Photochemical Nitration by Tetranitromethane. Part XXXIV.[†] The Photochemical Reactions of Pentamethylbenzene and Hexamethylbenzene with Tetranitromethane. The Formation and Rearrangement of Labile Adducts from Pentamethylbenzene

Lennart Eberson,[a,*] Michael P. Hartshorn,[b,*] and David J. Timmerman-Vaughan[b]

[a]Department of Chemistry, Lund University, PO Box 124, S-221 00 Lund, Sweden and [b]Department of Chemistry, University of Canterbury, Christchurch, New Zealand
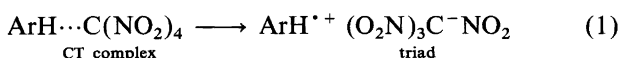
Eberson, L., Hartshorn, M. P., and Timmerman-Vaughan, D. J., 1996. Photochemical Nitration by Tetranitromethane. Part XXXIV. The Photochemical Reactions of Pentamethylbenzene and Hexamethylbenzene with Tetranitromethane. The Formation and Rearrangement of Labile Adducts from Pentamethylbenzene – Acta Chem. Scand. 50: 1121–1136. © Acta Chemica Scandinavica 1996.

The photolysis of the charge transfer (CT) complex of tetranitromethane and pentamethylbenzene (13) in dichloromethane at −50 or −78 °C gives the labile epimeric 1,2,3,4,6-pentamethyl-3-nitro-6-trinitromethylcyclohexa-1,4-dienes 18 and 19. Adduct 18 rearranges rapidly in [$^2H_2$]dichloromethane at 22 °C (half-life 9 min) to give 2,3,4,5-tetramethyl-1-(2′,2′,2′-trinitroethyl)benzene (21), 2,3,4,5-tetramethylphenylnitromethane (26), 2,3,4,5-tetramethylbenzyl nitrate (32) and 2,3,4,5-tetramethylbenzyl nitrite (36). The photolysis of the tetra-nitromethane–13 CT complex in dichloromethane at 20 °C gives compounds 21, 26, 32 and 36, in addition to their 2,3,4,6-tetramethyl analogues 20, 25, 31 and 35, the latter set of products probably arising from the rearrangement of the highly labile epimeric 1,2,3,5,6-pentamethyl-3-nitro-6-trinitromethylcyclohexa-1,4-dienes 54. The photolysis of the tetranitromethane–13 CT complex in acetonitrile gives mainly the phenylnitromethane 26, while similar reaction in 1,1,1,3,3,3-hexafluoropropan-2-ol yields pentamethylnitrobenzene 24, the latter by a nitrosation/oxidation sequence. Reaction of 13 with nitrogen dioxide in dichloromethane gives mainly compounds 26 and 30.

No adducts were detected in the photolysis of the CT complex of hexamethylbenzene 14 in dichloromethane at accessible reaction temperatures (⩾ −20 °C), but products of side-chain modification 37–46 were formed. In acetonitrile similar reaction gave in addition to the above products 37–46 the N-nitrosoacetamide 47 and its precursor 49. Compounds 47 and 49 are also formed, along with the major products pentamethylbenzyl nitrate 39 and the mono- and di-nitromethyl compounds 40 and 43, on reaction of 14 with nitrogen dioxide in acetonitrile.

EPR spectroscopic examination of the photolysis of acidic (trifluoroacetic acid, 0.4 mol dm^{-3}) solutions of tetranitromethane and 13 or 14 demonstrated the formation of the corresponding radical cation or a transformation product thereof, i.e. the 1,2,3,4,5,6,7,8-octamethylanthracene radical cation from 13 or 14[·+] from 14.

The photochemical addition of tetranitromethane to aromatic compounds (ArH) by excitation of the ArH–tetranitromethane 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[·+], trinitromethanide ion, and nitrogen dioxide.

$$ArH \cdots C(NO_2)_4 \longrightarrow ArH^{·+} \ (O_2N)_3C^-NO_2 \qquad (1)$$

CT complex   triad

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

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

$$Ar(H)C(NO_2)_3^· + NO_2 \longrightarrow adducts \qquad (3)$$

[†] Part XXXIII, see Ref. 1.
[*] To whom correspondence should be addressed.
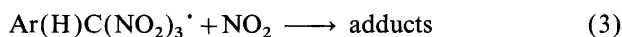
In determining the structures of the adducts formed, the first bond formation involving reaction of trinitromethanide ion with ArH $\cdot$ $^+$ is crucial. In the reaction of trinitromethanide ion with 1,2,3-trimethylbenzene radical cation **1** the initial bond formation occurs at each of the unoccupied ring positions, C4 and C5, to give the two delocalized carbon radicals **2** (27%) and **3** (61%) (Scheme 1), but no detectable coupling *ipso* to the methyl substituents.[3] This regiochemistry can be accounted for in terms of the relative energies of the various delocalized carbon radicals which determine the reaction pathways followed.[4] These relative energies will be affected both by the steric interactions between the trinitromethyl group and the remainder of the molecule, and the extent of the stabilization of the discrete carbon radical by substituents. The two delocalized carbon radicals **4** and **5** will be subject to some steric compression arising from the *ipso*-attachment of the trinitromethyl group, but more seriously from the interaction between the bulky trinitromethyl group and β-methyl group(s).[4,5] Although carbon radical **2** might be expected to gain some stabilization from the two appropriately situated methyl groups, this is offset by the steric interaction between the trinitromethyl group and the β-methyl group. For carbon radical **3**, stabilization of the radical system is afforded by only one methyl group, but steric interactions between the trinitromethyl group and the remainder of the molecule are minimal.

The formation of adducts, or products of adduct decomposition, in the reaction of 1,2,3,4-tetramethylbenzene radical cation **6** with trinitromethanide ion arises predominantly (65%) from trinitromethanide ion attack at an unoccupied ring position to give carbon radical **7**; only a small extent of reaction *ipso* to one of the flanking methyl groups to give carbon radical **8** (5%) was observed (Scheme 2).[6] In both carbon radicals, **7** and **8**, there is steric interaction between the trinitromethyl group and a β-methyl group, but radical **8** has the additional steric compression arising from the *ipso* attachment of the trinitromethyl group.

