4.6)
	3.64	5.03 (9.3)
	4.91	5.77 (2.1)
	5.03	3.64 (1.3)
	5.77	1.80 (1.1); 4.91 (2.7)
11	1.82	5.68 (4.2)
	3.63	4.97 (9.5)
	4.81	4.97 (2.3); 5.68 (1.7)
	4.97	3.63 (1.4)
	5.68	4.81 (2.2); 1.82 (0.9)
12	1.45	1.95 (1.3)
	1.95	1.45 (0.9); 5.45 (4.5)
	3.66	4.71 (5.7)
	4.71	3.66 (1.2); 5.45 (2.4)
	5.45	1.95 (0.7); 4.71 (1.3)
13	1.94	5.40 (3.9)
	3.63	4.66 (2.5)
	4.61	3.63 (0.6)
14	2.34	6.96 (5.3)
	3.84	6.87 (9.7)
	6.87	3.84 (1.4)
	6.96	2.34 (0.7)
15	3.80	6.65 (5.4)
	6.65	3.80 (0.9); 6.92 (10.2)
	6.92	6.65 (5.5)
16	2.02	2.21 (1.5)
	2.21	2.02 (1.1)
	3.91	6.83 (7.1)
	6.83	3.91 (1.5); 7.11 (11.3)
	7.11	6.83 (5.3)
19	2.21	2.33 (1.1)
	2.33	2.21 (0.9); 7.56 (7.5)
	3.88	7.42 (10.8)
	7.42	3.88 (1.4)
	7.56	2.33 (1.1)
20	1.55	2.16 (1.5)
	2.16	1.55 (0.8); 6.38 (5.8)
	3.94	6.44 (10.3)
	6.38	2.16 (0.8)
	6.44	3.94 (1.0)
21	1.76	5.87 (9.8)
	1.86	4.99 (5.2); 5.87 (9.8)
	3.63	5.03 (13.3)
	5.87	1.76 (0.5); 1.86 (1.3)
22	1.80	5.96 (7.9)
	1.86	4.87 (5.7); 5.96 (7.4)
	3.66	5.15 (12.1)
23	2.10	7.18 (5.5)
	2.27	7.18 (4.4)
	3.79	6.66 (13.5)
	6.66	3.79 (1.1)
	7.18	2.10 (1.3); 2.27 (1.0)
26	2.24	3.87 (0.2); 7.07 (2.6)
	2.53	7.07 (3.6)
	3.87	2.24 (0.3); 7.50 (8.0)
	7.07	2.24 (0.8); 2.53 (0.8)
	7.50	3.87 (0.8)

General procedure for the photonitration of 2,3-dimethylanisole (**6**) *with tetranitromethane.* A solution of 2,3-dimethylanisole (**6**) (500 mg, 0.46 mol dm^{-3}) and tetranitromethane (0.92 mol dm^{-3}) in dichloromethane (at 20 or −20 °C), acetonitrile (20 or −20 °C), or HFP (20 °C) was irradiated with filtered light ($\lambda_{cut\text{-}off}$ 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 4–6).

Photochemistry of 2,3-dimethylanisole (**6**) *in dichloromethane at 20 °C and the identification of products* (**10–20**). Reaction of 2,3-dimethylanisole–tetranitromethane in dichloromethane at 20 °C, as above, for 8 h resulted in essentially complete conversion into a product which was shown by ^{1}H NMR spectra to be a mixture of nitro–trinitromethyl adducts **10** (15%) and **11** (9%), hydroxy–trinitromethyl adducts **12** (3%) and **13** (1%), and aromatic compounds **14** (10%), **15** (1%), **16** (7%), **17** (42%), **18** (5%), **19** (1%) and hydroxy dinitro compound **20** (1%) (Table 4). HPLC allowed the partial separation of these products in the elution order given below.

5,6-Dimethyl-3-trinitromethylanisole (**14**), m.p. 94 °C (decomp.) (Insufficient for elemental analysis. Found: M^+ 285.0593. $C_{10}H_{11}N_3O_7$ requires 285.0597). IR: ν_{max} (KBr) 1614, 1587 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.22 (s, 6-Me), 2.34 (s, 5-Me), 3.84 (s, OMe), 6.87 (d, $J_{H2,H4}$ 2.5 Hz, H2), 6.96 (d, $J_{H4,H2}$ 2.5 Hz, H4). Nuclear Overhauser experiments, see Table 10. ^{13}C NMR ($CDCl_3$) δ 12.2 (6-Me), 20.4 (5-Me), 55.9 (OCH_3), 108.1 (C2), 119.6 (C3), 123.5 (C4), 133.4 (C5), 139.2 (C6), 157.9 (C1); a resonance for $C(NO_2)_3$ was not observed. The above assignments were confirmed by reverse detected heteronuclear correlation spectra (HMBC, HMQC).

