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Photochemical Nitration by Tetranitromethane. Part XXXIII.† Adduct Formation in the Photochemical Reactions of 1,2,4,5- and 1,2,3,5-Tetramethylbenzene

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The photolysis of the charge-transfer complex of tetranitromethane and 1,2,4,5-tetramethylbenzene in dichloromethane or acetonitrile gives the epimeric 1,3,4,6-tetramethyl-3-nitro-6-trinitromethylcyclohexa-1,4-dienes **8** and **9**, in addition to products of nuclear nitration **12** and side-chain modification **10**, **11**, and **13–18**. Similar reactions of 1,2,3,5-tetramethylbenzene gave *trans*-1,3,5,6-tetramethyl-6-nitro-3-trinitromethylcyclohexa-1,4-diene **30** and two isomeric 'double' adducts **31** and **32**, in addition to products of nuclear nitration **27** and side-chain modification **26**, **28** and **29**. The eliminative rearrangements of adducts **8** and **30** to give re-aromatized products in acetonitrile or [$^2H_3$]acetonitrile and in [^2H]chloroform are reported. The photolysis of the charge-transfer complexes of tetranitromethane with either 1,2,4,5-tetramethylbenzene or 1,2,3,5-tetramethylbenzene in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) gives a marked increase in the yields of ring-nitration products **12** or **27**, respectively, reactions presumed to proceed via a nitrosation–oxidation sequence. Reaction of 1,2,4,5-tetramethylbenzene with excess nitrogen dioxide in HFP also results in extensive ring nitration to give **12** and 2,3,5,6-tetramethyl-1,4-dinitrobenzene (**25**); the latter compound is seen as arising via the 2,3,5,6-tetramethyl-1,4-dinitrosobenzene (**34**). Similar reaction of 1,2,3,5-tetramethylbenzene gives ring-nitration product **27** as the major product. X-Ray crystal structures are reported for 2,4,6-trimethyl-1-(2′,2′,2′-trinitroethyl)benzene (**26**) and *trans*-1,3,5,6-tetramethyl-6-nitro-3-trinitromethyl-cyclohexa-1,4-diene (**30**).

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 $ArH^{\bullet+}$, trinitromethanide ion, and nitrogen dioxide.

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

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

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

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

Although no adducts were reported to be formed in the photochemical reactions of 1,3,5-trimethylbenzene (**1**), 1,2,4,5-tetramethylbenzene (**2**), pentamethylbenzene (**3**), or hexamethylbenzene (**4**) with tetranitromethane,[3] adducts and products of their secondary reactions were identified in the analogous reactions of benzene,[4] 1,2,3-trimethylbenzene (**5**),[5] and in 1,2,3,4-tetramethylbenzene (**6**).[6]

We now report the results of a re-examination of the photochemical reactions of 1,2,4,5-tetramethylbenzene (**2**) (durene) with tetranitromethane, and the corresponding reactions of 1,2,3,5-tetramethylbenzene (**7**) (isodurene). Such reaction of 1,2,4,5-tetramethylbenzene at −50 °C in dichloromethane for 4 h gave two unstable adducts (total absolute yield 38%), while 1,2,3,5-tetramethylbenzene under the same conditions showed a somewhat lower conversion into adducts (30%).

† Part XXXII, see Ref. 1.
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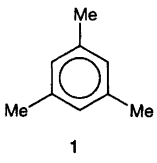
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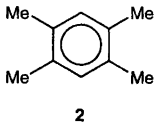
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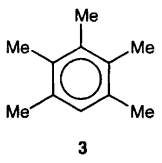
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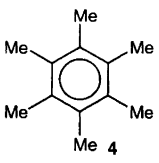
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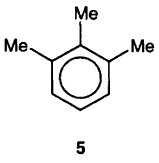
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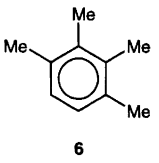
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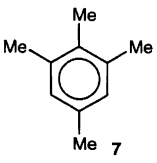
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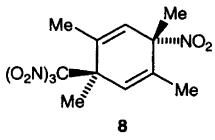
Results

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,[7] 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 $\leqslant 0\,^{\circ}C$. The crude product mixtures were stored at $-78\,^{\circ}C$ and were analysed (^1H NMR spectroscopy, see Experimental section; Tables 1–4, 8, and 9) as soon as possible.

Photochemistry of 1,2,4,5-tetramethylbenzene (**2**) *in dichloromethane at* $-50\,^{\circ}C$ *and the identification of adducts* **8** *and* **9**. A solution of **2** (0.47 mol dm^{-3}) and tetranitromethane (0.94 mol dm^{-3}) in dichloromethane was irradiated at $-50\,^{\circ}C$. The composition of the mixture was monitored by NMR spectral analysis (Table 1). The final solution (after 4 h, conversion 71%) contained the epimeric 1,3,4,6-tetramethyl-3-nitro-6-trinitromethylcyclohexa-1,4-dienes **8** (46%) and **9** (7%), aromatic compounds **10–17** (total 41%) and unidentified aromatic compounds (total 6%). The adducts **8** and **9** were separated partially by HPLC on a cyanopropyl column using hexane–dichloromethane mixtures as the eluting solvents. The first material eluted was a mixture of aromatic compounds, the separation and identification of which is given below.

Adducts **8** and **9** were assigned the epimeric 1,3,4,6-tetramethyl-3-nitro-6-trinitromethylcyclohexa-1, 4-diene structures from of a consideration of their spectroscopic data (Experimental section). The connectivity of each of adducts **8** and **9** was established from the results of nuclear Overhauser experiments and long-range reverse-detected heteronuclear correlation spectra (HMBC, HMQC). The ^1H and ^{13}C NMR spectra for adducts **8** and **9**, so assigned, were closely similar as expected for epimeric compounds. Of particular relevance were the ^{13}C NMR resonances for C3 and C6 for **8** (δ 88.3 and 51.2) and **9** (δ 85.4 and 50.6), which indicated the attachment of nitro and trinitromethyl groups, respectively, at those ring positions. The relative stereo-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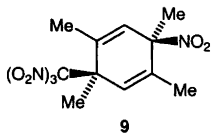
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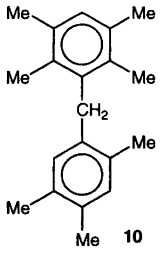
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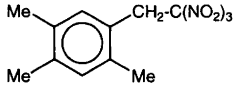
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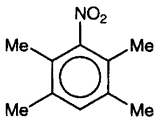
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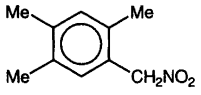
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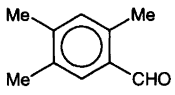
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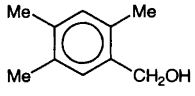
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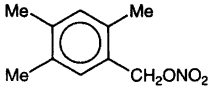
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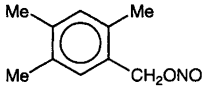
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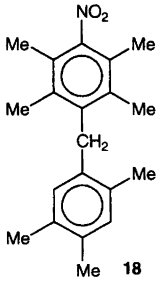
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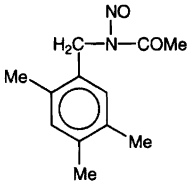
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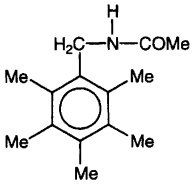
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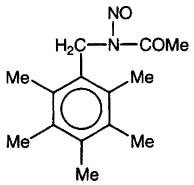
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Table 1. Overview of yields of products from the photolysis of 1,2,4,5-tetramethylbenzene (**2**) (0.47 mol dm^{-3}) and tetranitromethane (0.94 mol dm^{-3}) in dichloromethane.

		Yield (%)										
t/h	Conversion (%)	(**8**)	(**9**)	(**10**)	(**11**)	(**12**)	(**13**)	(**14**)	(**15**)	(**16**)	(**17**)	Unknown aromatics
At 20 °C												
1	42	11.8	3.5	1.2	26.1	9.9	10.8	13.0	0.8	14.7	3.0	5.2
2	69	9.8	3.5	0.8	24.5	9.4	12.7	6.6	0.5	24.0	2.9	5.3
4	87	4.8	2.1	0.5	27.4	5.4	15.4	5.3	0.5	30.7	2.7	5.2
At −50 °C												
2	46	50.3	7.9	2.2	6.3	0.6	13.0	1.2	0.8	9.3	1.3	7.1
4	71	46.1	7.1	1.1	6.0	0.9	17.7	0.6	1.2	13.0	2.8	5.9

Table 2. Overview of yields of products from the photolysis of 1,2,4,5-tetramethylbenzene (**2**) (0.47 mol dm^{-3}) and tetranitromethane (0.94 mol dm^{-3}) in 1,1,1,3,3,3-hexafluoropropan-2-ol at 20 °C.

		Yield (%)								
t/h	Conversion (%)	(**10**)	(**11**)	(**12**)	(**13**)	(**14**)	(**15**)	(**16**)	(**18**)	Unknown aromatics
0.5	3	4.5	0.8	60.0	1.7	8.8	10.2	3.2	trace	10.8
1	7	5.2	1.6	57.0	2.2	4.6	9.5	4.5	1.5	13.9
2	13	7.3	2.0	62.4	2.5	3.1	5.8	4.8	3.1	9.0
4	21	8.5	4	61.5	3.0	1.4	6.1	3.9	2.8	8.8
20	87	2.5	8.8	53.3	6.8	2.0	1.5	3.0	7.8	14.3

Table 3. Overview of yields of products from the photolysis of 1,2,4,5-tetramethylbenzene (**2**) (0.47 mol dm^{-3}) and tetranitromethane (0.94 mol dm^{-3}) in acetonitrile.

		Yield (%)											
t/h	Conversion (%)	(**8**)	(**9**)	(**10**)	(**11**)	(**12**)	(**13**)	(**14**)	(**15**)	(**16**)	(**18**)	(**19**)	Unknown aromatics
At 20 °C													
2	30	trace	trace	3.8	5.5	2.0	44.6	1.6	4.2	22.8	1.0	9.6	4.9
4	52	trace	trace	1.7	4.5	2.9	47.5	1.9	2.5	23.5	1.1	9.4	5.0
At −20 °C													
2	31	10.5	4.7	4.0	21.7	1.5	15.5	4.6	4.8	23.8	–	1.6	7.3
4	49	9.6	4.9	2.4	6.2	3.9	19.0	3.2	1.8	25.1	–	4.2	19.7

chemistry of **8** and **9** was assigned on the basis of their elution order from a cyanopropyl HPLC column with the dichloromethane–hexane solvent system, *trans*-1-trinitromethyl-4-nitro adducts being less polar than their *cis*-isomers.[5,7] Adduct **9** was obtained only in admixture with **8**, but its spectroscopic data were obtained by subtraction of the known spectra for adduct **8**. The connectivity of each of adducts **8** and **9** was established from the results of nuclear Overhauser experiments and long-range reverse-detected heteronuclear correlation spectra (HMBC, HMQC). Although confirmation of the molecular formula of **8** was not possible by either elemental analysis or by mass spectrometry, due to its instability, the structures assigned to adducts **8** and **9** appear secure.