The reactions of the isomeric tetramethylbenzene radical cations **9** and **12** with trinitromethanide ion document further the importance of steric effects on the
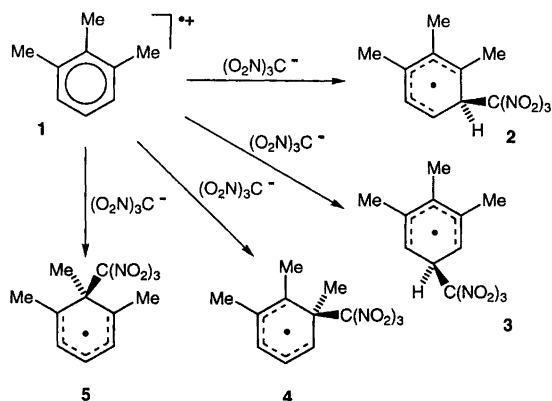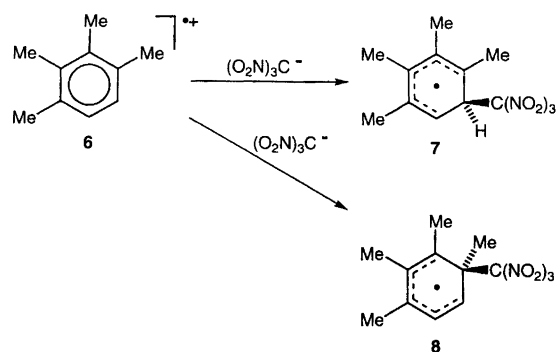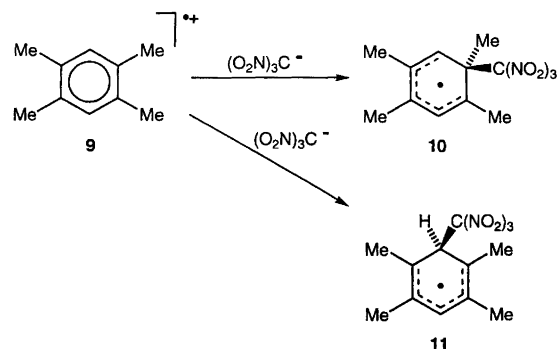
Scheme 2

course of this type of reaction.[1] For the reaction of the radical cation of 1,2,4,5-tetramethylbenzene (**9**) the only adducts (58%; at −50 °C) which could be detected arose from trinitromethanide ion attack *ipso* to one of the methyl groups (and β- to a second methyl group) to give delocalized carbon radical **10** (Scheme 3); products were not observed which might have arisen by initial attack of trinitromethanide ion at an unsubstituted ring carbon atom to give delocalized carbon radical **11** with two β-methyl/trinitromethyl steric interactions. The yields of adducts from the photolysis of the CT complex of 1,2,3,5-tetramethylbenzene with tetranitromethane were low, but those which did form arose from trinitromethanide ion attack on the radical cation of 1,2,3,5-tetramethylbenzene **12** *ipso* either to one of the flanking methyl groups or to the 5-methyl group, with the latter predominating.

In the light of the foregoing, we re-examined the photolyses of the CT complexes of tetranitromethane with pentamethylbenzene (**13**) and hexamethylbenzene (**14**) with the intention of detecting the presence of labile adducts among the reaction products. These reactions had been studied earlier but only at ambient temperatures.[7] However, we were aware at the outset that the epimeric adducts **15** derived from 1,2,4,5-tetramethylbenzene **16** were labile in solution at 20 °C. Given the close structural similarities between adducts **15** and the most likely adduct structures **17** to be formed from pentamethylbenzene (**13**), we anticipated that the adducts **17** might be detectable only at low reaction

Scheme 1

Scheme 3

temperatures. In the event, adducts **17** were detectable, if transiently at −50 °C, and isolated as labile materials from a reaction at −78 °C. Unfortunately the low solubility of hexamethylbenzene **14** precluded the use of such low temperature reactions for that substrate. 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,[8] 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 ≤0 °C. The crude product mixtures were stored at −78 °C and were analysed (¹H NMR spectroscopy; see Experimental, Tables 1–3 and 5–7 as soon as possible.
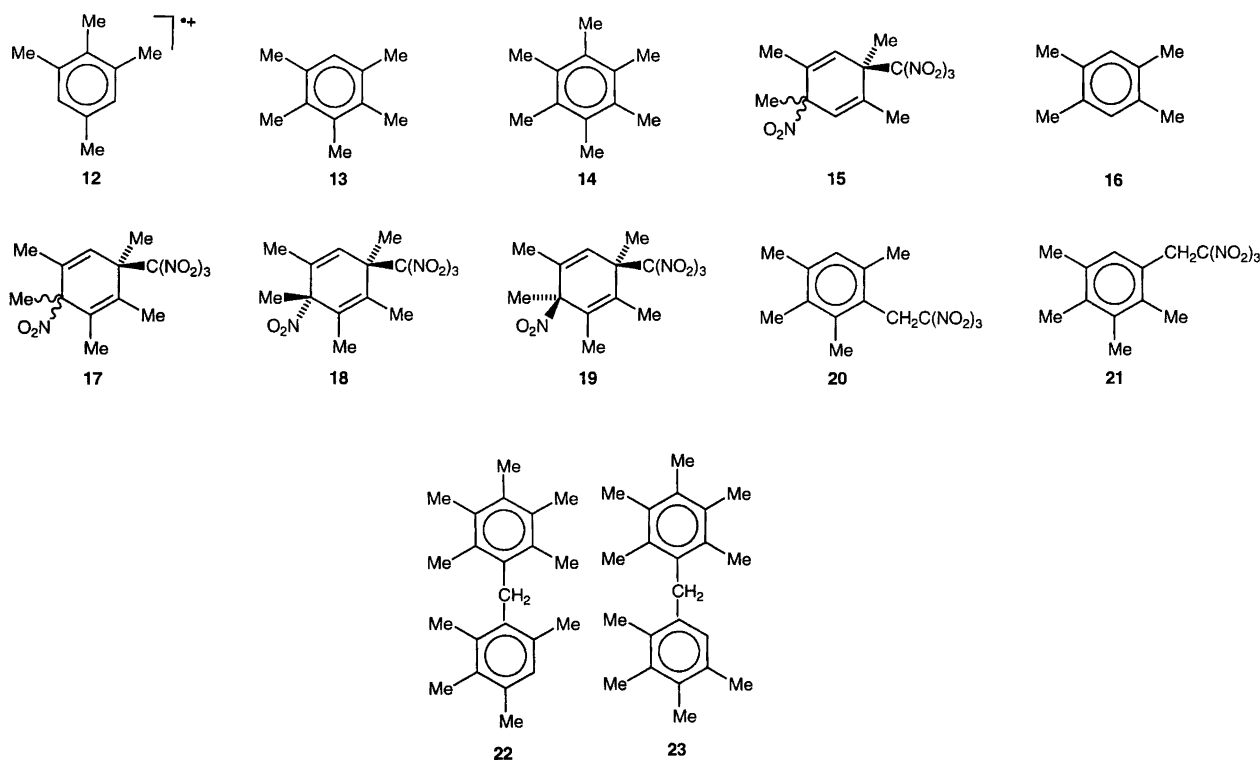
(A) Reactions of pentamethylbenzene 13

Photochemistry in dichloromethane at −78 °C and the identification of adducts **18** *and* **19**. A solution of **13** (0.42 mol dm⁻³) and tetranitromethane (0.84 mol dm⁻³) in dichloromethane was irradiated at −78 °C. The composition of the mixture was monitored by withdrawing samples for NMR spectral analysis (Table 1). The final solution (after 3 h) after work-up contained the epimeric 1,2,3,4,6-pentamethyl-3-nitro-6-trinitromethylcyclohexa-1,4-dienes (**18**) (15%) and **19** (1%), aromatic compounds **20–32** (total 79%), and unidentified aromatic compounds

(5%). Adduct **18** was separated partially by HPLC on a cyanopropyl column cooled to 0 °C using hexane–dichloromethane mixtures as the eluting solvents. The first material eluted was a mixture of aromatic compounds, the separation of which is given below.