4-Methoxy-2,3-dimethylbenzonitrile N-*oxide* (**15**), m.p. 112 °C (sublim.) (Insufficient for elemental analysis. Found: M^+ 177.0790. $C_{10}H_{11}NO_2$ requires 177.0790). IR: (KBr) 2280, 1263 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.15 (s, 3-Me), 2.24 (s, 2-Me), 3.80 (s, OMe), 6.65 (d, $J_{H5,H6}$ 8.8 Hz, H5), 6.92 (d, $J_{H6,H5}$ 8.8 Hz, H6). Nuclear Overhauser experiments, see Table 10. ^{13}C NMR ($CDCl_3$) δ 12.3 (3-Me), 15.2 (2-Me), 55.7 (OCH_3), 108.3 (C5), 122.8 (C6), 124.9 (C1), 126.3 (C3), 132.3 (C2), 155.3 (C4); a resonance for $C(NO_2)_3$ was not observed. The above assignments were confirmed by reverse detected heteronuclear correlation spectra (HMBC, HMQC).

2,3-Dimethyl-4-trinitromethylanisole (**16**), m.p. 58–59 °C (Insufficient for elemental analysis. Found: No parent ion visible, M^+-NO_2 239.0664. $C_{10}H_{11}N_2O_5$ requires 239.0668). IR: ν_{max} (KBr) 1622, 1580 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.02 (s, 3-Me), 2.21 (s, 2-Me), 3.91 (s, OMe), 6.83 (d, $J_{H6,H5}$ 8.8 Hz, H6), 7.11 (d, $J_{H5,H6}$ 8.8 Hz, H5). Nuclear Overhauser experiments, see Table 10. ^{13}C NMR ($CDCl_3$) δ 12.0 (2-Me), 18.2 (3-Me), 55.8 (OCH_3), 107.7 (C6), 113.7 (C4), 128.7 (C2), 129.0 (C5), 139,5 (C3), 161.5 (C1); a resonance for $C(NO_2)_3$ was not observed. The above assignments were confirmed by reverse detected heteronuclear correlation spectra (HMBC, HMQC).

2,3-Dimethyl-4-nitroanisole (**17**), m.p. 71–72 °C (Lit.[4] m.p. 70–73 °C) identical with authentic material.

5,6-Dimethyl-2,4-dinitrophenol (**18**), m.p. 84–85.5 °C (Lit.[5] m.p. 86.5–87 °C). IR: ν_{max} (KBr) 3209, 1614, 1591, 1549, 1522, 1354 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.37, 2.54 (both s, 5-Me, 6-Me), 8.61 (s, H3), 11.32 (br s, OH).

3-Methoxy-4,5-dimethylbenzoic acid (**19**), m.p. 153–154 °C (Insufficient for elemental analysis. Found: M^+ 180.0782. $C_{10}H_{12}O_3$ requires 180.0786). IR: ν_{max} (KBr) 3421, 1684 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.21 (s, 4-Me), 2.33 (s, 5-Me), 3.88 (s, OMe), 7.42 (br s, H2), 7.56 (br s, H6). Nuclear Overhauser experiments, see Table 10.

1-Methoxy-5,6-dimethyl-t-*6-nitro*-r-*3-trinitromethylcyclohexa-1,4-diene* (**10**), as an oil containing an impurity (5%). IR: ν_{max} (liquid film) 1599, 1558 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.80 (dd, $J_{5\text{-}Me,H4}$ 1.5 Hz, $J_{5\text{-}Me,\ H3}$ 1.4 Hz, 5-Me), 1.82 (s, 6-Me), 3.64 (s, OMe), 4.91 (br s, H3), 5.03 (dd, $J_{H2,H3}$ 3.9 Hz, $J_{H2,H4}$ 1.5 Hz, H2), 5.77 (ddq, $J_{H4,H3}$ 3.4 Hz, $J_{H4,H2}$ 1.5 Hz, $J_{H4,5\text{-}Me}$ 1.5 Hz, H4); the spin–spin coupling patterns above were confirmed by double irradiation experiments. Nuclear Overhauser experiments, see Table 10. ^{13}C NMR ($CDCl_3$) δ 18.0 (5-Me), 21.9 (6-Me), 43.6 (C3), 55.9 (OCH_3), 88.5 (C2), 89.1 (C6), 117.3 (C4), 140.5 (C5), 158.3 (C1); a resonance for $C(NO_2)_3$ was not observed. The above assignments were confirmed by reverse detected heteronuclear correlation spectra (HMBC, HMQC).