Photochemistry of 1,2,4,5,-tetramethylbenzene (**2**) *in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) at 20 °C and the identification of the aromatic products* **10–15** *and* **18**. Photolysis of the CT complex of **2**–tetranitromethane in HFP at 20 °C, as above, gave a mixture of the aromatic compounds **10–16** and **18** (Table 2). The degree of conversion was 87% after 20 h. Chromatography of this mixture on a silica gel Chromatotron plate allowed the separation of compounds **10–15** and **18**, with the benzylic nitrate **16** being presumably hydrolysed during the chromatography to give further benzylic alcohol **15**. Of the products isolated, compounds **10** and **12–15** were identified by comparison with authentic material (Experimental section). Compounds **11** and **18** were isolated only in small quantities, but their respective molecular formulae were established from mass spectra and their structures from a consideration of their spectroscopic data. For each of **11** and **18**, the connectivity in the structures was established by a combination of the results of nuclear Overhauser experiments, and long-range reverse-detected heteronuclear correlation spectra (HMBC, HMQC). The presence of 2,4,5-trimethylbenzyl nitrate (**16**) in the reaction mixture was inferred from the ^{1}H NMR spectroscopic signal due to the -CH_2-ONO_2 group.[3]

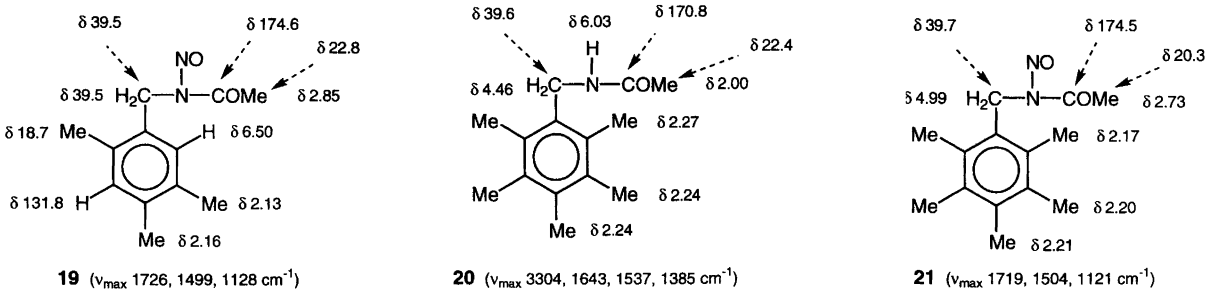
Photochemistry of 1,2,4,5-tetramethylbenzene (**2**) *in acetonitrile at 20 °C and the identification of the* N*-nitrosoacetamide* (**19**). Photolysis of the CT complex of **2**–tetranitromethane in acetonitrile at 20 °C, as above, gave 52% conversion after 4 h into a mixture of the aromatic compounds **10–16** and **18** (total 86%), the *N*-nitrosoacetamide **19** (9%) and unidentified aromatic products (5%) (Table 3). Chromatography of this mixture on a silica gel Chromatotron plate gave a small amount of **19** in a fraction eluted immediately before the aldehyde **14**. The molecular formula, $C_{12}H_{16}N_2O_2$, of **19** was obtained from its mass spectrum, and the attachment of three methyl groups and a methylene function to the aromatic ring was indicated by the results of nuclear Overhauser experiments. The remainder of the structure of **19** was assigned by analogy with the spectroscopic data for pentamethylbenzylacetamide (**20**) and its *N*-nitroso derivative **21**.[8] Comparative IR, ^{1}H and ^{13}C NMR spectroscopic data are presented in Fig. 1 for the two *N*-nitroso compounds **19** and **21**,[8] and the parent compound **20** of the latter. It should be emphasized that only small quantities of the two *N*-nitroso compounds **19** and **21**[8] could be isolated by rapid chromatography on silica gel Chromatotron plates of mixtures containing significant quantities of each compound. In particular, the *N*-nitrosoacetamide structure **19** is in accord with the carbonyl stretching frequency (1726 cm^{-1}), reflecting the effect of the electron-withdrawing *N*-nitroso group.[9] Further, the ^{13}C NMR resonances δ 174.6 (amide carbonyl carbon), δ 22.8 (CH_3-CO-) and δ 39.5 (CH_2) are consistent with the *N*-(2,4,5-trimethylbenzyl)-*N*-nitrosoacetamide structure. Finally, **19** would be expected to suffer a ready loss of a fragment of mass 30 (NO) in the mass spectrum, as is observed. The above assignments were confirmed by long-range reverse-detected heteronuclear correlation spectra (HMBC, HMQC).

Photochemistry of 1,2,4,5-tetramethylbenzene (**2**) *in dichloromethane at 20 °C.* Photolysis of the CT complex of **2**–tetranitromethane in dichloromethane for 4 h at 20 °C, as above, gave mixtures of products, the composition of which are summarized in Table 1.

Photochemistry of 1,2,4,5-tetramethylbenzene (**2**) *in dichloromethane containing trifluoroacetic acid (0.7 M) at 20 °C.* Photolysis of the CT complex of **2**–tetranitromethane, as above, in dichloromethane containing trifluoroacetic acid (0.7 M) gave a mixture of the aromatic compounds **10–14**, **16** and **18**, and unidentified aromatic products (20%) (Table 4). Notable among these products is the side-chain trinitromethyl derivative **11**, formed in 3% absolute yield after 4 h.

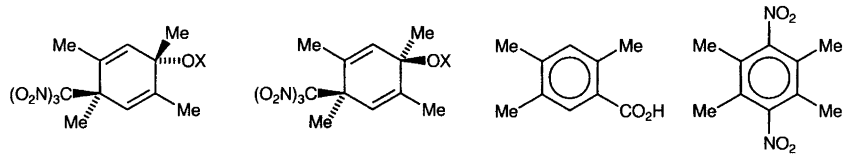
*Eliminative rearrangement of 1,3,4,6-tetramethyl-*r*-3-nitro-*t*-6-trinitromethylcyclohexa-1,4-diene* (**8**) *in acetonitrile at 20 °C.* A solution of **8** in acetonitrile was stored in the dark at 20 °C; aliquots were removed at appropriate time intervals and the solvent was removed at ≤0 °C to give residues, the composition of which was determined by ^{1}H NMR spectral analysis. Initially (within 5 min) adduct **8** underwent epimerization to give adduct **9**, and also nitro–nitrito rearrangement to give the epimeric trinitromethyl nitrite esters **22a** and **23a**. During the workup procedure **22a** and **23a** were hydrolysed to give the corresponding trinitromethyl alcohols **22b** and **23b**, the ^{1}H NMR spectra of which are given in the Experimental section. Subsequently (over ca. 1 h) the equilibrium mixture of **8**, **9**, **22a** and **23a** was converted into a mixture of **11** (14%), **12** (18%), **13** (11%), **15** (7%), **16** (3%) and unidentified aromatic products (total 33%).

*Eliminative rearrangement of 1,3,4,6-tetramethyl-*r*-3-nitro-*t*-6-trinitromethylcyclohexa-1,4-diene* (**8**) *in [^{2}H] chloroform at 20 °C.* A solution of **8** in [^{2}H]chloroform was



19 (ν_{max} 1726, 1499, 1128 cm^{-1}) **20** (ν_{max} 3304, 1643, 1537, 1385 cm^{-1}) **21** (ν_{max} 1719, 1504, 1121 cm^{-1})

Fig. 1. IR, ^1H and ^{13}C NMR data for compounds **19–21**.



22 a X = NO, b X = H **23** a X = NO, b X = H **24** **25**

stored in the dark at 20 °C and the ^1H NMR spectrum of the solution monitored at appropriate time intervals. In this solvent **8** epimerized only slowly, equilibrium with its epimer **9** being established after 90 h. The trinitromethyl nitrite esters **22a** and **23a** were not observed in this rearrangement, **8** and **9** being slowly converted (25 days) into a mixture of **11** (52%), **13** (18%), **14** (6%), **16** (10%) and some unidentified aromatic compounds (total 13%).

Reaction of 1,2,4,5-tetramethylbenzene (**2**) *with nitrogen dioxide in dichloromethane at 20 °C.* A solution of **2** in dichloromethane saturated with nitrogen dioxide was irradiated with filtered light ($\lambda_{cut\text{-}off}$ 435 nm) at 20 °C. A similar mixture was stored in the dark at 20 °C. Aliquots were removed at appropriate time intervals and the excess nitrogen dioxide and solvent were removed under reduced pressure at ≤0 °C. The product compositions were determined by ^1H NMR spectral analysis and are given in Table 5. After reaction for 4 h the two product compositions were similar, viz. 2,4,5-trimethylbenzyl nitrate **16** (ca. 70%), 2,4,5-trimethylphenylnitromethane **13** (ca. 20%), with small amounts of aromatic compounds **10**, **14** and **15**, and unidentified compounds. These results are comparable with those reported recently by Bosch and Kochi,[10] except that they also observed a low yield of the nuclear nitration product **12**.

Reaction of 1,2,4,5-tetramethylbenzene (**2**) *with nitrogen dioxide in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) at 20 °C.* A solution of **2** in HFP saturated with nitrogen dioxide was irradiated with filtered light ($\lambda_{cut\text{-}off}$ 435 nm) at 20 °C. A similar mixture was stored in the dark at 20 °C. After 0.5 h, at which time all of **2** in both reactions had been consumed, the excess nitrogen dioxide and solvent were removed under reduced pressure at ≤0 °C. The product compositions, determined by ^1H NMR spectral analysis, were similar, viz. **12** (ca. 72%), **24** (ca. 16%) and **25** (ca. 4%) with small amounts of aromatic compounds **13** and **14**, and unidentified compounds.

EPR spectroscopic studies of the photochemical reaction between 1,2,4,5-tetramethylbenzene (**2**) *and tetranitromethane.* We have previously shown[11] that radical cations that are not too reactive can be observed by EPR spectroscopy in irradiated solutions of ArH–tetranitromethane–trifluoroacetic acid (0.8 mol dm^{-3}) in dichloromethane at low temperature (usually −60 to −70 °C); without acid present the spectrum was either much weaker or not observable at all. This behaviour was interpreted as being caused by protonation of trinitromethanide ion, which thus is removed from the triad and replaced by the much weaker nucleophile, nitroform.

Application of this method to 1,2,4,5-tetramethylbenzene **2** showed no sign of its radical cation $\mathbf{2}^{\bullet+}$ at −70 °C, without or with trifluoroacetic acid (0.8 mol dm^{-3}) present. Evidently, both reaction (2) and the $ArH^{\bullet+}$–NO_2 reaction are very fast under these conditions. In neat TFA at −12 °C, irradiation of **2** and tetranitromethane again failed to produce an EPR spectrum of $\mathbf{2}^{\bullet+}$; however, when the light was switched off, a weak EPR spectrum of a radical cation formed by further transformation of $\mathbf{2}^{\bullet+}$, $(1,2,4,5,6,8\text{-hexamethylanthracene})^{\bullet+}$, slowly developed. The formation of this radical cation was previously[12] demonstrated in the oxidation of **10** in trifluoroacetic acid, either photochemically or by 2,3-dichloro-4,5-dicyanobenzoquinone (DDQ). The same radical cation was also obtained and detected by EPR spectroscopy[13] by irradiation of **2**-tetranitromethane–trifluoroacetic acid (0.4 mol dm^{-3}) in HFP at 22 °C.

Attempts were also made to detect the putative Ar–NO intermediate from the **2**–NO_2 reaction in HFP. A solution of NO_2 (5 mmol dm^{-3}) and **2** (100 mmol dm^{-3}) in

Table 4. Overview of yields of products from the photolysis of 1,2,4,5-tetramethylbenzene (**2**) (0.47 mol dm^{-3}) and tetranitromethane (0.94 mol dm^{-3}) in dichloromethane containing trifluoroacetic acid (0.7 mol dm^{-3}) at 20 °C.

		Yield (%)							
t/h	Conversion (%)	(**10**)	(**11**)	(**12**)	(**13**)	(**14**)	(**16**)	(**18**)	Unknown aromatics
0.5	9	31.0	22.3	4.3	6.0	5.8	17.0	0.4	13.2
1	16	32.7	18.5	4.0	7.4	3.2	20.0	0.9	13.3
2	22	31.9	12.8	4.5	9.2	4.5	21.9	1.6	13.6
4	38	22.2	8.1	7.6	9.7	7.4	22.1	2.7	20.2

Table 5. Overview of yields of products from the reaction of 1,2,4,5-tetramethylbenzene (**2**) (0.47 mol dm^{-3}) in dichloromethane saturated with nitrogen dioxide at 20 °C.