Adduct **18** was assigned the 1,2,3,4,6-pentamethyl-3-nitro-6-trinitromethylcyclohexa-1,4-diene structure on the basis of a consideration of its spectroscopic data (Experimental). The assignment of adduct **18** as the *trans*-isomer was made from a comparison of its ¹H NMR data and the chemical shift of the olefinic proton (the only signal clearly identifiable in the reaction mixture) for the *cis*-isomer **19** with the ¹H NMR data for the epimeric adducts **33** and **34** derived from 1,2,4,5-tetramethylbenzene **16**¹ (Fig. 1).

Photochemistry in dichloromethane at 20 °C and the identification of the aromatic products **20–30**. Photolysis of the CT complex of **13**–tetranitromethane in dichloromethane at 20 °C for 3 h, as above, gave a mixture of the aromatic compounds **20–30** (Table 1). The yields of compounds **24** and **28** could not be assessed individually from ¹H NMR spectra because of overlapping signals, but these are included within the column 'Total aromatics.' Chromatography of this mixture on a silica gel Chromatotron plate allowed the separation of compounds **20–30** (for the elution order, see Experimental), the benzyl nitrates **31** and **32**, and the benzyl nitrites **35** and **36** being presumably hydrolysed to give the respective benzyl alcohols **29** and **30**.

The structures of the isomeric 2′,2′,2′-trinitroethyl aromatic compounds **20** and **21** were established from their

<table>
<tr><td>12</td><td>13</td><td>14</td><td>15</td><td>16</td></tr>
<tr><td>17</td><td>18</td><td>19</td><td>20</td><td>21</td></tr>
<tr><td colspan="5">22   23</td></tr>
</table>

Table 1. Overview of yields of products from the photolysis of pentamethylbenzene (13) (0.42 mol dm^{-3}) and tetranitromethane (0.84 mol dm^{-3}) in dichloromethane.

t/h	Conversion (%)	Yield (%)																Total aromatics
		(18)	(19)	Total adducts	(20)	(21)	(22)	(23)	(25)	(26)	(27)	(29)	(30)	(31)	(32)	(35)	(36)	
20 °C																		
0.5	30	—	—	—	23.5	5.2	trace	1.9	1.0	39.9	—	0.7	0.3	5.0	20.4	0.1	0.3	100
1	49	—	—	—	17.3	3.7	trace	1.0	0.9	52.0	0.2	0.4	0.5	4.7	16.9	0.5	0.6	100
2	78	—	—	—	11.9	3.6	0.1	1.1	1.9	40.3	0.6	0.1	0.1	6.3	28.9	0.7	2.0	100
3	89	—	—	—	9.7	3.5	0.1	0.5	1.9	40.7	1.1	0.3	0.2	6.5	29.9	0.9	2.8	100
−20 °C																		
0.5	56	8.4	—	8.4	10.4	2.4	—	1.7	1.3	22.9	—	0.4	trace	8.9	40.9	—	—	91.6
1	78	—	—	—	9.4	3.7	—	3.6	2.3	36.1	0.1	1.1	trace	8.6	29.6	0.4	3.6	100
2	96	—	—	—	9.0	3.1	—	0.5	3.1	47.3	0.2	0.4	0.2	7.5	24.5	0.6	2.3	100
3	99	—	—	—	8.8	3.2	—	0.1	2.7	45.7	0.2	0.3	0.2	7.6	27.3	0.6	1.6	100
−50 °C																		
0.5	26	25.2	1.4	26.6	6.7	1.1	—	9.4	6.0	14.9	0.4	0.4	0.4	12.9	14.5	0.7	0.5	73.4
1	41	33.0	2.2	35.2	8.4	1.3	0.3	3.9	8.0	14.7	0.2	0.2	0.2	8.4	11.2	2.2	1.9	64.8
2	69	2.1	—	2.1	9.2	4.5	0.2	11.3	10.8	23.6	0.6	0.2	0.1	6.7	15.2	4.9	6.3	97.9
3	79	—	—	—	7.7	3.4	0.1	7.4	10.0	25.6	0.6	0.3	0.1	8.3	21.1	3.9	8.7	100
−78 °C																		
0.5	36	31.8	1.8	33.6	6.1	1.6	0.3	14.6	4.3	9.5	—	0.3	trace	14.6	8.7	0.5	1.2	66.4
1	48	46.2	2.1	48.3	5.1	1.6	0.3	7.0	5.3	8.9	trace	0.1	0.1	10.8	7.1	1.0	1.9	51.7
2	64	37.2	2.2	39.4	6.0	1.9	0.4	4.3	6.1	13.5	trace	0.1	0.1	11.6	8.4	1.8	2.3	60.6
3	76	14.9	0.8	15.7	6.2	3.2	0.4	8.3	6.6	18.5	0.2	trace	0.4	12.4	13.7	2.5	6.9	84.3

Table 2. Overview of yields of products from the photolysis of pentamethylbenzene (13) (0.42 mol dm^{-3}) and tetranitromethane (0.84 mol dm^{-3}) in acetonitrile.

t/h	Conversion (%)	Yield (%)											Total aromatics
		(20)	(21)	(22)	(23)	(25)	(26)	(27)	(29)	(30)	(31)	(32)	
20 °C													
0.5	28	3.1	1.3	—	6.3	2.9	75.6	—	1.6	0.7	3.4	1.1	100
1	54	2.7	1.1	—	2.8	3.1	78.7	0.1	1.2	0.4	3.3	1.3	100
2	69	2.2	1.0	trace	1.4	3.1	81.4	0.1	0.9	0.5	3.1	1.7	100
3	83	1.9	1.3	0.1	1.0	2.8	68.7	0.2	0.8	0.4	2.8	13.2	100
−20 °C													
1	21	5.0	1.5	—	14.8	3.7	46.9	—	0.7	1.2	7.0	10.4	100
2	36	2.8	0.4	0.1	6.1	6.1	58.0	—	0.4	0.8	8.0	9.1	100
3	45	2.4	0.2	0.1	3.4	7.2	67.4	0.3	0.2	0.3	7.9	5.0	100

Table 3. Overview of yields of products from the photolysis of pentamethylbenzene (13) (0.42 mol dm^{-3}) and tetranitromethane (0.84 mol dm^{-3}) in dichloromethane containing trifluoroacetic acid (0.7 M) at 20 °C.

t/h	Conversion (%)	Yield (%)											Total aromatics
		(20)	(21)	(22)	(23)	(25)	(26)	(27)	(29)	(30)	(31)	(32)	
0.5	7	26.0	6.2	5.1	24.3	0.7	21.8	—	0.5	0.5	0.6	1.4	100
1	11	24.0	5.7	8.0	28.4	0.6	21.6	—	0.7	0.8	0.7	1.2	100
2	17	20.9	5.0	10.2	30.0	0.6	19.0	0.6	0.8	1.2	0.9	1.8	100
3	26	19.6	4.7	8.9	31.4	0.6	18.3	1.4	1.0	1.1	1.2	1.7	100

molecular formular (mass spectra) and a consideration of their NMR spectra. In each case the connectivity was established from the results of nuclear Overhauser experiments, with confirmation of the assignment of chemical shifts by heteronuclear correlation spectra (HMBC, HMQC).