1-Methoxy-5,6-dimethyl-c-*6-nitro*-r-*3-trinitromethylcyclohexa-1,4-diene* (**11**), as an oil containing an impurity (5%). IR: ν_{max} (liquid film) 1601, 1556 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.82 (dd, $J_{5\text{-}Me,H4}$ 1.4 Hz, $J_{5\text{-}Me,H3}$ 1.4 Hz, 5-Me), 1.85 (s, 6-Me), 3.63 (s, OMe), 4.81 (br s, H3), 4.97 (dd, $J_{H2,H3}$ 3.4 Hz, $J_{H2,H4}$ 2.0 Hz, H2), 5.68 (ddq, $J_{H4,H3}$ 2.9 Hz, $J_{H4,H2}$ 2.0 Hz, $J_{H4,5\text{-}Me}$ 1.4 Hz, H4; the spin–spin coupling patterns above were confirmed by double irradiation experiments. Nuclear Overhauser experiments, see Table 10. ^{13}C NMR ($CDCl_3$) δ 18.0 (5-Me), 21.4 (6-Me), 42.6 (C3), 55.9 (OCH_3), 88.5 (C2, C6), 117.2 (C4), 139.3 (C5), 157.7 (C1); a resonance for $C(NO_2)_3$ was not observed. The above assignments were confirmed by reverse detected heteronuclear correlation spectra (HMBC, HMQC).

2-Methoxy-1,6-dimethyl-t-*4-trinitromethylcyclohexa-2,5-dien*-r-*1-ol* (**12**), isolated only in admixture with hydroxy–trinitromethyl adduct **13** (15%) below. IR: ν_{max} (liquid film) 3460, 1597, 1576 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.45 (s, 1-Me), 1.95 (d, $J_{6\text{-}Me,H5}$ 1.5 Hz, 6-Me), 3.66 (s, OMe), 4.71 (d, $J_{H4,H5}$ 2.9 Hz, H4), 4.71 (s, H3), 5.45

(dq, $J_{H5,H4}$ 2.9 Hz, $J_{H5,6\text{-}Me}$ 1.5 Hz, H5); the spin–spin coupling patterns above were confirmed by double irradiation experiments. Nuclear Overhauser experiments, see Table 10. ^{13}C NMR ($CDCl_3$) δ 17.5 (6-Me), 26.9 (1-Me), 43.9 (C4), 55.4 (OCH_3), 68.6 (C1), 84.6 (C3), 112.2 (C5), 147.2 (C6), 163.6 (C2); a resonance for $C(NO_2)_3$ was not observed. The above assignments were confirmed by reverse detected heteronuclear correlation spectra (HMBC, HMQC).

*2-Methoxy-1,6-dimethyl-*c*-4-trinitromethylcyclohexa-2,5-dien-*r*-1-ol* (**13**), isolated only as the minor component in admixture with hydroxy–trinitromethyl adduct (**12**) above. ^1H NMR ($CDCl_3$) δ 1.45 (1-Me), 1.94 (dd, $J_{6\text{-}Me,H5}$ 1.5 Hz, $J_{6\text{-}Me,H4}$ 1.5 Hz, 6-Me), 3.63 (s, OMe), 4.61 (ddq, $J_{H4,H5}$ 3.0 Hz, $J_{H4,H3}$ 2.5 Hz, $J_{H4,6\text{-}Me}$ 1.5 Hz, H4), 4.66 (dd, $J_{H3,H4}$ 2.5 Hz, $J_{H3,H5}$ 2.0 Hz, H3), 5.40 (ddq, $J_{H5,H4}$ 3.0 Hz, $J_{H5,H3}$ 2.5 Hz, $J_{H5,6\text{-}Me}$ 1.5 Hz, H5; the spin–spin coupling patterns above were confirmed by double irradiation experiments. Nuclear Overhauser experiments, see Table 10. ^{13}C NMR ($CDCl_3$) δ 17.7 (6-Me), 24.4 (1-Me), 42.8 (C4), 55.4 (OMe), 85.2 (C3), 112.7 (C5); the above assignments were confirmed by reverse detected heteronuclear correlation spectra (HMQC); resonances for C1, C2, C6 and $C(NO_2)_3$ were not observed for a sample in which adduct (**5**) was the minor component.