		Yield (%)					
t/h	Conversion (%)	(**10**)	(**13**)	(**14**)	(**15**)	(**16**)	Unknown aromatics
In the dark							
0.5	16	1.0	21.8	4.9	2.6	67.6	2.1
1	24	1.1	23.0	4.3	2.5	67.0	2.1
2	32	1.0	21.6	7.5	1.7	66.1	2.1
4	60	1.1	22.7	5.6	1.2	67.6	1.8
Irradiation with filtered light ($\lambda_{cut\text{-}off}$ 435 nm)							
0.5	18	1.0	22.2	5.3	3.3	67.0	1.2
1	28	1.3	22.8	3.3	2.6	69.2	0.8
2	45	0.9	20.7	5.8	1.2	69.7	1.7
4	68	0.7	19.9	7.0	0.5	69.5	2.4

HFP was allowed to stand at 22 °C for 10 min, after which time Tl^{III} trifluoroacetate was added (this procedure is known to convert 2,3,5,6-tetramethylnitrosobenzene into its radical cation[13]). However, the thermal reaction with the Tl^{III} reagent gave no EPR signal; only irradiation by UV light caused the EPR spectrum of $(2,3,5,6\text{-tetramethylnitrosobenzene})^{\cdot+}$ to appear. The same spectrum was obtained in the same way when the reagents were added in the reverse order, i.e. **2** was first treated with Tl^{III} trifluoroacetate for 10 min and then NO_2 was added.

Photochemistry of 1,2,3,5-tetramethylbenzene **7** *in dichloromethane at 20 °C and the identification of aromatic compounds* **26–29**, *adduct* **30** *and 'double adducts'* **31** *and* **32**. Photolysis of the CT complex of **7**–tetranitromethane in dichloromethane for 6 h at 20 °C, as above, gave a mixture of 2,4,6-trimethyl-1-(2′,2′,2′-trinitroethyl)benzene (**26**, 10%), 2,3,4,6-tetramethylnitrobenzene (**27**, 24%), 3,4,5-trimethylphenylnitromethane (**28**, 6%), 2,3,5-trimethylphenylnitromethane (**29**, 9%), *trans*-1,3,5,6-tetramethyl-6-nitro-3-trinitromethylcyclohexa-1, 4-diene (**30**, 14%), the isomeric 1,2,4,6-tetramethyl-2,5-dinitro-6-trinitromethylcyclohex-3-en-1-ols (**31**, 2%) and (**32**, 1.5%), unidentified adducts (total 18%) and unidentified aromatic compounds (total 16%). This mixture was partially separated into its components by chromatography on a silica gel Chromatotron plate. The first compound eluted was 2,4,6-trimethyl-1-(2′,2′,2′-trinitroethyl)benzene (**26**), $C_{11}H_{13}N_3O_6$, the structure of which was determined for a crystal of poor quality by single-crystal X-ray analysis; a perspective drawing is presented in Fig. 2, and the corresponding atomic coordinates are given in Table 6. The structure consists of two crystallographically independent molecules, the two molecules differing in the orientation of the aromatic ring (see superposition, Fig. 3); this difference is of no chemical significance. The spectroscopic data for the trinitromethyl compound **26** were in accord with the established structure.

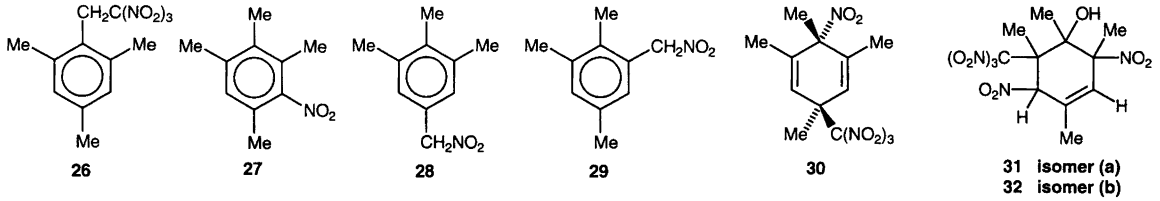
2,3,4,6-Tetramethylnitrobenzene **27** and 3,4,5-trimethylphenylnitromethane **28** were identified by comparison with authentic material.[14] 2,3,5-Trimethylphenylnitromethane **29** could not be isolated in a pure state, but its structure was established by the results of nuclear Overhauser experiments and reverse-detected heteronuclear correlation spectra (HMQC) (Experimental section).

The structure of the next compound eluted was determined by single-crystal X-ray analysis. A perspective drawing of *trans*-1,3,5,6-tetramethyl-6-nitro-3-trinitromethylcyclohexa-1,4-diene (**30**, $C_{11}H_{14}N_4O_8$) is presented in Fig. 4, and the corresponding atomic coordinates are given in Table 7. The structure consists of two crystallographically independent molecules. The differences between the two molecules lie both in the conforma-

Table 6. Fractional coordinates for atoms in 2,4,6-trimethyl-1-(2′,2′,2′-trinitroethyl)-benzene (**26**).[a]

Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	$10^3U/Å^2$
Molecule 1				
O(11)	9152(3)	6551(6)	315(2)	57(1)
O(12)	9466(3)	7883(5)	1176(2)	55(1)
O(21)	6798(3)	5932(5)	−37(2)	46(1)
O(22)	7376(3)	7966(5)	−337(2)	47(1)
O(31)	6523(3)	9077(5)	757(2)	54(1)
O(32)	8045(4)	9832(6)	1033(3)	87(2)
N(1)	8899(3)	7278(5)	738(2)	36(1)
N(2)	7266(3)	7063(5)	63(2)	30(1)
N(3)	7442(4)	8925(5)	864(2)	39(1)
C(1)	7997(4)	6403(5)	1938(2)	23(1)
C(2)	7605(4)	7280(5)	2384(2)	23(1)
C(3)	8098(4)	7315(5)	3019(2)	26(1)
C(4)	8972(4)	6505(5)	3233(2)	24(1)
C(5)	9320(3)	5613(5)	2787(2)	25(1)
C(6)	8862(3)	5541(5)	2142(2)	24(1)
C(7)	7460(4)	6296(5)	1240(2)	25(1)
C(8)	6651(4)	8167(6)	2208(3)	33(1)
C(9)	9502(4)	6579(6)	3926(2)	35(1)
C(10)	9299(4)	4509(6)	1704(2)	33(1)
C(11)	7778(4)	7367(5)	759(2)	24(1)
Molecule 2				
O(11′)	3218(3)	5524(4)	1464(2)	41(2)
O(12′)	1760(3)	5499(5)	827(2)	50(1)
O(21′)	1307(3)	8590(5)	186(2)	60(1)
O(22′)	2273(3)	7095(5)	−239(2)	49(1)
O(31′)	3852(3)	8975(5)	421(2)	51(1)
O(32′)	4445(3)	6963(5)	857(2)	60(1)
N(1′)	2568(3)	6044(5)	1050(2)	32(1)
N(2′)	2030(4)	7805(5)	208(2)	39(1)
N(3′)	3781(3)	7837(5)	701(2)	33(1)
C(1′)	3021(3)	8518(5)	2056(2)	22(1)
C(2′)	3895(4)	9353(5)	2267(2)	25(1)
C(3′)	4359(4)	9264(5)	2910(2)	26(1)
C(4′)	3996(4)	8377(5)	3350(2)	26(1)
C(5′)	3124(4)	7584(5)	3133(2)	25(1)
C(6′)	2621(4)	7640(5)	2498(2)	25(1)
C(7′)	2459(4)	8670(6)	1363(2)	26(1)
C(8′)	4348(4)	10400(6)	1835(3)	35(1)
C(9′)	4524(4)	8274(7)	4041(2)	38(1)
C(10′)	1660(4)	6766(6)	2331(3)	32(1)
C(11′)	2721(4)	7599(6)	864(2)	29(1)

[a]The equivalent isotropic temperature factor in Tables 7 and 8 is defined as one-third of orthogonalized U_{ij} tensor ($Å^2$).



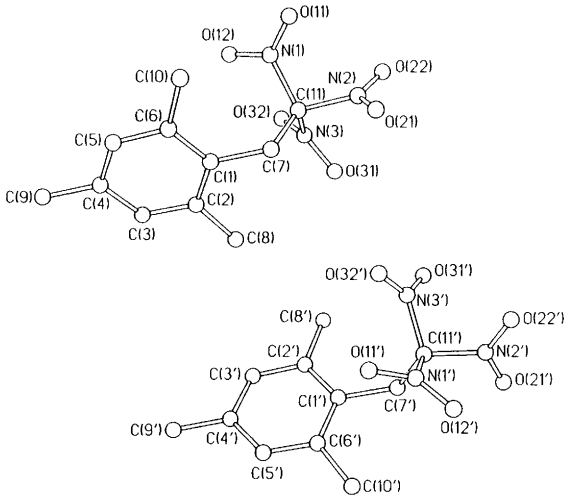


Fig. 2. Perspective drawing of compound **26**.

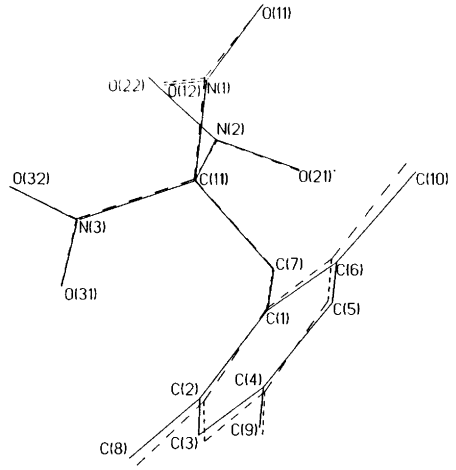


Fig. 3. Superposition of molecules 1 and 2 of compound **26**.

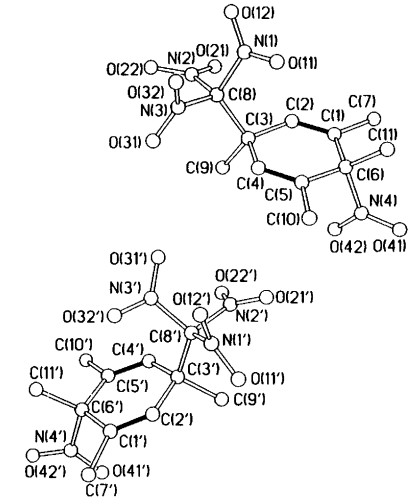


Fig. 4. Perspective drawing of compound **30**. Double bonds are shown in black.

Table 7. Fractional coordinates for atoms in *trans*-1,3,5,6 - tetramethyl - 6 - nitro - 3 - trinitromethylcyclohexa-1,4-diene (**30**).

Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	$10^3U/Å^2$
Molecule 1				
O(11)	7798(2)	11246(2)	3895(2)	49(1)
O(12)	6363(2)	12315(2)	3413(2)	53(1)
O(21)	4493(2)	10710(2)	1251(2)	50(1)
O(22)	3108(2)	11110(2)	2421(2)	70(1)
O(31)	3663(2)	9795(2)	3597(2)	54(1)
O(32)	5247(3)	11259(2)	4768(2)	57(1)
O(41)	9914(3)	6837(2)	1819(2)	89(1)
O(42)	7621(2)	6721(1)	1081(2)	45(1)
N(1)	6641(2)	11429(2)	3445(2)	35(1)
N(2)	4208(3)	10784(2)	2113(2)	42(1)
N(3)	4687(2)	10519(2)	3840(2)	37(1)
N(4)	8785(3)	7242(2)	1731(2)	40(1)
C(1)	8228(3)	9030(2)	1695(2)	30(1)
C(2)	6936(3)	9394(2)	1625(2)	29(1)
C(3)	5837(2)	9281(2)	2260(2)	27(1)
C(4)	6491(3)	8851(2)	3116(2)	28(1)
C(5)	7783(3)	8489(2)	3226(2)	28(1)
C(6)	8806(3)	8529(2)	2505(2)	30(1)
C(7)	9201(3)	9081(2)	951(2)	46(1)
C(8)	5358(3)	10455(2)	2880(2)	29(1)
C(9)	4468(3)	8440(2)	1405(2)	39(1)
C(10)	8280(3)	7993(2)	4050(2)	43(1)
C(11)	10387(3)	9018(3)	3199(3)	57(1)
Molecule 2				
O(11')	5589(2)	4732(1)	3840(2)	39(1)
O(12')	5159(2)	6431(2)	4656(2)	51(1)
O(21')	5936(2)	5832(2)	2428(2)	50(1)
O(22')	3876(2)	5539(2)	1178(2)	49(1)
O(31')	3076(2)	7100(2)	2998(2)	54(1)
O(32')	2010(2)	6201(2)	3739(2)	48(1)
O(41')	−694(2)	1692(2)	1118(2)	58(1)
O(42')	−2612(2)	2381(2)	1570(2)	65(1)
N(1')	4928(2)	5510(2)	3869(2)	31(1)
N(2')	4603(2)	5605(2)	2069(2)	33(1)
N(3')	2845(2)	6308(2)	3202(2)	36(1)
N(4')	−1299(2)	2463(2)	1613(2)	38(1)
C(1')	1028(3)	3473(2)	3024(2)	30(1)
C(2')	2392(2)	3764(2)	3004(2)	28(1)
C(3')	2775(2)	4153(2)	2171(2)	25(1)
C(4')	1397(2)	4211(2)	1375(2)	25(1)
C(5')	15(2)	3955(2)	1391(2)	27(1)
C(6')	−319(2)	3641(2)	2291(2)	29(1)
C(7')	776(3)	2973(3)	3810(2)	48(1)
C(8')	3736(2)	5339(2)	2804(2)	27(1)
C(9')	3670(3)	3297(2)	1476(2)	32(1)
C(10')	−1287(3)	3976(2)	511(2)	38(1)
C(11')	−1219(3)	4446(2)	2983(2)	49(1)

tions of the alicyclic rings [torsional angles: molecule 1, C(1)–C(2)–C(3)–C(4) 8.3(3)°; C(2)–C(1)–C(6)–C(5) −0.9(3)°. molecule 2, C(1′)–C(2′)–C(3′)–C(4′) −9.1(3)°; C(2′)–C(1′)–C(6′)–C(5′) 11.1(3)°] and in the orientations of the trinitromethyl groups relative to the alicyclic rings [torsional angles: molecule 1, N(2)–C(8)–C(3)–C(9) −40.1(3)°. molecule 2, N(2′)–C(8′)–C(3′)–C(9′) 41.4(2)°]. These differences are not chemically significant. The spectroscopic data for the adduct **30** were consistent with the established structure.

The isomeric 'double' adducts **31** and **32** were eluted in the later fractions from the HPLC column as slightly impure oils which could not be induced to crystallize. Although extensive spectroscopic data are available (Experimental section) and the implied connectivity appears certain, the stereochemistry of the two isomers could not be assigned. However, it is clear that the two isomers **31** and **32** are 'double' adducts, i.e. products derived by addition of nitrogen dioxide to initially formed hydroxytrinitromethyl- or nitrotrinitromethylcyclohexa-1,3-dienes (Ref. 5).

Photochemistry of 1,2,3,5-tetramethylbenzene (**7**) *in dichloromethane at −20 or −50 °C.* Photolysis of the CT complex of **7**–tetranitromethane in dichloromethane for 6 h at −20 or −50 °C, as above, gave mixtures of products, the composition of which are summarized in Table 8.

Photochemistry of 1,2,3,5-tetramethylbenzene (**7**) *in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) at 20 °C.* Photolysis of the CT complex of **7**–tetranitromethane in HFP for 1 h at 20 °C, as above, resulted in a 30% conversion into predominantly 1,2,3,5-tetramethylnitrobenzene (**27**, 76%), together with minor amounts of compounds **26** and **28–32**, and other unidentified aromatic compounds (total 7%) and unidentified adducts (total 9%).

Photochemistry of 1,2,3,5-tetramethylbenzene (**7**) *in dichloromethane containing trifluoroacetic acid (0.7 M) at 20 °C.* Photolysis of the CT complex of **7**–tetranitromethane in dichloromethane containing trifluoroacetic acid (0.7 M) for 1 h at 20 °C, as above, resulted in a 30% conversion into predominantly 1,2,3,5-tetra methylnitrobenzene **27** (56%), together with lesser amounts of compounds **26** (3%), **28** (5%), **29** (3%), traces of compounds **30–32**, and other unidentified aromatic compounds (total 7%) and unidentified adducts (total 9%).

Photolysis of 1,2,3,5-tetramethylbenzene **7** *in acetonitrile at 20 or −20 °C.* Photolysis of the CT complex of **7**–tetranitromethane in acetonitrile at either 20 or −20 °C, as above, for 6 h resulted in the formation of the products **26–32** (Table 9).

Reaction of 1,2,3,5-tetramethylbenzene (**7**) *with nitrogen dioxide in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) at 20 °C.* A solution of **7** in HFP saturated with nitrogen dioxide was irradiated with filtered light ($\lambda_{cut\text{-}off}$ 435 nm) at 20 °C. A similar mixture was stored in the dark at 20 °C. After 2 h, after which time all of **7** in both reactions had been consumed, the excess nitrogen dioxide and solvent were removed under reduced pressure at ≤0 °C. The product compositions, determined by ^{1}H NMR spectral analysis, were similar, viz. **27** (ca. 43%), **28** (ca. 13%), **29** (ca. 3%), **33** (12%), and unidentified compounds.

Table 8. Overview of yields of products from the photolysis of 1,2,3,5-tetramethylbenzene (**7**) (0.47 mol dm^{-3}) and tetranitromethane (0.94 mol dm^{-3}) in dichloromethane.

	Yield (%)								
t/h	(**26**)	(**27**)	(**28**)	(**29**)	Unknown aromatics	(**30**)	(**31**)	(**32**)	Unknown adducts
At 20 °C									
1	20.3	15.4	1.6	3.7	8.8	13.5	1.9	1.5	33.3
2	14.2	25.8	1.1	4.6	8.7	13.1	1.9	1.5	29.1
4	11.6	22.3	4.6	7.5	15.7	14.2	2.1	1.5	20.5
6	10.0	23.6	5.7	9.2	16.0	13.8	2.1	1.5	18.1
At −20 °C									
1	8.4	34.3	12.4	9.7	7.1	5.4	–	–	22.6
2	7.0	30.7	11.5	10.2	6.8	6.0	0.3	0.6	26.8
4	7.5	19.8	14.2	17.3	5.8	8.1	0.4	0.4	26.5
6	9.0	16.9	17.5	17.0	4.9	8.8	1.1	0.6	24.2
At −50 °C									
1	4.5	54.8	6.7	2.7	6.4	4.7	0.7	–	19.5
2	5.6	38.1	8.3	4.3	6.2	7.3	0.4	0.3	29.6
4	7.2	22.7	11.0	7.3	7.4	11.4	1.2	0.8	31.0
6	6.8	22.2	10.4	7.1	9.4	12.6	1.5	0.6	29.5

Table 9. Overview of yields of products from the photolysis of 1,2,3,5-tetramethylbenzene (**7**) (0.47 mol dm^{-3}) and tetranitromethane (0.94 mol dm^{-3}) in acetonitrile.

	Yield (%)							
t/*h*	(**26**)	(**27**)	(**28**)	(**29**)	Unknown aromatics	(**30**)	(**31**)	(**32**)	Unknown adducts
At 20 °C									
1	2.2	62.8	11.4	2.4	4.2	4.4	0.2	0.3	12.0
2	2.5	41.1	20.0	4.0	5.1	8.4	0.4	0.3	18.2
4	3.0	28.2	24.9	7.1	6.1	11.4	0.4	0.5	18.4
6	3.1	23.1	23.7	10.3	9.6	10.1	0.9	0.6	18.6
At −20 °C									
1	2.4	62.9	1.4	3.6	9.2	3.4	1.0	0.4	15.6
2	4.1	42.5	2.6	6.6	5.9	7.8	1.7	0.6	28.2
4	5.9	28.4	4.2	8.9	9.2	9.5	0.8	0.7	32.4
6	6.8	18.0	5.2	9.2	9.1	13.1	1.3	0.8	36.4

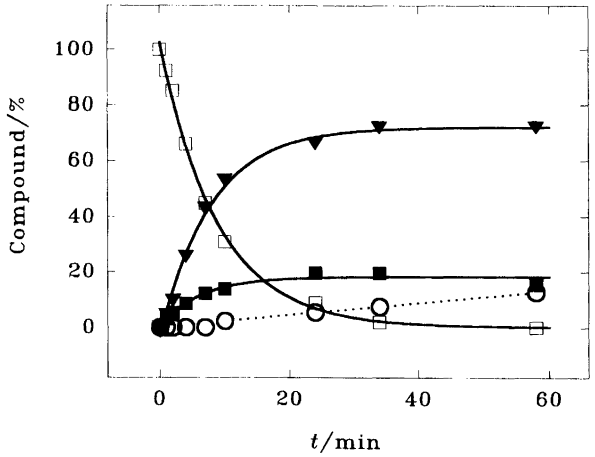


Fig. 5. Kinetics of rearrangement of adduct **30** in ($^2H_3$)acetonitrile at 22 °C. Empty squares, **30**; filled squares, **26**; triangles, **28**; circles, unidentified compounds. The solid lines represent the best fits to first-order expressions with rate constants as given in the text. The dotted line is only intended for improving readability.

Eliminative rearrangement of trans-*1,3,5,6-tetramethyl-6-nitro-3-trinitromethylcyclohexa-1,4-diene* (**30**) *in* [$^2H_3$]*acetonitrile at 22 °C.* A solution of **30** in [$^2H_3$]acetonitrile was stored at 22 °C and the ^{1}H NMR spectrum monitored at appropriate time intervals. Adduct **30** decomposed with a rate constant of 0.114(4) h^{-1} and the major product, formed with a rate constant of 0.13(1) h^{-1}, was 3,4,5-trimethylphenylnitromethane (**28**). In the later stages of the rearrangement process, 2,4,6-trimethyl-1-(2′,2′,2′-trinitroethyl)benzene (**26**) appeared among the products (Fig. 5) with a rate constant of 0.16(3) h^{-1}.

Attempted eliminative rearrangement of trans-*1,3,5,6-tetramethyl-6-nitro-3-trinitromethylcyclohexa-1,4-diene* (**30**) *in* [^2H]*chloroform or in* [$^2H_2$]*dichloromethane at 22 °C.* Solutions of **30** in either [^{2}H]chloroform or [$^2H_2$]dichloromethane were unchanged over a period of 4 days at 22 °C.

Discussion

The formation of adducts in the photolysis of the CT complexes of tetranitromethane with 1,2,4,5-tetramethylbenzene (**2**) *and 1,2,3,5-tetramethylbenzene* (**7**). Although the epimeric 1,3,4,6-tetramethyl-3-nitro-6-trinitromethylcyclohexa-1,4-dienes **8** and **9** were detected among the photolysis products of the CT complex of tetranitromethane and **2** in both dichloromethane and acetonitrile solution at 20 °C, the yields of these labile adducts **8** and **9** were considerably higher at lower reaction temperatures, reaching a total yield of 53% in dichloromethane at −50 °C. In acetonitrile solution lower reaction temperatures were limited to −20 °C (total yield of adducts 15%) because of the limited solubility of the substrate **2** in that medium. The pattern of adduct yields found for photolyses in dichloromethane

or acetonitrile solution (Tables 1 and 3) is understandable in the light of the rearrangement of the nitro–trinitromethyl adducts **8** and **9** in acetonitrile and [^{2}H]chloroform at ca. 20 °C, the rearrangement of nitro–trinitromethyl adduct **8** being complete in 1 h in acetonitrile (half-life ca. 0.1 h) but considerably slower in [^{2}H]chloroform (half-life ca. 72 h). These rates of rearrangement of nitro–trinitromethyl adduct **8** probably reflect lower limits for the rates of rearrangement during the photolysis reactions of the CT complex of **2** with tetranitromethane; cf. results of the photolysis of the CT complex of tetranitromethane with 1,2,3-trimethylbenzene.[5]

The rearrangement of adduct **8** to aromatic products, with initial equilibration to its epimer **9** and nitrites **22a** and **23a**, is analogous to the rearrangement of the 1,4-nitro–trinitromethyl adduct of 1,4-dimethylnaphthalene, previously studied in some detail.[15] In this case it was concluded that the epimerization would occur in a polar step, whereas the nitro–nitrito rearrangement probably was of radical nature. The characteristics of the **8** rearrangement are similar and the same conclusions are probably valid.