Table 4. Overview of yields of products from the reaction of pentamethylbenzene (**13**) (0.42 mol dm^{-3}) in dichloromethane saturated with nitrogen dioxide at 20 °C.

| t/h	Conversion (%)	Yield (%)									Total aromatics
		(22)	**(23)**	**(25)**	**(26)**	**(27)**	**(29)**	**(30)**	**(31)**	**(32)**	
In the dark											
0.5	31	—	1.1	2.2	33.9	1.5	0.3	0.1	14.4	44.5	100
1	42	—	1.2	2.6	34.6	1.6	0.4	0.2	13.7	43.9	100
2	47	trace	0.8	2.0	36.5	2.2	0.8	0.4	13.7	41.3	100
3	53	0.1	0.9	2.2	38.6	2.3	1.2	0.6	13.6	39.1	100
Irradiation with filtered light ($\lambda_{cut-off}$ 435 nm)											
0.5	38	—	1.0	1.9	27.3	1.5	0.6	0.2	14.3	50.0	100
1	51	—	0.9	2.1	28.4	1.6	0.7	0.3	14.2	50.3	100
2	68	trace	0.7	1.7	31.4	1.7	0.4	0.2	13.7	48.3	100
3	76	0.1	0.6	1.9	31.9	2.0	0.7	0.3	13.0	47.5	100
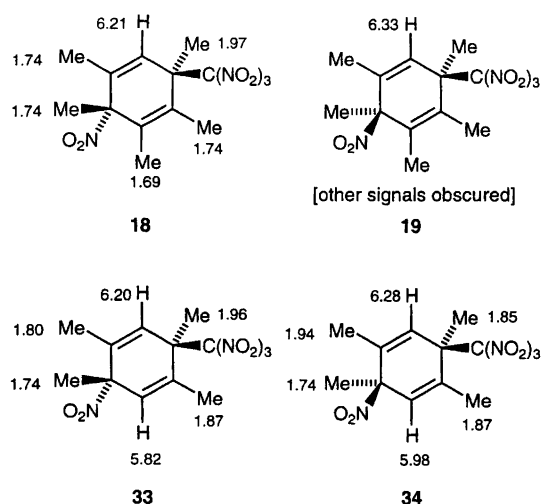
Fig. 1. ^{1}H NMR spectroscopic data for nitro–trinitromethyl adducts **18, 19, 33** and **34**.

The structures of the related 2,3,4,6-tetramethylphenyl-nitromethane (**25**) and 2,3,4,6-tetramethylbenzyl alcohol (**30**) were also established from their mass spectra, NMR data (including the results of nuclear Overhauser experiments) and heteronuclear correlation spectra (HMBC, HMQC) (Experimental).

The remaining compounds **22–24** and **26–29** were identified by comparison with authentic materials. Four compounds, the labile isomeric benzyl nitrates **31** and **32**, and benzyl nitrites **35** and **36**, were apparently hydrolysed on the silica gel plate and augmented the yields of the isomeric benzyl alcohols **29** and **30**. Compounds **31** and **32** were identified in the reaction mixture from their characteristic ^{1}H NMR resonances for the CH$_2$–O–NO$_2$ function,[9] and the benzyl nitrites similarly from the broad singlets for the CH$_2$–O–NO function.[7]

Photochemistry in acetonitrile. Photolysis of the CT complex of **13** and tetranitromethane in acetonitrile at either
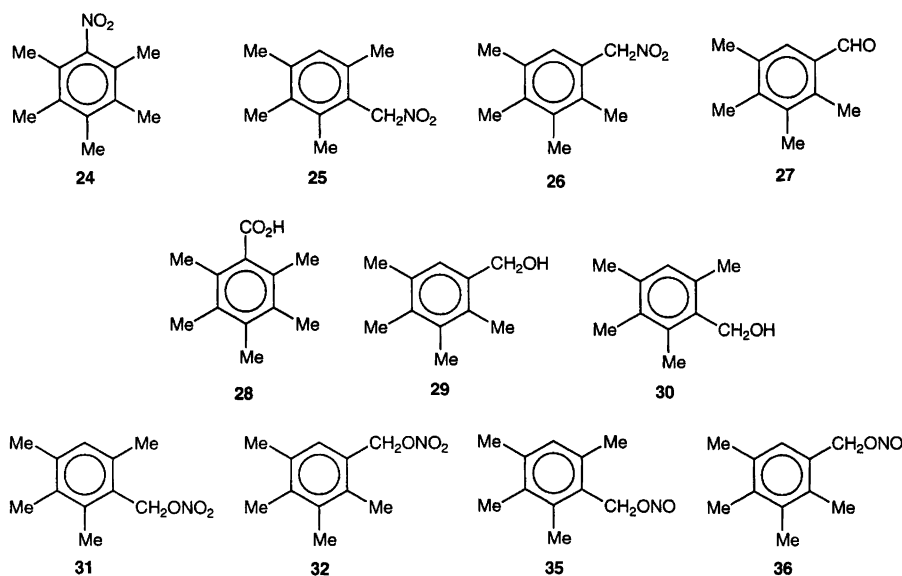
20 or $-20\,^{\circ}\mathrm{C}$ yielded a broadly similar pattern of products (Table 2). Worthy of comment is the higher yield of 2,3,4,5-tetramethylphenylnitromethane **26** in acetonitrile solution, and the absence of any traces of adducts **18** and **19** even at $-20\,^{\circ}\mathrm{C}$.

Photochemistry in dichloromethane containing trifluoroacetic acid ($0.7\ mol\ dm^{-3}$). Photolysis of the CT complex of **13** and tetranitromethane in dichloromethane containing trifluoroacetic acid $(0.7\ \mathrm{mol}\ \mathrm{dm}^{-3})$ at $20\,^{\circ}\mathrm{C}$ for 3 h gave a low conversion (ca. 26%) into a mixture of products **20–23, 25–27** and **29–32** (Table 3). In this reaction the yields of the diphenylmethanes **22** and **23** were higher than was found for reaction in pure dichloromethane, and correspondingly the yields of the phenylnitromethane **26** and the benzyl nitrate **32** were much reduced. Notable were the essentially unchanged yields of the two $2',2',2'$-trinitroethylbenzene derivatives **20** and **21**.