2-(4′-Hydroxy-3′-methoxy-4′,5′-dimethylcyclohexa-2′,5′-dienylidene)-1,1-dinitroethene (**20**), as an oil (Insufficient for elemental analysis. Found: M^+ 256.0693. $C_{10}H_{12}N_2O_6$ requires 256.0695). IR: ν_{max} (liquid film) 3427, 1657, 1541 cm^{-1}. UV: λ_{max} (ethanol) 386 nm (ε 32 400), 342 nm (sh, ε 23 600). ^1H NMR ($CDCl_3$) δ 1.55 (s, 4′-Me), 2.16 (d, $J_{5'\text{-}Me,H6'}$ 1.0 Hz, 5′-Me), 2.43 (br s, 4′-OH), 3.94 (s, OMe), 6.38 (dq, $J_{H6',H2'}$ 1.5 Hz, $J_{H6',5'\text{-}Me}$ 1.0 Hz, H6′), 6.44 (d, $J_{H2',H6'}$ 1.5 Hz, H2′); the spin–spin coupling patterns above were confirmed by double irradiation experiments. Nuclear Overhauser experi-ments, see Table 10. ^{13}C NMR ($CDCl_3$) δ 18.6 (5′-Me), 27.2 (4′-Me), 56.9 (OCH_3), 70.9 (C4′), 89.9 (C2′), 114.9 (C6′), 146.6 (C2), 158.5 (C5′), 175.8 (C3′); a resonance for $C(NO_2)_2$ was not observed. The above assignments were confirmed by reverse detected heteronuclear correlation spectra (HMBC, HMQC).

Photochemistry of 2,3-dimethylanisole (**6**) *in HFP at 20 °C.* Reaction of 2,3-dimethylanisole–tetranitromethane in HFP at 20 °C, as above, for 24 h gave a product which was shown by ^1H NMR spectra to be a mixture of nitro–trinitromethyl adducts (**10**) (1%) and (**11**) (2%), hydroxy–trinitromethyl adducts (**12**) (0.3%) and (**13**) (trace), and aromatic compounds (**14**) (19%), (**16**) (4%), (**17**) (61%), (**18**) (0.3%), and unidentified aromatic compounds (12%) (Table 6). After a reaction time of 8 h the conversion of 2,3-dimethylanisole (**6**) into products was ca. 30%, in contrast to essentially complete conversion in dichloromethane at 20 °C.

Photochemistry of 2,3-dimethylanisole (**6**) *in dichloromethane containing trifluoroacetic acid (0.7 M) at 20 °C.* Reaction of 2,3-dimethylanisole–tetranitromethane in dichloromethane containing trifluoroacetic acid (0.7 M) at 20 °C, as above, for 8 h resulted in ca. 20% conversion into a mixture of nitro–trinitromethyl adducts **10** (3%) and **11** (0.5%), aromatic compounds **14** (42%), **15** (7%), **16** (8%), **17** (23%), **18** (2%), and unidentified aromatic compounds (15%) (Table 7).

General procedure for the photonitration of 2,4-dimethylanisole (**7**) *with tetranitromethane.* A solution of 2,4-dimethylanisole (**7**) (500 mg, 0.46 mol dm^{-3}) and tetranitromethane (0.92 mol dm^{-3}) in dichloromethane (at 20, −20, −50 or −78 °C), acetonitrile (at 20 or −20 °C), or HFP (20 °C) was irradiated with filtered light ($\lambda_{cut\text{-}off} < 435$ 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 (dichloromethane reactions, Table 8; acetonitrile reactions, Table 9).

Photochemistry of 2,4-dimethylanisole (**7**) *in dichloromethane at 20 °C and the identification of adducts* **21** *and* **22**. Reaction of 2,4-dimethylanisole–tetranitromethane in dichloromethane at 20 °C, as above, for 3 h resulted in partial conversion (ca. 81%) (^1H NMR spectra) into nitro–trinitromethyl adducts **21** (15%) and **22** (2%), unidentified adducts (total 8%), 4,6-dimethyl-3-trinitromethylanisole (**23**) (30%), 4,6-dimethyl-2-nitrophenol (**24**) (9%), 4,6-dimethyl-2-trinitromethylanisole (**25**) (5%), 4,6-dimethyl-3-nitroanisole (**26**) (1.5%), 4,6-dimethyl-2-nitroanisole (**27**) (11%), 2,4-dimethyl-4-nitrocyclohexa-2,5-dienone (**28**) (14%), and unidentified aromatic compounds (total 5%) (Table 8). The nitro–trinitromethyl adducts **21** and **22** were partially separated by HPLC and gave in elution order:

A mixture of aromatic compounds **23–27** which were separated from a mixture from a reaction in dichloromethane at −78 °C by chromatography on a silica gel Chromatotron plate, below.