In contrast to the marked lability of the nitro–trinitromethyl adducts **8** and **9**, the nitro–trinitromethyl adduct **30** and the 'double' adducts **31** and **32** obtained from **7** were relatively stable in solution. Adduct **30** was stable in [^{2}H]chloroform or [$^2H_2$]dichloromethane at 22 °C for 4 days and rearranged in [$^2H_3$]acetonitrile with a half-life of 6.0 h at 22 °C (Fig. 5). Accordingly, adduct yields from **7** were significant even at 20 °C in both dichloromethane and acetonitrile.

The addition of a protic acid to photolyses of charge-transfer complexes of aromatic molecules with tetranitromethane has been shown to convert trinitromethanide ion, one component of the triad [$ArH^{\bullet+}$ $(O_2N)_3C^-$ NO_2], into the less nucleophilic nitroform, resulting in the predominant recombination process $ArH^{\bullet+}/NO_2$ being observed.[11,13] The photolysis of the CT complex of **2** in dichloromethane containing trifluoroacetic acid (0.7 M) at 20 °C proceeded more slowly than the reaction without added acid and gave aromatic compounds **10–14**, **16** and **18**, but adducts **8** and **9** were not detected.

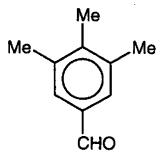
It should be noted that 2,4,5-trimethyl-1-(2′,2′,2′-trinitroethyl)benzene (**11**) was still formed in reasonable yield (Tables 1 and 4), in spite of the fact that the trinitromethanide ion concentration has been almost completely suppressed by protonation. However, since the side-chain products must be derived from the 2,4,5-trimethylbenzyl cation, it is reasonable to assume that nitroform can react as a nucleophile with this carbocation with its higher charge density at a single carbon, compared to the situation in $\mathbf{2}^{\bullet+}$.

Similar reaction of 1,2,3,5-tetramethylbenzene (**7**) resulted in a marked reduction in the yields of the trinitromethyl derivatives **26**, and **30–32**, and a substantial increase in the yield of 2,3,4,6-tetramethylnitrobenzene **27**, presumably as the result of $ArH^{\bullet+}/NO_2$ coupling.

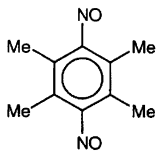
Reaction chemistry in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP). HFP has been found to strongly stabilize radical cations,[16] partly by rendering any nucleophilic species present exceedingly unreactive.[16e] We therefore anticipated that in the present work HFP would inhibit the attack of trinitromethanide ion on the radical cation and by default favour the occurrence of the $ArH^{\bullet+}/NO_2$ coupling process. In the event, the photolysis of the CT complex of tetranitromethane with **2** in HFP at 20 °C was slow, yielded no adducts **8** and **9**, a limited yield of the trinitromethyl side-chain derivative **11**, and 2,3,5,6-tetramethylnitrobenzene (**12**) as the major product (ca. 60%) (Table 2).

Reaction of **2** with a saturated solution of nitrogen dioxide in HFP, either on irradiation with filtered light ($\lambda_{cut\text{-}off}$ 435 nm) or in the dark at 20 °C, was complete in <0.5 h and gave 2,3,5,6-tetramethylnitrobenzene **12** as the major product (ca. 74%) and 2,3,5,6-tetramethyl-1,4-dinitrobenzene (**25**, 4%) as a minor product. This result is in marked contrast to the outcome of the analogous reactions of **2** with a saturated solution of nitrogen dioxide in dichloromethane at 20 °C, either on irradiation with filtered light ($\lambda_{cut\text{-}off}$ 435 nm) or in the dark, in which 2,4,5-trimethylbenzyl nitrate (**16**, ca. 70%) and 2,4,5-trimethylphenylnitromethane (**13**, ca. 20%) were the significant products. It appears that the 'dark' and 'light' reaction conditions of the reactions of nitrogen dioxide in dichloromethane, above, have resulted in thermal nitration of **2**, the product composition being broadly in agreement with product ratios for thermal nitration using nitrogen dioxide in dichloromethane in the dark reported recently by Bosch and Kochi.[10]

In contrast, the formation of ring-substituted nitration products **12** and **33** in the reactions of **2** with nitrogen dioxide in HFP is consistent with the reaction sequence of nitrosation (by NO^+), followed by oxidation of the nitrosoarene to the nitroarenes; it seems probable that the 1,4-dinitro compound **33** is formed by sequential nitrosation of 1,2,4,5-tetramethylbenzene (**2**), followed by oxidation of the 1,4-dinitroso compound **34**.



33



34

What then is the role of HFP in promoting the nitrosation of 1,2,4,5-tetramethylbenzene (**2**)? Bosch and Kochi[10] recently proposed the following equilibrium [eqn. (4)] arising in the interaction between the 'head-to-tail' coupled form of nitrogen dioxide and an aromatic molecule.

$$ONO\text{-}NO_2 \rightleftharpoons NO^+NO_3^- \overset{ArH}{\rightleftharpoons} [ArH, NO^+]\,NO_3^- \quad (4)$$

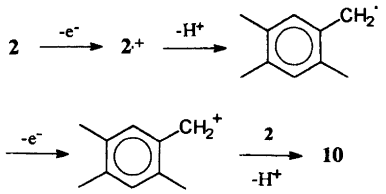
Given the propensity of HFP for essentially sequestering

nucleophilic species, it appears likely that the effect of HFP in promoting aromatic nitrosation arises from its effect on the equilibrium in eqn. (4) in favour of the [ArH, NO^+] species with the counter-ion NO_3^- deactivated by interaction with the solvent.* Under these circumstances, and in the presence of excess nitrogen dioxide in HFP, nitrosation appears the likely reaction, as is found.

Returning now to the consideration of the outcome of the photolysis of the CT complex of **2** with tetranitromethane in HFP which results in extensive ring nitration, it appears that not only does HFP markedly reduce the nucleophilic reactivity of trinitromethanide ion, but also promotes nitrosation of ArH by nitrogen dioxide, as outlined above. In this connection, it should be noted that the conversion of **2** into products in this photolysis reaction with tetranitromethane in HFP is a slow process (Table 2).

The reactions of 1,2,3,5-tetramethylbenzene (**7**) in HFP, either of the photolysis of the charge-transfer complex with tetranitromethane or 'light' or 'dark' reactions with excess nitrogen dioxide, broadly parallel those reported above for **2**, i.e. a substantial increase in overall ring nitration to give 2,3,4,6-tetramethylnitrobenzene (**27**).

The EPR spectroscopic results and their implications. The radical cation of 1,2,4,5-tetramethylbenzene, $\mathbf{2}^{\bullet+}$, is a very reactive species which has only been detected in solution by EPR spectroscopy using Co^{III} trifluoroacetate as the oxidant in a flow method,[17] or using either Hg^{II} trifluoroacetate UV irradiation[18] at low temperature or Tl^{III} trifluoroacetate oxidation[19] at ambient temperature as methods of generation. The success of the latter method probably depends on the fact that the EPR experiment actually monitors the *slow formation* of the radical cation, as demonstrated for hexamethylbenzene radical cation.[20] Thus the experiments designed to use photolysis of **2**-tetranitromethane in the presence of trifluoroacetic acid failed to produce any detectable concentrations of $\mathbf{2}^{\bullet+}$. However, since the photolysis reaction gives **10** as one of the products, most likely via the reaction sequence shown in eqn. (5),[21] it still becomes possible to indirectly observe the consequences of the formation of $\mathbf{2}^{\bullet+}$; the oxidation of **10** will produce the 1,2,4,5,6,8-hexamethylanthracene radical cation which gives a characteristic EPR spectrum.[12] It should be noted that this radical cation is sensitive toward the light used in the photolysis and is therefore best observed immediately after the light has been switched off (see Experimental).



(5)

Thus weak spectra of the 1,2,4,5,6,8-hexamethylanthracene radical cation were observed from the photolysis of **2** and tetranitromethane in both neat trifluoroacetic acid at −12 °C and HFP–trifluoroacetic acid (0.4 mol dm^{-3}) at 22 °C, implying that the acidic medium protonates trinitromethanide ion und thus leaves $\mathbf{2}^{\bullet+}$ to engage in competing, slower reactions.

The experiments designed to possibly detect 2,3,5,6-tetramethylnitrosobenzene as its radical cation from the reaction between **2** and NO_2 in HFP cannot be unambiguously interpreted. The EPR spectrum of the nitroso compound was indeed detected, but since the reaction between an arylthallium(III) trifluoroacetate and NO_2 is a synthetic pathway to nitrosoarenes,[22,23] it is not possible to know with certainty which sequence of events has led to the appearance of the EPR spectra observed.

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, 1,2,4,5- and 1,2,3,5-tetramethylbenzene were purchased from Aldrich. Dichloromethane (AR) and acetonitrile (HiPerSolv) were from BDH and 1,1,1,3,3,3-hexafluoropropan-2-ol from Sigma or of Merck UVASOL quality.

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.[24]

General procedure for the photonitration of 1,2,4,5-tetramethylbenzene (**2**) *and 1,2,3,5-tetramethylbenzene* (**7**) *with tetranitromethane.* A solution of **2** or **7** (500 mg, 0.47 mol dm^{-3}) and tetranitromethane (0.94 mol dm^{-3}) in dichloromethane (at 20, −20 or −50 °C), acetonitrile (20 or −20 °C), or 1,1,1,3,3,3-hexafluoropropan-2-ol (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 1–4, 7 and 10).

* The reaction between nitrate ion and the tris(4-bromophenyl)aminium ion in HFP is very slow,[16g] as expected slower than those of chloride and bromide ion ($k \approx 10^{-4}$ dm^3 mol^{-1} s^{-1}).[16e]

Table 10. Nuclear Overhauser effects for compounds isolated.