Photochemistry in $1,1,1,3,3,3$-hexafluoropropan-2-ol (HFP) at $20\,^{\circ}C$. The photolysis of the CT complex of **13** and tetranitromethane in HFP at $20\,^{\circ}\mathrm{C}$, as above, was a slow process, resulting in only a low conversion (ca. 17%) after 3 h. After 24 h the product was shown to consist of a mixture of predominantly 2,3,4,5,6-pentamethylnitrobenzene **(24)** (68%), 2,3,4,5-tetramethyl-1-($2',2',2'$-trinitroethyl)benzene **(21)** (8%), 2,3,4,5-tetramethylphenylnitromethane **(26)** (11%), and minor amounts of compounds **20, 23, 25–27, 29** and **30** (total 8%).

*Reactions of **13** with nitrogen dioxide in dichloromethane at $20\,^{\circ}C$.* A solution of **13** $(0.42\ \mathrm{mol}\ \mathrm{dm}^{-3})$ in dichloromethane saturated with nitrogen dioxide was stored in the dark at $20\,^{\circ}\mathrm{C}$. A similar solution was irradiated with filtered light ($\lambda_{\mathrm{cut\text{-}off}}$ 435 nm) also at $20\,^{\circ}\mathrm{C}$. Aliquots were removed from each solution at appropriate time intervals, and after work-up (Experimental) the product composition was determined by $^{1}\mathrm{H}$ NMR spectral analysis (Table 4). The products formed after 3 h for the two reactions were shown to be similar, viz. 2,3,4,5-tetramethylphenylnitromethane **(26)** (dark, 39%; light, 32%), the benzyl nitrates **31** (dark, 14%; light, 13%) and **32** (dark, 39%; light, 48%), and small amounts of compounds **22, 23, 25, 27, 29** and **30**.

Eliminative rearrangement of trans-$1,2,3,4,6$-pentamethyl-3-nitro-6-trinitromethylcyclohexa-1,4-diene **(18)** *in $[^{2}H_{2}]$dichloromethane at $22\,^{\circ}C$.* A solution of **18** in $[^{2}\mathrm{H}_{2}]$dichloromethane was stored in the dark at $22\,^{\circ}\mathrm{C}$ and its $^{1}\mathrm{H}$ NMR spectrum monitored at appropriate time intervals. The rearrangement of the adduct **18** was rapid (ca. 26% after 2 min), including the establishment of equilibrium between the epimeric adducts **18** and **19** during that period, the ratio of **18**:**19** being ca. 9. The rate constants of disappearance of **18** and **19** were the same, 0.074(3) and 0.067(6) min^{-1}, respectively, and those of the appearance of products **21, 26** and **(32 + 35)** approximately the same [0.088(7), 0.044(7) and 0.057(6)

min^{-1}]. The rearrangement was complete in 1 h (Fig. 2) to give 2,3,4,5-tetramethyl-1-($2',2',2'$-trinitroethyl)benzene **(21)** (11%), 2,3,4,5-tetramethylphenylnitromethane **(26)** (49%), 2,3,4,5-tetramethylbenzyl nitrate **(32)** (9%) and 2,3,4,5-tetramethylbenzyl nitrite **(35)** (26%).

*EPR spectroscopy of pentamethylbenzene (**13**) in the presence of tetranitromethane.* The radical cation of **13** is a reactive species, which under the conditions of the usual methods of radical cation generation partly undergoes a characteristic transformation into the persistent 1,2,3,4,5,6,7,8-octamethylanthracene radical cation $(\mathrm{OMA}^{\bullet+})$.[10,11] $\mathrm{OMA}^{\bullet+}$ is very light-sensitive,[12] and **13**$^{\bullet+}$ can therefore be observed during photo-oxidation of **13** by $\mathrm{Tl}^{\mathrm{III}}$ trifluoroacetate in trifluoroacetic acid at $-15\,^{\circ}\mathrm{C}$. When the irradiation is discontinued, the EPR spectrum of $\mathrm{OMA}^{\bullet+}$ appears strongly within a few min.

We have previously[13] shown that the photolysis $(\lambda > 430\ \mathrm{nm})$ of tetranitromethane and **13** gives intense spectra of $\mathrm{OMA}^{\bullet+}$ in dichloromethane–trifluoroacetic acid $(0.8\ \mathrm{mol}\ \mathrm{dm}^{-3})$ at low temperatures, $-(40\text{–}60)\,^{\circ}\mathrm{C}$, and in HFP or HFP–trifluoroacetic acid $(0.4\ \mathrm{mol}\ \mathrm{dm}^{-3})$ at $22\,^{\circ}\mathrm{C}$, immediately after switching off the light source. No spectrum of **13**$^{\bullet+}$ was seen under these conditions, signifying that its reaction with trinitromethanide ion and/or NO_2 must be too fast for accumulation of **13**$^{\bullet+}$.

(B) Reactions of hexamethylbenzene (**14**)

*Photochemistry in dichloromethane at $-20\,^{\circ}C$ and the identification of aromatic products **37–45**.* A solution of **14** $(0.39\ \mathrm{mol}\ \mathrm{dm}^{-3})$ and tetranitromethane $(0.78\ \mathrm{mol}\ \mathrm{dm}^{-3})$ in dichloromethane was irradiated at $-20\,^{\circ}\mathrm{C}$. The composition of the mixture was monitored by withdrawing samples for NMR spectral analysis (Table 5). The final solution (after 3 h) after work-up contained pentamethyl-($2',2',2'$-trinitroethyl)benzene **(37)** (10%), pentamethylbenzyl nitrite **(38)** (6%), pentamethylbenzyl nitrate **(39)** (42%), pentamethylphenylnitromethane **(40)** (40%), and small amounts of compounds **41–45**. The components of this mixture were separated by HPLC on a cyanopropyl column using hexane–dichloromethane mixtures as the eluting solvents. The majority of the products (**37–41, 43** and **45**) were identified by comparison of their spectroscopic data with those for authentic material.

The small amount of 3,4,5,6-tetramethyl-2-nitromethylbenzyl nitrate **(42)** was identified from its spectroscopic data. The molecular formula was given by the mass spectrum, the functionality was indicated by the infrared spectrum (1628, 1279, 858 cm^{-1}, nitrate ester; 1541 cm^{-1}, nitro), and the connectivity was established from the results of nuclear Overhauser experiments.