*1-Methoxy-4,6-dimethyl-*t*-6-nitro-*r*-3-trinitromethylcyclohexa-1,4-diene* (**21**), as a yellow oil containing impurities (ca. 10%). ^1H NMR ($CDCl_3$) δ 1.76 (s, 6-Me), 1.86 (d, $J_{Me,H5}$ 1.5 Hz, 4-Me), 3.63 (s, OMe), 4.99 (br d, $J_{H3,H2}$ 3.9 Hz, H3), 5.03 (d, $J_{H2,H3}$ 3.9 Hz, H2), 5.87 (q, $J_{H5,Me}$ 1.5 Hz, H5); assignments confirmed where possible by double irradiation experiments. Nuclear Overhauser experiments, see Table 10. ^{13}C NMR ($CDCl_3$) δ 20.9 (4-Me), 23.2 (6-Me), 46.6 (C3), 55.2 (OCH_3), 86.2 (C6), 89.5 (C2), 128.7 (C4), 131.3 (C5), 157.3 (C1); a resonance for $C(NO_2)_3$ was not observed. The above assignments were confirmed by reverse detected heteronuclear correlation spectra (HMBC, HMQC).

*1-Methoxy-4,6-dimethyl-*c*-6-nitro-*r*-3-trinitromethylcyclohexa-1,4-diene* (**22**), as an oil containing impurities (ca. 10%). ^{1}H NMR ($CDCl_3$) δ 1.80 (s, 6-Me), 1.85 (app br s, 4-Me), 3.66 (s, OMe), 4.87 (d, $J_{H3,H2}$ 3.9 Hz, H3), 5.15 (d, $J_{H2,H3}$ 3.9 Hz, H2), 5.96 (q, $J_{H5,Me}$ 1.5 Hz, H5); assignments confirmed where possible by double irradiation experiments. Nuclear Overhauser experiments, see Table 10. ^{13}C NMR ($CDCl_3$) δ 21.3 (4-Me), 23.8 (6-Me), 46.9 (C3), 55.7 (OCH_3), 84.8 (C6), 89.1 (C2), 130.3 (C4), 131.5 (C5), 157.0 (C1); a resonance for $C(NO_2)_3$ was not observed. The above assignments were confirmed by reverse detected heteronuclear correlation spectra (HMBC, HMQC).

Photochemistry of 2,4-dimethylanisole (**7**) *in dichloromethane at −78 °C and the identification of aromatic compounds* **23–28**. Reaction of 2,4-dimethylanisole–tetranitromethane in dichloromethane at −78 °C, as above, for 3 h resulted in partial conversion (ca. 65%) (^{1}H NMR spectra) into nitro–trinitromethyl adducts **21** (39%) and **22** (4%), unidentified adducts (total 7%), aromatic compounds **23** (2%), **24** (2%), **25** (1%), **26** (4%), **27** (8%), nitrodienone **28** (22%), and unidentified aromatic compounds (total 10%) (Table 8). Chromatography of this mixture on a silica gel Chromatotron plate gave in elution order:

4,6-Dimethyl-3-trinitromethylanisole (**23**), m.p. 75–78 °C (decomp.) (Insufficient for elemental analysis, crystals inadequate for X-ray crystallography. Found: M^+ 285.0596. $C_{10}H_{11}N_3O_7$ requires 285.0597). IR: ν_{max} (KBr) 1618, 1591, 1560 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.10, 2.27 (both s, 4-Me, 6-Me), 3.79 (s, OMe), 6.66 (s, H2), 7.18 (s, H5). Nuclear Overhauser experiments, see Table 10.

4,6-Dimethyl-2-nitrophenol (**24**), m.p. 68–69 °C (Lit.[14] 70–71 °C). IR: ν_{max} (KBr) 1541 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 4-Me, 6-Me), 7.26 (d, $J_{H5,H3}$ 1.0 Hz, H5), 7.74 (d, $J_{H3,H5}$ 1.0 Hz, H3), 10.77 (s, OH).