Compound	Irradiated at δ (ppm)	Enhancement(s) (%) at δ (ppm)
8	1.74	5.82 (4.0)
	1.80	6.20 (4.4)
	1.87	5.82 (4.9)
	1.96	6.20 (4.1)
	5.82	1.74 (0.3); 1.87 (0.7)
	6.20	1.80 (0.7); 1.96 (0.2)
9	1.74	1.94 (0.5); 5.98 (5.2)
	1.85	6.28 (3.6)
	1.87	5.98 (3.9)
	1.94	6.28 (3.2)
	5.98	1.74 (0.6); 1.87 (0.9)
	6.28	1.94 (1.3)
10	2.04	6.28 (7.2)
	2.06	2.27 (1.1); 3.87 (6.4)
	2.18	6.97 (5.0)
	2.27	2.06 (1.4); 6.94 (9.0)
	2.36	3.87 (3.4); 6.97 (5.5)
	3.87	2.06 (2.6); 2.36 (2.9)
	6.28	2.04 (1.0)
	6.94	2.27 (1.7)
	6.97	2.18 (1.0); 2.36 (1.2)
11	2.17	4.38 (1.3); 7.00 (4.1)
	2.18	6.82 (3.9)
	2.21	7.00 (3.8)
	4.38	2.17 (1.6); 6.82 (4.0)
	6.82	2.18 (0.6); 4.38 (0.6)
	7.00	2.17 (0.6); 2.21 (0.2)
12	2.25	7.04 (4.4)
	7.04	2.25 (0.3)
13	2.23	7.02 (2.3); 7.10 (2.7)
	2.31	5.41 (0.8); 7.02 (2.5)
	5.41	2.31 (0.5); 7.10 (3.6)
	7.02	2.23 (0.2); 2.31 (0.5)
	7.10	5.41 (0.7)
14	2.29	7.03 (2.3); 7.55 (2.3)
	2.60	7.03 (2.3); 10.19 (1.7)
	7.03	2.29 (0.1); 2.60 (0.3)
	7.55	2.29 (0.2); 10.19 (2.0)
	10.19	2.60 (0.2); 7.55 (1.4)
15	2.22	6.95 (2.5); 7.08 (2.3)
	2.28	4.61 (0.6); 6.95 (2.2)
	4.61	2.28 (0.3); 7.08 (2.1)
	6.95	2.22 (0.4); 2.28 (0.4)
	7.08	2.22 (0.1); 4.61 (0.4)
18	2.08	6.20 (6.5)
	2.11	3.88 (4.1); 2.19 6.99 (5.0)
	2.36	3.88 (2.1); 6.99 (5.9)
	3.88	2.11 (2.6); 2.36 (2.5); 6.20 (1.7)
	6.20	2.08 (1.2)
	6.99	2.19 (0.4); 2.36 (1.2)
19	2.13	6.50 (4.2)
	2.16	6.90 (3.5)
	2.31	4.86 (1.3); 6.90 (3.7)
	4.86	2.31 (1.2); 6.50 (2.7)
	6.50	2.13 (0.9); 4.86 (0.5)
	6.90	2.16 (0.6); 2.31 (0.8)
26	2.17	4.70 (2.8); 6.88 (3.9)
	2.26	6.88 (4.2)
	4.70	2.17 (1.8)
	6.88	2.17 (1.1); 2.26 (1.1)
29	5.43	2.32 (0.4); 7.10 (3.3)
	7.03	2.24 (0.3)
	7.10	2.24 (0.4); 5.43 (0.7)
30	1.79	5.94 (7.7)
	5.94	1.79 (0.5)
31	1.26	4.93 (3.1)
	1.34	4.93 (5.1)
	1.95	6.24 (3.5)
	2.07	4.94 (2.2); 6.24 (3.5)
	4.93	1.26 (0.7); 1.34 (0.6); 2.07 (0.6)
	6.24	1.95 (0.4); 2.07 (0.5)
32	1.29	4.94 (3.8)
	1.31	1.90 (1.1); 4.94 (4.9)
	1.90	1.29 (0.5); 1.31 (0.8); 6.10 (3.8)
	2.11	1.29 (0.5); 4.94 (4.1); 6.10 (3.7)
	4.94	1.29 (0.7); 1.31 (0.5); 2.11 (0.7)
	6.10	1.29 (0.5); 1.90 (0.5); 2.11 (0.6)

Photochemistry of 1,2,4,5-tetramethylbenzene (**2**) *in dichloromethane at −50 °C and the identification of adducts* **8** *and* **9**. Reaction of **2**–tetranitromethane in dichloromethane at −50 °C, as above, for 4 h gave a product which was shown by ^{1}H NMR spectra to be a mixture of adducts **8** (46%) and **9** (7%), aromatic compounds **10–17** (total 41%), and unidentified aromatic products (6%). The mixture was partially separated into its components by HPLC and gave the following in elution order:

The first material eluted was a mixture of aromatic compounds.

*1,3,4,6-Tetramethyl-*r*-3-nitro-*t*-6-trinitromethylcyclohexa-1,4-diene* (**8**), as an unstable oil (elemental analysis not possible because of instability; parent ion not visible in mass spectrum). IR: ν_{max} (liquid film) 1599, 1583, 1549 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.74 (s, 3-Me), 1.80 (d, $J_{4\text{-Me,H5}}$ 1.5 Hz, 4-Me), 1.87 (d, $J_{1\text{-Me,H2}}$ 1.5 Hz, 1-Me), 1.96 (s, 6-Me), 5.82 (q, $J_{H2,1\text{-Me}}$ 1.5 Hz, H2), 6.20 (q, $J_{H5,4\text{-Me}}$ 1.5 Hz, H5). Nuclear Overhauser experiments, see Table 10. ^{13}C NMR ($CDCl_3$) δ 18.3 (4-Me), 19.1 (1-Me), 23.3 (3-Me, 6-Me), 51.2 (C6), 88.3 (C3), 126.0 (C5), 130.2 (C2), 134.1 (C1), 136.2 (C4), resonance for $C(NO_2)_3$ not observed. The above assignments were confirmed by long-range reverse-detected heteronuclear correlation spectra (HMBC,HMQC).

*1,3,4,6-Tetramethyl-*r*-3-nitro-*c*-6-trinitromethylcyclohexa-1,4-diene* (**9**), as an oil in admixture with adduct (**8**) (5%). ^{1}H NMR ($CDCl_3$) δ 1.74 (s, 3-Me), 1.85 (s, 6-Me), 1.87 (d, $J_{1\text{-Me, H2}}$ 1.5 Hz, 1-Me). 1.94 (d, $J_{4\text{-Me,H5}}$

1.5 Hz, 4-Me), 5.98 (q, $J_{H2,1\text{-}Me}$ 1.5 Hz, H2), 6.28 (q, $J_{H5,4\text{-}Me}$ 1.5 Hz, H5). Nuclear Overhauser experiments, see Table 10. ^{13}C NMR ($CDCl_3$) δ 18.7 (4-Me), 18.9, 23.7 (1-Me, 6-Me), 25.6 (3-Me), 50.6 (C6), 85.4 (C3), 126.4 (C5), 130.3 (C2), 134.4 (C1), 136.3 (C4), resonance for $\mathbf{C}(NO_2)_3$ not observed. The above assignments were confirmed by long-range reverse-detected heteronuclear correlation spectra (HMBC,HMQC), and comparison with data for the epimer **8**.

Photochemistry of 1,2,4,5-tetramethylbenzene (**2**) *in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) at 20 °C and the identification of the aromatic products* (**10–16** and **18**). Reaction of **2**–tetranitromethane in HFP at 20 °C, as above, gave a mixture of the aromatic compounds **10–16** and **18** (Table 2). Chromatography of the crude product on a silica gel Chromatotron plate allowed the separation of aromatic compounds **10–15** and **18**, compound **16** not being eluted from the plate, in elution order:

2,2',3,4',5,5',6-Heptamethyldiphenylmethane (**10**), m.p. 139 °C (decomp.) (Found: M^+ 266.2034. $C_{20}H_{26}$ requires 266.20345). ^1H NMR ($CDCl_3$) δ 2.04 (s, 5'-Me), 2.06 (s, 6H, 2-Me, 6-Me), 2.18 (s, 4'-Me), 2.27 (s, 6H, 3-Me, 5-Me), 2.36 (s, 2'-Me), 3.87 (s, CH_2), 6.28 (s, H6'), 6.94 (s, H4), 6.97 (s, H3'), identical with an authentic sample available from earlier work.[20] Nuclear Overhauser experiments, see Table 10. ^{13}C NMR ($CDCl_3$) δ 15.7 (2-Me, 6-Me), 19.1, 19.2 (2'-Me, 4'-Me), 19.3 (5'-Me), 20.6 (3-Me, 5-Me), 32.7 ($\mathbf{C}H_2$), 127.9 (C6), 129.8 (C4), 131.2 (C3'), 133.2, 133.5 (C2, C3, C5, C5', C6), 133.8 (C4'), 135.3 (C2'), 136.7 (C1). The above assignments were confirmed by long-range reverse-detected heteronuclear correlation spectra (HMQC, HMBC).

2,4,5-Trimethyl-1-(2',2',2'-trinitroethyl)benzene (**11**), m.p. 70–73 °C (insufficient for elemental analysis; Found: M^+ 283.0804. $C_{11}H_{13}N_3O_6$ requires 283.0804). IR: ν_{max} (KBr) 1605, 1578 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.17 (s, 2-Me), 2.18 (s, 5-Me), 2.21 (s, 4-Me), 4.38 (br s, $\mathbf{C}H_2$), 6.82 (s, H6), 7.00 (s, H3). Nuclear Overhauser experiments, see Table 10. ^{13}C NMR ($CDCl_3$) δ 18.6 (5-Me), 19.2 (4-Me), 19.4 (2-Me), 36.3 ($\mathbf{C}H_2$), 122.4 (C1 or C2), 130.4 (C6), 132.7 (C3), 135.4 (C2 or C1, and C4 or C5), 138.3 (C5 or C4), resonance for $\mathbf{C}(NO_2)_3$ not observed. The above assignments were confirmed by long-range reverse-detected heteronuclear correlation spectra (HMBC, HMQC).

2,3,5,6-Tetramethylnitrobenzene (**12**), m.p. 109–114 °C, identical with an authentic sample.[25] IR: ν_{max} (KBr) 1520 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.12 (s, 6H, 2-Me, 6-Me), 2.25 (s, 6H, 3-Me, 5-Me), 7.04 (s, H4). Nuclear Overhauser experiments, see Table 10.

2,4,5-Trimethylphenylnitromethane (**13**),[3] isolated as an oil (Found: M^+ 179.0944. $C_{10}H_{13}NO_2$ requires 179.0946). IR: ν_{max} (liquid film) 1543, 1369 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.23 (s, 6H, 4-Me, 5-Me), 2.31 (s, 2-Me), 5.41 (s, $\mathbf{C}H_2$), 7.02 (s, H3), 7.10 (s, H6). Nuclear Overhauser experiments, see Table 10.

2,2',3,4',5,5'6-Heptamethyl-4-nitrodiphenylmethane (**18**), m.p. 157 °C (decomp.) (insufficient for elemental analysis. Found: M^+ 311.1885. $C_{20}H_{25}NO_2$ requires 311.1885). IR: ν_{max} (KBr) 1524 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.08 (s, 5'-Me), 2.11 (s, 6H, 2-Me, 6-Me), 2.19 (s, 9H, 3-Me, 4'-Me, 5-Me), 2.36 (s, 2'-Me), 3.88 (s, $\mathbf{C}H_2$), 6.20 (s, H6'), 6.99 (s, H3'). Nuclear Overhauser experiments, see Table 10. ^{13}C NMR ($CDCl_3$) δ 15.0 (3-Me or 4'-Me), 16.2 (2-Me), 19.1 (2'-Me and 4'-Me or 3-Me), 19.3 (5'-Me), 33.1 ($\mathbf{C}H_2$), 127.5 (C6'), 131.4 (C3'), 133.2 (C1' or C2'), 133.9 (C2' or C1'),135.1 (C2), 138.9 (C1), signals due to C3, C4, C4' and C5' could not be assigned. The above assignments were confirmed by long-range reverse-detected heteronuclear correlation spectra (HMBC, HMQC).

2,4,5-Trimethylbenzaldehyde (**14**), isolated as an oil (Found: M^+ 148.0886. $C_{10}H_{12}O$ requires 148.0888. Fragmentation pattern identical with an authentic sample). IR: ν_{max} (liquid film) 2754, 1697 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.29 (s, 6H, 4-Me, 5-Me), 2.60 (s, 2-Me), 7.03 (s, H3), 7.55 (s, H6), 10.19 (s, **C**HO). Nuclear Overhauser experiments, see Table 10.

2,4,5-Trimethylbenzyl alcohol (**15**), isolated as an oil (Found: M^+ 150.1040. $C_{10}H_{14}O$ requires 150.1045. Fragmentation pattern identical with an authentic sample). IR: ν_{max} (liquid film) 3379 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.22 (s, 6H, 4-Me, 5-Me), 2.28 (s, 2-Me), 4.61 (s, $\mathbf{C}H_2$), 6.95 (s, H3), 7.08 (s, H6). Nuclear Overhauser experiments, see Table 10.