Similarly, the structure of 3,4,5,6-tetramethyl-2-nitromethylbenzyl alcohol **(44)** was established from its spectroscopic data. The functionality was indicated

Table 5. Overview of yields of products from the photolysis of hexamethylbenzene (14) (0.39 mol dm⁻³) and tetranitromethane (0.78 mol dm⁻³) in dichloromethane.

t/h	Yield (%) (37)	(38)	(39)	(40)	(41)	(42)	(43)	(44)	(45)	(46)	Unidentified aromatics
20 °C											
1	18.6	3.3	33.4	32.0	—	—	trace	—	—	trace	12.7
3	17.1	9.7	34.3	32.7	—	0.4	0.9	—	—	0.8	4.1
5	15.7	8.1	31.3	32.1	trace	1.6	2.5	trace	trace	1.9	6.8
−20 °C[a]											
1	12.6	1.4	25.0	51.7	—	trace	0.1	—	—	—	9.2
3	12.4	4.5	25.0	56.4	—	0.2	0.8	—	—	—	0.7
5	10.4	5.7	37.0	44.5	trace	0.4	0.9	—	—	—	1.1
8	9.8	5.9	41.8	39.6	0.2	0.8	1.5	trace	trace	—	0.4

[a] Some substrate remained undissolved throughout the reaction.

Table 6. Overview of yields of products from the photolysis of hexamethylbenzene (14) (0.39 mol dm⁻³) and tetranitromethane (0.78 mol dm⁻³) in acetonitrile at 20 °C.[a]

t/h	Yield (%) (37)	(38)	(39)	(40)	(41)	(42)	(43)	(44)	(45)	(47)	(48)	(49)	Unidentified aromatics
1	9.1	trace	30.6	52.9	0.4	0.8	0.8	0.5	—	trace	—	3.8	1.1
3	6.5	0.4	28.1	51.4	0.3	1.0	3.4	0.2	—	0.5	trace	4.0	4.2
5	8.6	0.1	28.0	47.0	0.7	1.8	4.0	0.9	—	0.9	0.1	3.3	4.6
8	8.7	1.0	20.9	40.4	0.5	3.0	10.4	0.7	trace	2.7	0.4	4.0	7.4

[a] Some substrate remained undissolved until a reaction time of 7 h.

Table 7. Overview of yields of products from the photolysis of hexamethylbenzene (14) (0.39 mol dm⁻³) and tetranitromethane (0.78 mol dm⁻³) in 1,1,1,3,3,3-hexafluoropropan-2-ol at 20 °C.[a]

t/h	Yield (%) (37)	(39)	(40)	(41)	(45)	Unidentified aromatics
1	47.6	11.4	21.6	—	8.7	10.7
3	49.9	7.9	20.6	—	8.3	13.3
5	51.8	6.2	19.8	—	7.5	14.7
8	55.9	5.5	19.7	trace	5.9	13.0
24	67.0	—	11.4	2.7	4.8	14.1

[a] Some substrate remained undissolved for the first 1 h of the reaction.

Fig. 2. Kinetics of the eliminative rearrangement of nitro-trinitromethyl adduct 18 in [²H₂]dichloromethane at 22 °C. Empty squares, adduct 18; filled squares, adduct 19; empty triangles, 21; filled triangles, 26; circles, 32 + 35. The curves represent the best-fitting exponentials, with rate constants given in the text.

from the infrared spectrum (3383 cm⁻¹, OH; 1551 cm⁻¹, nitro), the connectivity determined from the results of nuclear Overhauser experiments, and the NMR assignments confirmed by heteronuclear correlation spectra (HMBC, HMQC).

Photochemistry in acetonitrile at 20 °C and the identification of aromatic products 47–49. A solution of 14 (0.39 mol dm⁻³) and tetranitromethane (0.78 mol dm⁻³) in dichloromethane was irradiated at 20 °C, as above, for 8 h to give a mixture of pentamethyl-(2′,2′,2′-trinitroethyl)benzene (37) (9%), pentamethylbenzyl
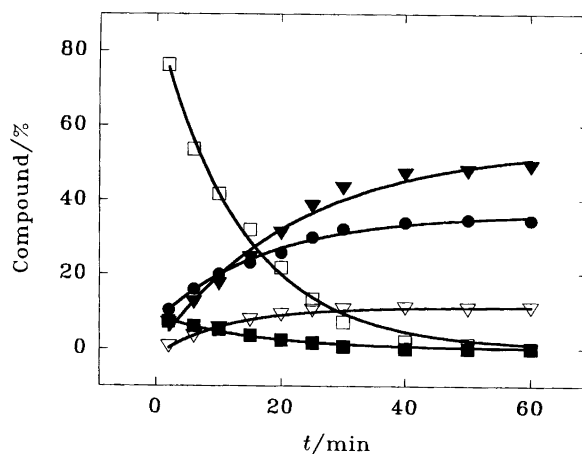
nitrate (39) (21%), pentamethylphenylnitromethane (40) (40%), 1,2-bis(nitromethyl)-3,4,5,6-tetramethylbenzene (43) (10%), and small amounts of compounds 38, 41, 42, 44, 45 and 47–49 (Table 6). This mixture was separated into its components by HPLC and gave the additional compounds 47–49. Pentamethylbenzyl acetate

(48) was identified by comparison with authentic material.[14]

Compounds 47 and 49, which were isolated only in low yield, were identified from their spectroscopic data as N-nitroso-N-(pentamethylbenzyl)acetamide and the parent compound N-(pentamethylbenzyl)acetamide respectively. The latter (49) gave ^{1}H NMR spectral data essentially identical with literature data,[15] and was further characterized by its infrared spectrum (3304, 1643 cm^{-1}, N-monosubstituted amide) and ^{13}C NMR resonances for the CH$_2$ (δ 39.6), C=O (δ 170.8) functions. The connectivity was confirmed from the results of nuclear Overhauser experiments (Experimental), and the NMR assignments by long-range reverse detected heteronuclear correlation spectra (HMBC, HMQC).

The structure of N-nitroso-N-(pentamethylbenzyl)acetamide (47) is supported by its mass spectrum, which includes a M$^+$-NO fragment, and its other spectroscopic data. The presence of the N-nitroso-disubstituted amide functionality followed from its infrared spectrum, which lacked the absorptions at 3304 and 1643 cm^{-1} found for the N-monosubstituted amide 49, but exhibited an absorption at 1719 cm^{-1}; such a shift from 1643 to 1719 cm^{-1} is characteristic for the carbonyl stretching frequency on the introduction of an electron-withdrawing substituent into a N-monosubstituted amide.[16] For this compound 47 the ^{13}C NMR resonances for the CH$_2$ and C=O atoms appeared at δ 39.7 and 174.5, respectively.

Photochemistry in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) at 20 °C. The photolysis of the CT complex of 14 and tetranitromethane in HFP at 20 °C, as above, was a slow process. After 24 h the product was shown to consist of a mixture of predominantly 2,3,4,5,6-pentamethyl-1-(2′,2′,2′-trinitroethyl)benzene (37) (67%), and 2,3,4,5,6-pentamethylphenylnitro-

methane (40) (11%), with minor amounts of compounds 41 (3%) and 2,3,4,5,6-pentamethylbenzyl alcohol (45) (5%), and unidentified aromatic compounds (total 14%) (Table 7).