4,6-Dimethyl-2-trinitromethylanisole (**25**), as an oil (Insufficient for elemental analysis. Parent ion not visible. Found: M^+–NO_2 239.06675. $C_{10}H_{11}N_2O_5$ requires 239.0668). ^{1}H NMR ($CDCl_3$) δ 2.17, 2.19 (both s, 4-Me, 6-Me), 3.91 (s, OMe), 6.81 (s, H3), 7.00 (s, H5).

4,6-Dimethyl-3-nitroanisole (**26**), isolated in low yield as an oil (Insufficient for elemental analysis. Found: M^+ 181.0738. $C_9H_{11}NO_3$ requires 181.0739). IR: ν_{max} (liquid film) 1518 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.24 (s, 6-Me), 2.53 (s, 4-Me), 3.87 (s, OMe), 7.07 (s, H5), 7.50 (s, H2). Nuclear Overhauser experiments, see Table 10.

4,6-Dimethyl-2-nitroanisole (**27**), isolated in low yield as an oil (Insufficient for elemental analysis. Found: M^+ 181.0736. $C_9H_{11}NO_3$ requires 181.0739). IR: ν_{max} (liquid film) 1531 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.32 (s, 4-Me, 6-Me), 3.86 (s, OMe), 7.21 (s, H5), 7.44 (s, H3).

2,4-Dimethyl-4-nitrocyclohexa-2,5-dienone (**28**) was detected in the reaction product prior to chromatography by its partial ^{1}H NMR spectrum ($CDCl_3$) δ 6.38 (d, $J_{H6,H5}$ 10.3 Hz, H6), 6.88 (dq, $J_{H3,H5}$ 2.9 Hz, $J_{H3,Me}$ 1.5 Hz, H3), 7.08 (dd, $J_{H5,H6}$ 10.3 Hz, $J_{H5,H3}$ 2.9 Hz, H5); Lit.[14] ^{1}H NMR (Ac_2O) δ 6.37 (d, $J_{H6,H5}$ 10 Hz, H6), 6.96 (dq, $J_{H3,H5}$ 3.2 Hz, $J_{H3,Me}$ 1.4 Hz, H3), 7.18 (dd, $J_{H5,H6}$ 10 Hz, $J_{H5,H3}$ 3.2 Hz, H5). During chromatography the nitro dienone **28** rearranged to give 4,6-dimethyl-2-nitrophenol (**24**) additional to that present initially.

Photochemistry of 2,4-dimethylanisole (**7**) *in HFP at 20 °C.* Reaction of 2,4-dimethylanisole–tetranitromethane in HFP at 20 °C, as above, for 3 h resulted in a lower conversion (ca. 46%; to be compared with ca. 81% in dichloromethane for 3 h at 20 °C) of 2,4-dimethylanisole (**7**) into nitro–trinitromethyl adducts **21** (1%) and **22** (1%), unidentified adducts (total 1%), aromatic compounds **23** (21%), **24** (6%), **25** (2%), **26** (16%), **27** (38%), and unidentified aromatic compounds (total 14%).

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 *K*α) 0.71069 Å, from a crystal monochromator] are given below. The space group was determined unambiguously as a result of the structure analysis reported below, but initially indicated by conditions limiting possible reflections. ω-Scans were used to collect reflection intensities out to a maximum Bragg angle $\theta = 25.02°$. The cell parameters were determined by least-squares refinements for which the setting angles of 32 accurately centred high-angle reflections were used.

Crystal data.

*1-Methoxy-6-methyl-*c*-6-nitro-*r*-3-trinitromethylcyclohexa-1,4-diene* (**9**), $C_9H_{10}N_4O_9$, M 318.21, triclinic, space group $P\bar{1}$, a 6.097(2), b 10.290(2), c 11.188(2) Å, α 73.23(1), β 86.80(2), γ 83.91(3)°; V 668.0(3) Å^3, D_c 1.582 g cm^{-3}, Z 2, μ(Mo *K*α) 1.44 cm^{-1}. The crystal was colourless and of approximate dimensions 0.90 × 0.48 × 0.16 mm. Data were collected at 166(2) K. Number of independent reflections measured 2345, 1699 with $I > 2\sigma(I)$. Absorption corrections were not applied; g_1 0.0531, g_2 0.4300; $R_{(obs)}$-factor 0.054, $wR_{(all\ data)}$ 0.130.

Structure determination. Full-matrix least-squares refinements (SHELXL-93)[22] 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. Final Fourier syntheses show no significant resuidual electron density, and there were no abnormal discrepancies between observed and calculated structure factors.

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