2,4,5-Trimethylbenzyl nitrate (**16**) was not eluted from the silica gel Chromatotron plate, being presumably hydrolysed to 2,4,5-trimethylbenzyl alcohol (**15**). The presence of 2,4,5-trimethylbenzyl nitrate (**16**) in the crude reaction mixture was inferred from the ^1H NMR signal due to the -$\mathbf{C}H_2$-ONO_2 group at δ 5.39.[3]

Photochemistry of 1,2,4,5-tetramethylbenzene (**2**) *in acetonitrile at 20 °C and the identification of the* N*-nitroso acetamide* (**19**). Reaction of **2**–tetranitromethane in acetonitrile at 20 °C, as above, for 4 h gave a product which was shown by ^1H NMR spectra to be a mixture of aromatic compounds **10–16**, and **18** (total 86%), the *N*-nitrosoacetamide **19** (9%) and unidentified aromatic products (5%) (Table 3). Chromatography of the reaction mixture on a silica gel Chromatotron plate gave the *N*-nitrosoacetamide **19** in a fraction eluted immediately before 2,4,5-trimethylbenzaldehyde (**14**):

N-nitrosoacetamide (**19**), isolated as an oil (insufficient for elemental analysis. Found: M^+ 220.12105. $C_{12}H_{16}N_2O_2$ requires 220.1211. Found: M^+-NO 190.1227. $C_{12}H_{16}NO$ requires 190.1227). IR: ν_{max} (liquid film) 1726, 1499, 1128, 912 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.13 (s, 5-Me), 2.16 (s, 4-Me), 2.31 (s, 2-Me), 2.85 (s, CH_3-CO), 4.86 (s, CH_2), 6.50 (s, H6), 6.90 (s, H3).

Nuclear Overhauser experiments, see Table 10. ^{13}C NMR ($CDCl_3$) δ 18.7 (2-Me), 19.2, 19.3 (4-Me, 5-Me), 22.8 (CH_3-CO), 39.5 (CH_2), 127.9 (C6), 129.4 (C2), 131.8 (C3), 133.0 (C1), 134.1 (C4), 135.8 (C5), 174.6 (amide C=O). The above assignments were confirmed by long-range reverse-detected heteronuclear correlation spectra (HMBC, HMQC).

Photochemistry of 1,2,4,5-tetramethylbenzene (**2**) *at 20 °C in dichloromethane containing trifluoroacetic acid (0.7 mol dm^{-3}).* Reaction of **2**–tetranitromethane in dichloromethane containing trifluoroacetic acid (0.7 mol dm^{-3}) at 20 °C, as above, for 4 h gave a product which was shown by ^1H NMR spectra to be a mixture of aromatic compounds **10–14**, **16** and **18** (total 80%), and unidentified aromatic products (20%) (Table 4).

*Rearrangement of 1,3,4,6-tetramethyl-*r*-3-nitro-*t*-6-trinitromethylcyclohexa-1,4-diene* (**8**) *in acetonitrile at 20 °C.* A solution of **8** (11 mg) in acetonitrile (11 ml) was stored in the dark at 20 °C. Aliquots were withdrawn from the reaction mixture at appropriate time intervals, the solvent removed under reduced pressure at ≤0 °C, and the composition of each residue determined by ^1H NMR spectral analysis. Within the first 5 min adduct **8** underwent epimerization to give adduct **9**, and also nitro–nitrito rearrangement to give the epimeric trinitromethyl nitrites **22a** and **23a**, equilibrium (**8**:**9**:**22a**:**23a** ≈3:1:4:1) between these species being reached after 3–5 min. During the workup procedure the trinitromethyl nitrites **22a** and **23a** were converted into the corresponding 1,2,4,5-tetramethyl-*t*-4-trinitromethylcyclohexa-2,5-dien-*r*-1-ol (**22b**), ^1H NMR ($CDCl_3$) δ 1.42 (s, 1-Me), 1.75 (s, 4-Me), 1.78 (d, $J_{2\text{-Me,H3}}$ 1.5 Hz, 2-Me), 1.92 (d, $J_{5\text{-Me,H6}}$ 1.5 Hz, 5-Me), 5.54 (q, $J_{H6,5\text{-Me}}$ 1.5 Hz, H6), 5.88 (q, $J_{H3,2\text{-Me}}$ 1.5 Hz, H3), and 1,2,4,5-tetramethyl-*c*-4-trinitromethylcyclohexa-2,5-dien-*r*-1-ol (**23b**), ^1H NMR ($CDCl_3$) δ 1.32 (s, 1-Me), 1.69 (s, 4-Me), 1.76 (br s, 2-Me), 1.90 (br s, 5-Me), 5.53 (q, $J_{H6,5\text{-Me}}$ 1.5 Hz, H6), 5.84 (q, $J_{H3,2\text{-Me}}$ 1.5 Hz, H3). Subsequently over ca. 1 h this equilibrium mixture of adducts **8**, **9**, **22a** and **23a** was converted into a mixture of 2,4,5-trimethyl-1-(2′,2′,2′-trinitroethyl)benzene (**11**, 16%), 2,3,5,6-tetramethylnitrobenzene (**12**, 21%), 2,4,5-trimethylphenylnitromethane (**13**, 13%), 2,4,5-trimethylbenzyl alcohol (**15**, 9%), 2,4,5-trimethylbenzyl nitrate (**16**, 4%), and unidentified aromatic products (total 37%).

*Rearrangement of 1,3,4,6-tetramethyl-*r*-3-nitro-*t*-6-trinitromethylcyclohexa-1,4-diene* (**8**) *in [^2H]-chloroform at 20 °C.* A solution of **8** in [^2H]chloroform was stored in the dark at 20 °C, and the ^1H NMR spectrum of the solution was monitored at appropriate time intervals. In comparison with the rearrangement of **8** in acetonitrile, above, the transformations of **8** in [^2H]chloroform occurred sluggishly, equilibrium with the epimer **9** (**8**:**9** ≈6:1) being established only after ca. 90 h, and the formation of products from the adduct mixture being complete after >14 days. In contrast to the rearrangement in acetonitrile, the trinitromethyl nitrites **22a** and **23a** were not detected in the rearrangement in [^2H]chloroform. The major products present after 25 days were 2,4,5-trimethyl-1-(2′,2′,2′-trinitroethyl)benzene (**11**, 52%), 2,4,5-trimethylphenylnitromethane (**13**, 18%), 2,4,5-trimethylbenzaldehyde (**14**, 6%), 2,4,5-trimethylbenzyl nitrate (**16**, 10%) and unidentified aromatic compounds (13%).

Nitration of 1,2,4,5-tetramethylbenzene (**2**) *with nitrogen dioxide in dichloromethane at 20 °C.* A solution of **2** (0.47 mol dm^{-3}) in dichloromethane saturated with nitrogen dioxide was stored at 20 °C in the dark. Aliquots were removed at appropriate time intervals, the excess nitrogen dioxide and solvent were removed under reduced pressure at ≤0 °C, and the product composition determined by ^1H NMR spectral analysis (Table 5). After 4 h the products formed were shown to be predominantly 2,4,5-trimethylbenzyl nitrate (**16**, 70%), and 2,4,5-trimethylphenylnitromethane (**13**, 20%) and small amounts of aromatic compounds **10**, **14** and **15**, and unidentified aromatic compounds.

Photochemical nitration of 1,2,4,5-tetramethylbenzene (**2**) *with nitrogen dioxide in dichloromethane at 20 °C.* A solution of **2** (0.47 mol dm^{-3}) in dichloromethane saturated with nitrogen dioxide was irradiated with filtered light ($\lambda_{cut\text{-}off}$ 435 nm) at 20 °C. Aliquots were removed at appropriate time intervals, the excess nitrogen dioxide and solvent were removed under reduced pressure at ≤0 °C, and the product composition determined by ^1H NMR spectral analysis (Table 5). After 4 h the products formed were shown to be similar to those of the 'dark' reaction, above, i.e. predominantly 2,4,5-trimethylbenzyl nitrate (**16**, 68%), and 2,4,5-trimethylphenylnitromethane (**13**, 23%) and small amounts of aromatic compounds **10**, **14** and **15**, and unidentified aromatic compounds.

Nitration of 1,2,4,5-tetramethylbenzene (**2**) *with nitrogen dioxide in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) at 20 °C.* A solution of **2** (0.47 mol dm^{-3}) in HFP saturated with nitrogen dioxide was stored at 20 °C in the dark. Aliquots were removed at appropriate time intervals, the excess nitrogen dioxide and solvent were removed under reduced pressure at ≤0 °C, and the product composition determined by ^1H NMR spectral analysis. Complete reaction of **2** had occurred after <0.5 h and the products formed were shown to be predominantly 2,3,5,6-tetramethylnitrobenzene (**12**, 71%), 2,4,5-trimethylbenzoic acid (**24**, 18%), 2,3,5,6-tetramethyl-1,4-dinitrobenzene (**25**, 4%), and small amounts of aromatic compounds **13** and **14**, and unidentified aromatic compounds.

Photochemical nitration of 1,2,4,5-tetramethylbenzene (**2**) *with nitrogen dioxide in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) at 20 °C.* A solution of **2** (0.47 mol dm^{-3}) in HFP saturated with nitrogen dioxide was irradiated with

filtered light ($\lambda_{cut\text{-}off}$ 435 nm) at 20 °C. Aliquots were removed at appropriate time intervals, the excess nitrogen dioxide and solvent were removed under reduced pressure at ≤0 °C, and the product composition determined by ^{1}H NMR spectral analysis. Complete reaction of **2** had occurred after <0.5 h and the products formed were shown to be similar to those of the 'dark' reaction, above, i.e. predominantly 2,3,5,6-tetramethylnitrobenzene (**12**, 74%), 2,4,5-trimethylbenzoic acid (**24**, 12%), 2,3,5,6-tetramethyl-1,4-dinitrobenzene (**25**, 4%), and small amounts of aromatic compounds **13** and **14**, and unidentified aromatic compounds.

Photochemistry of 1,2,3,5-tetramethylbenzene (**7**) *in dichloromethane at 20 °C and the identification of aromatic compounds* **26–29**, *adduct* **30** *and 'double adducts'* **31** *and* **32**. Reaction of **7**–tetranitromethane in dichloromethane at 20 °C, as above, for 6 h gave a product which was shown by ^{1}H NMR spectra to be a mixture of aromatic compounds **26–29** (total 49%), adduct **30** (14%), adducts **31** and **32** (total 4%), unidentified aromatic compounds (total 16%), and unidentified adducts (total 18%) (Table 6). The mixture was partially separated into its components by HPLC and gave the following in elution order:

2,4,6-Trimethyl-1-(2',2',2'-trinitroethyl)benzene (**26**), m.p. 83 °C (decomp.) (X-ray crystal structure determined, see below). IR: ν_{max} (KBr) 1601 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.17 (s, 2-Me, 6-Me), 2.26 (s, 4-Me), 4.70 (br s, $\mathbf{CH_2}$), 6.88 (s, H3, H5). Nuclear Overhauser experiments, see Table 10. ^{13}C NMR ($CDCl_3$) δ 20.0 (2-Me, 6-Me), 20.9 (4-Me), 123.2 (C2, C6), 130.0 (C3, C5), 138.3 (C1), 139.2 (C4), resonance for $\mathbf{C}(NO_2)_3$ not observed. The above assignments were confirmed by long-range reverse-detected heteronuclear correlation spectra (HMBC, HMQC).