Reactions of hexamethylbenzene (14) with nitrogen dioxide in dichloromethane at 20 °C. A solution of 14 (0.39 mol dm^{-3}) in dichloromethane saturated with nitrogen dioxide was stored in the dark at 20 °C. A similar solution was irradiated with filtered light ($\lambda_{cut-off}$ 435 nm) also at 20 °C. Aliquots were removed from each solution at appropriate time intervals and after work-up (Experimental) the product composition was determined by ^{1}H NMR spectral analysis (Table 8). The products formed after 8 h for the two reactions were shown to be similar, viz. 2,3,4,5,6-pentamethylbenzyl nitrate (39) (dark, 50%; light, 56%), 2,3,4,5,6-pentamethylphenylnitromethane 40 (dark, 40%; light, 35%) and a small amount of 2,3,4,5,6-pentamethylbenzyl nitrite (38) (dark, 7%; light, 4%).

Reactions of hexamethylbenzene (14) with nitrogen dioxide in acetonitrile at 20 °C. A solution of hexamethylbenzene (14) (0.39 mol dm^{-3}) in acetonitrile saturated with nitrogen dioxide was stored in the dark at 20 °C. A similar solution was irradiated with filtered light ($\lambda_{cut-off}$ 435 nm) also at 20 °C. Reaction was complete in 1 h, and after work-up (Experimental) the product composition was determined by ^{1}H NMR spectral analysis. The products formed for the two reactions were shown to be similar, viz. 2,3,4,5,6-pentamethylbenzyl nitrate (39) (dark, 19%; light, 13%), 2,3,4,5,6-pentamethylphenylnitromethane (40) (dark, 63%; light, 63%), 1,2-bis(nitromethyl)-3,4,5,6-tetramethylbenzene (43) (dark, 9%; light, 11%), and N-nitrosoacetamide (47) (dark, 4%; light, 2%).
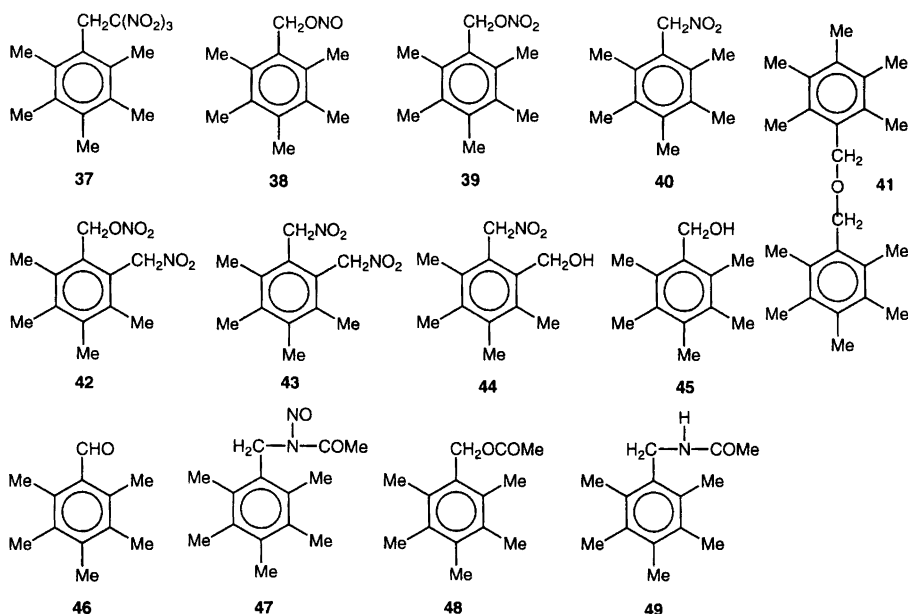
Table 8. Overview of yields of products from the reaction of hexamethylbenzene (14) (0.39 mol dm^{-3}) in dichloromethane saturated with nitrogen dioxide at 20 °C.

t/h	Yield (%)									
	(38)	(39)	(40)	(41)	(42)	(43)	(44)	(45)	(46)	Unidentified aromatics
In the dark										
1	3.9	53.9	41.0	—	—	0.1	—	0.6	0.3	0.2
3	4.9	53.3	40.2	trace	trace	0.1	—	0.6	0.6	0.3
5	6.2	51.3	40.3	0.1	0.1	0.1	—	0.9	0.6	0.4
8	6.7	50.0	40.4	0.1	0.1	0.1	—	1.6	0.6	0.4
Irradiation with filtered light ($\lambda_{cut-off}$ 435 nm)										
1	2.9	57.8	38.0	trace	trace	0.1	—	0.4	0.6	0.2
3	3.1	58.1	36.2	0.2	0.1	0.2	—	0.8	0.8	0.5
5	3.3	57.9	35.0	0.5	0.2	0.3	—	0.8	1.6	0.4
8	3.4	56.4	35.3	0.4	0.5	1.0	trace	trace	2.0	1.0

EPR spectroscopy of hexamethylbenzene (14) in the presence of tetranitromethane. The radical cation of **14** is a reactive species,[12,13] which could not be observed upon irradiation of solutions of **14** and tetranitromethane in dichloromethane–trifluoroacetic acid (0.8 mol dm^{-3}) at −60 °C, nor was it observable in HFP at 22 °C. In HFP–trifluoroacetic acid (0.4 mol dm^{-3}) a very weak signal of **14**·$^{+}$ built up upon irradiation at 22 °C. At 0 °C, a stronger signal was seen ($a^{H} = 0.66$ mT, a^{H} in TFA 0.651 mT[17]) under these conditions.

The use of a stronger acid in HFP (methanesulfonic acid, 0.4 mol dm^{-3}) at 22 °C led to the development of a weak OMA·$^{+}$ spectrum. A control experiment showed that OMA by itself in HFP at 22 °C was thermally oxidized to OMA·$^{+}$.
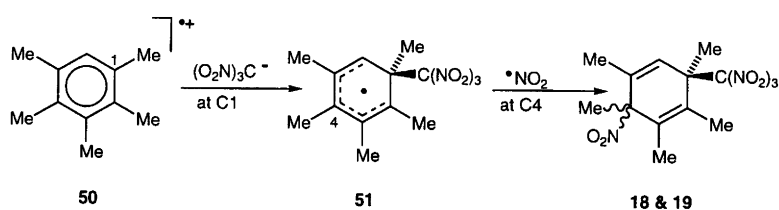
Discussion

The formation and eliminative rearrangement of nitro–trinitromethyl adducts 18 and 19 in the photolysis of the charge-transfer complex of pentamethylbenzene 13 and tetranitromethane. The nitro–trinitromethyl adducts **18** and **19** formed in the photolysis of the CT complex of **13** and tetranitromethane arise by initial attack of trinitromethanide ion *ipso* to one of the flanking methyl groups in the radical cation **50** to give the delocalized carbon radical **51** (Scheme 4). Radical coupling of the delocalized carbon radical **51** with nitrogen dioxide at C4 with C–N bond formation would then give the nitro–trinitromethyl adducts **18** and **19**. Adducts **18** and **19** are notably unstable, being undetectable in photolysis reac-

tions in dichloromethane solution of the charge-transfer complex of pentamethylbenzene **13** and tetranitromethane at 20 °C, transiently detectable at −20 °C, and still clearly labile during photolyses even at −50 or −78 °C. These observations reflect a far greater lability for the pentamethyl adducts **18** and **19** than for the tetramethyl adducts **33** and **34** (Fig. 1), a point which will be referred to again below in the discussion of the photolysis of the CT complex of **14** and tetranitromethane.