2,3,4,6-Tetramethylnitrobenzene (**27**), identical with an authentic sample.[14]

3,4,5-Trimethylphenylnitromethane (**28**), identical with an authentic sample.[14]

2,3,5-Trimethylphenylnitromethane (**29**), as an oil containing an impurity (5%). ^{1}H NMR ($CDCl_3$) δ 2.24 (s, 3-Me, 5-Me), 2.32 (s, 2-Me), 5.43 (s, $\mathbf{CH_2}NO_2$), 7.03 (s, H4), 7.10 (s, H6). Nuclear Overhauser experiments, see Table 10. ^{13}C NMR ($CDCl_3$) δ 18.4 (2-Me), 19.0, 19.4 (3-Me, 5-Me), 77.6 ($\mathbf{CH_2}NO_2$), 132.2 (C4), 132.6 (C6); signals at δ 125.7, 129.4, 135.2, 138.9 could not be assigned. The above assignments were confirmed by long-range reverse-detected heteronuclear correlation spectra (HMQC).

trans-*1,3,5,6-Tetramethyl-6-nitro-3-trinitromethylcyclohexa-1,4-diene* (**30**), m.p. 66–68 °C (X-ray crystal structure determined, see below). IR: ν_{max} (KBr) 1583, 1547 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.79 (br s, 1-Me, 3-Me, 5-Me, 6-Me), 5.94 (br s, H2, H4). Nuclear Overhauser experiments, see Table 10. ^{13}C NMR ($CDCl_3$) δ 18.4 (1-Me, 5-Me), 20.6, 25.5 (3-Me, 6-Me), 47.6 (C3), 90.9 (C6), 124.1 (C2, C4), 137.0 (C1, C5), resonance for $\mathbf{C}(NO_2)_3$ not observed. The above assignments were confirmed by long-range reverse-detected heteronuclear correlation spectra (HMBC, HMQC).

1,2,4,6-Tetramethyl-2,5-dinitro-6-trinitromethylcyclohex-3-en-1-ol (**31**), isolated as an oil containing an impurity (5%). IR: ν_{max} (liquid film) 3693, 1601, 1560 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.26 (s, 1-Me), 1.34 (s, 6-Me), 1.95 (s, 3-Me), 2.07 (d, $J_{4\text{-}Me,H3}$ 1.5 Hz, 4-Me), 4.93 (s, H5), 6.24 (q, $J_{H3,4\text{-}Me}$ 1.5 Hz, H3). Nuclear Overhauser experiments, see Table 10. ^{13}C NMR ($CDCl_3$) δ 18.6 (1-Me), 20.3 (4-Me), 22.0 (2-Me), 22.3 (6-Me), 45.1 (C6), 51.7 (C1), 86.1 (C2), 96.0 (C5), 128.3 (C3), 130.2 (C4), resonance for $\mathbf{C}(NO_2)_3$ not observed. The above assignments were confirmed by long-range reverse-detected heteronuclear correlation spectra (HMBC, HMQC).

1,2,4,6-Tetramethyl-2,5-dinitro-6-trinitromethylcyclohex-3-en-1-ol (**32**), isolated as an oil containing an impurity (10%). IR: ν_{max} (liquid film) 3445, 1576, 1553 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.29 (s, 1-Me), 1.31 (s, 6-Me), 1.90 (s, 2-Me), 2.11 (d, $J_{4\text{-}Me,H3}$ 1.5 Hz, 4-Me), 4.94 (s, H5), 6.10 (q, $J_{H3,4\text{-}Me}$ 1.5 Hz, H3. Nuclear Overhauser experiments, see Table 10. ^{13}C NMR ($CDCl_3$) δ 20.7 (1-Me), 22.2 (4-Me), 24.9 (6-Me), 26.2 (2-Me), 47.6 (C6), 62.3 (C1), 88.5 (C2), 96.8 (C5), 128.8 (C3), 133.4 (C4), resonance for $\mathbf{C}(NO_2)_3$ not observed. The above assignments were confirmed by long-range reverse-detected heteronuclear correlation spectra (HMBC, HMQC).

Photochemistry of 1,2,3,5-tetramethylbenzene (**7**) *in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) at 20 °C.* Reaction of **7**-tetranitromethane in HFP at 20 °C, as above, after 1 h gave a mixture of the aromatic compounds **26** (1%), **27** (76%), **28** (0.4%), **29** (1%), adduct **30** (2%), adducts **31** (0.6%) and **32** (2%), unidentified aromatic compounds (total 7%), and unidentified adducts (total 9%).

Photochemistry of 1,2,3,5-tetramethylbenzene (**7**) *at 20 °C in dichloromethane containing trifluoroacetic acid (0.7 mol dm^{-3}).* Reaction of **7**–tetranitromethane in dichloromethane containing trifluoroacetic acid (0.7 mol dm^{-3}) at 20 °C, as above, for 1 h gave a product which was shown by ^{1}H NMR spectra to be a mixture of the aromatic compounds **26** (3%), **27** (56%), **28** (5%), **29** (3%), adduct **30** (0.8%), adducts **31** (0.4%) and **32** (0.2%), unidentified aromatic compounds (total 14%), and unidentified adducts (total 17%).

Nitration of 1,2,3,5-tetramethylbenzene (**7**) *with nitrogen dioxide in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) at 20 °C.* A solution of **7** (0.47 mol dm^{-3}) in HFP saturated with nitrogen dioxide was stored at 20 °C in the dark. Aliquots were removed at appropriate time intervals, the excess nitrogen dioxide and solvent were removed under reduced pressure at ≤0 °C, and the product composition

determined by ^{1}H NMR spectral analysis. Essentially complete reaction of **7** had occurred after 2 h and the products formed were shown to be predominantly 2,3,4,6-tetramethylnitrobenzene (**27**, 42%), 3,4,5-trimethylphenylnitromethane (**28**, 12%), 2,3,5-trimethylphenylnitromethane (**29**, 3%), 3,4,5-trimethylbenzaldehyde (**33**, 10%), and unidentified products (33%).

Photochemical nitration of 1,2,3,5-tetramethylbenzene (**7**) *with nitrogen dioxide in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) at 20 °C.* A solution of **7** (0.47 mol dm^{-3}) in HFP saturated with nitrogen dioxide was irradiated with filtered light ($\lambda_{cut\text{-}off}$ 435 nm) at 20 °C. Aliquots were removed at appropriate time intervals, the excess nitrogen dioxide and solvent were removed under reduced pressure at $\leqslant$0 °C, and the product composition determined by ^{1}H NMR spectral analysis. Essentially complete reaction of **7** had occurred after 2 h and the products formed were shown to be similar to those of the 'dark' reaction, above, i.e. predominantly 2,3,4,6-tetramethylnitrobenzene (**27**, 44%), 3,4,5-trimethylphenylnitromethane (**28**, 13%), 2,3,5-trimethylphenylnitromethane (**29**, 3%), 3,4,5-trimethylbenzaldehyde (**33**, 13%), and unidentified products (27%).

Rearrangement of trans-*1,3,5,6-tetramethyl-6-nitro-3-trinitromethylcyclohexa-1,4-diene* (**30**) *in* [$^2H_3$]*acetonitrile at 22 °C.* A solution of the adduct **30** in [$^2H_3$]acetonitrile was stored in the dark at 22 °C and the ^{1}H NMR spectrum monitored at appropriate time intervals. Initially (0–7 h) adduct **30** rearranged to give 3,4,5-trimethylphenylnitromethane (**28**) and some unidentified material. At longer reaction times the conversion of the adduct **30** into the nitromethyl compound **28** and unidentified compounds continued, but 2,4,6-trimethyl-1-(2′,2′,2′-trinitroethyl)benzene (**26**) appeared among the products. The kinetic evaluation is presented in Fig. 4.

The attempted rearrangement of trans-*1,3,5,6-tetramethyl-6-nitro-3-trinitromethylcyclohexa-1,4-diene* (**30**) *in* [^2H]*chloroform or in* [$^2H_2$]*dichloromethane at 22 °C.* Solutions of the adduct **30** in either [^{2}H] chloroform or [$^2H_2$]dichloromethane were stable for greater than 4 days at 22 °C.

EPR spectroscopy. EPR spectra were recorded by the Upgrade Version ESP 3220–200SH of a Bruker ER-200D spectrometer, equipped with a photolysis cavity. The light source was the 50 W high-pressure Hg lamp from Bruker (ER 202) and the filter was from Schott, Germany (cut-off at 430 nm).

Control experiments established that the Hg^{II} trifluoroacetate–UV light[18] (at −12 °C) and Tl^{III} trifluoroacetate method[19] (at −12 and 0 °C) gave excellent spectra of $\mathbf{2}^{\bullet+}$ in neat trifluoroacetic acid or HFP, the latter solvent being used in the 0 °C runs. As in the case of pentamethylbenzene,[21] the Tl^{III} method could be performed photochemically with advantage.

The attempts to generate and detect $\mathbf{2}^{\bullet+}$ by photolysis of **2** (ca. 40 mmol dm^{-3}) in the presence of tetranitromethane (0.4 mol dm^{-3}) by light of $\lambda > 435$ nm were performed in dichloromethane and dichloromethane–trifluoroacetic acid (0.8 mol dm^{-3}) at −70 °C, in trifluoroacetic acid at −12 °C, and in HFP and HFP–trifluoroacetic acid (0.4 mol dm^{-3}) at 22 °C. Only in the acidic solutions was any radical cation detectable, and then in the form of the transformation product, (1,2,4,5,6,8-hexamethylanthracene)$^{\bullet+}$, characterized previously.[12]

The attempts to detect 1-nitroso-2,3,5,6-tetramethylbenzene were made on solutions of **2** (100 mol dm^{-3}) in HFP, to which a small volume (maximum 3% of the total volume) of NO_2 in dichloromethane was added to make up an intial [NO_2] of 5 mmol dm^{-3}. No EPR signal was detectable. After 10 min Tl^{III} trifluoroacetate was added. Again, the thermal reaction gave no EPR signal, whereas irradiation by UV light generated the EPR spectrum of (2,3,5,6-tetramethylnitrosobenzene)$^{\bullet+}$ (Refs. 13 and 26). This spectrum disappeared immediately after discontinuation of the irradiation. Inverse addition of the reagents gave the same result.

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) 0.71073 Å from a crystal monochromator] are given below. The space group was determined unambiguously as a result of the structure analysis 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

2,4,6-Trimethyl-1-(2′,2′,2′-trinitroethyl)-benzene (**26**), $C_{11}H_{13}N_3O_6$, *M* 283.24, monoclinic, space group $P\,2_1/c$, *a* 13.399(6), *b* 9.217(4), *c* 20.976(8) Å, *β* 99.56(3)°; *V* 2555(2) Å^3, D_c 1.473 g cm^{-3}, *Z* 8, μ(Mo Kα) 1.22 cm^{-1}. The crystal was colourlesss and of approximate dimensions 1.0 × 0.8 × 0.4 mm. Data were collected at 158(2) K out to a maximum Bragg angle θ = 28.5 °. Number of independent reflections measured 3340, 2368 with $I > 2\sigma(I)$. Absorption corrections were not applied; g_1 0.1122, g_2 6.1900; $R_{(obs)}$-factor 0.074, $wR_{(all\ data)}$ 0.23.

trans-*1,3,5,6-Tetramethyl-6-nitro-3-trinitromethylcyclohexa-1,4-diene* (**30**), $C_{11}H_{14}N_4O_8$, *M* 330.26, triclinic, space group $P\,\bar{1}$, *a* 9.344(3), *b* 13.228(4), *c* 13.459(3) Å, *α* 113.99(2), *β* 102,68(2), *γ* 92,47(2)°; *V* 1466.4(7) Å^3, D_c 1.496 g cm^{-3}, *Z* 4, μ(Mo Kα) 1.29 cm^{-1}. The crystal was colourless and of approximate dimensions 0.90 × 0.86 × 0.84 mm. Data were collected at 163(2) K out to a maximum Bragg angle θ = 25°. Number of

independent reflections measured 4984, 3420 with $I > 2\sigma(I)$. Absorption corrections were not applied; g_1 0.0946, g_2 0.0000; $R_{(obs)}$-factor 0.053, $wR_{(all\ data)}$ 0.138.

Structure determination. Full-matrix least-squares refinements (SHELXL-93)[27] 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.

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