In accord with the discussion above, nitro–trinitromethyl adduct **18** underwent a rapid eliminative rearrangement in [^{2}H$_2$]dichloromethane (Fig. 2) at 22 °C to give 2,3,4,5-tetramethyl-1-(2′,2′,2′-trinitroethyl)benzene (**21**), 2,3,4,5-tetramethylphenylnitromethane (**26**), 2,3,4,5-tetramethylbenzyl nitrate (**32**) and 2,3,4,5-tetramethylbenzyl nitrite (**35**), all products isolated from the photolysis reactions of the CT complex of **13** and tetranitromethane. Although not established with certainty, it appears that on dissolution in [^{2}H$_2$]dichloromethane the *trans*-adduct **18** epimerized to give an equilibrium mixture with the *cis*-adduct **19** within 2 min (**18**:**19**≈9), similarly but very much more rapidly than that seen for nitro–trinitromethyl adducts **52** and **53** in the 1,4-dimethylnaphthalene series.[18] Subsequently this equilibrium mixture of adducts **18** and **19** rearranged to yield the products, above.

What are the implications of this marked lability of nitro–trinitromethyl adducts **18** and **19** for the mode of formation of the non-adduct products from the photolysis of the CT complex of **13** and tetranitromethane? From an inspection of the yields after 1 and 3 h of

50   **51**   **18 & 19**

Scheme 4

52 53

54 55
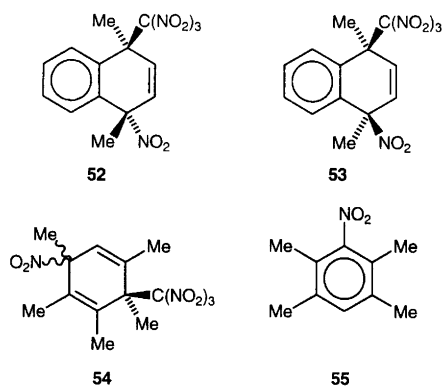
adducts **18** and **19**, and other products **21, 26, 32** and **36**, for the photolysis reactions at -50 and $-78\,^\circ$C it appears likely that products **21, 26, 32** and **36** are formed largely if not exclusively by rearrangement of nitro–trinitromethyl adducts **18** and **19**.

On the reasonable assumption that the 2,3,4,5-tetramethylbenzyl derivatives **21, 26, 32** and **36** are formed by rearrangement of adducts **18** and **19** during the photolysis of the charge-transfer complex of pentamethylbenzene **13** and tetranitromethane, what then is the origin of the 2,3,4,6-tetramethylbenzyl derivatives **20, 25, 31** and **35**? An attractive postulate would be analogous rearrangement of the 1,2,3,4,6-penta-methyl-3-nitro-6-trinitromethylcyclohexa-1,4-dienes **54**. Certainly the steric compression in the region of the trinitromethyl group would be expected to render this type of nitro–trinitromethyl adduct **54** highly susceptible to rearrangement initiated by cleavage of the C–C(NO$_2$)$_3$ bond.

The photolysis of the CT complex of **13** *and tetranitromethane either in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) or in dichloromethane containing trifluoroacetic acid (TFA, 0.7 M).* Under these reaction conditions the reaction of trinitromethanide ion with the radical cation of pentamethylbenzene **(50)** would be expected to be at least partially suppressed by the solvent (HFP)[19] or by protonation (TFA).[20] In the event, both reactions were slow, resulting in low conversion of substrate into products after the normal reaction time of 3 h (HFP, 17%; TFA present, 26%).

Notable in the photolysis reaction in HFP was the formation of a significant yield of 2,3,4,5,6-pentamethylnitrobenzene **(24)** (68%). This is analogous to the formation of 2,3,5,6-tetramethylnitrobenzene **(55)** on photolysis of the charge-transfer complex of 1,2,4,5-tetramethylbenzene **(16)** and tetranitromethane in HFP, a reaction seen as HFP-promoted nitrosation of the aromatic substrate followed by oxidation of the nitroso compound so formed.[1]

Results of EPR spectroscopic examination of the photolysis of pentamethylbenzene **13** *and tetranitromethane.* The

protonation of trinitromethanide ion in the triad of eqn. (1) has been shown to lead to complete or almost complete elimination of the addition pathway.[20] The alternative process, coupling between ArH$^{\cdot+}$ and NO$_2$, then can occur, but since it is slower than the ArH$^{\cdot+}$-trinitromethanide reaction, the radical cation often will accumulate and be observed by its EPR spectrum. In some cases the primary radical cations ArH$^{\cdot+}$ are too reactive to be observed but undergo fast further transformations, so that secondary, more stable radical cations are formed. One such further reaction is dehydrodimerization, for example of methylated naphthalenes to their corresponding 1,1'-binaphthalenes.[21] In the case of pentamethylbenzene **(13)**, the radical cation is easily converted into the radical cation of 1,2,3,4,5,6,7,8-octamethylanthracene (OMA$^{\cdot+}$) which can be used as a marker for **13**$^{\cdot+}$.

Thus the fact that **13** and tetranitromethane upon irradiation by light of $\lambda > 430$ nm in dichloromethane at $-70\,^\circ$C or HFP at 22 $^\circ$C, gave rise to the EPR spectrum of neither **13**$^{\cdot+}$ nor that of OMA$^{\cdot+}$ shows that **13**$^{\cdot+}$ must be consumed in fast reactions with trinitromethanide and/or NO$_2$. OMA in itself gave an EPR spectrum under these conditions and could not have been formed from **13**$^{\cdot+}$.

In contrast, when trifluoroacetic acid was present in these experiments, a strong signal of OMA$^{\cdot+}$ appeared, demonstrating that **13**$^{\cdot+}$ must have had a long enough lifetime to make the pathway to OMA$^{\cdot+}$ competitive. Most likely, the enhancement of the lifetime is caused by the elimination of the **13**$^{\cdot+}$-trinitromethanide pathway. It should be noted that the **13**$^{\cdot+}\rightarrow$OMA$^{\cdot+}$ pathway is only a minor one, since no OMA or products thereof were observed in the preparative photochemical experiments in dichloromethane–trifluoroacetic acid.

The photolysis of the CT complex of hexamethylbenzene **(14)** *and tetranitromethane.* The study of these photolytic reactions was hampered considerably by the low solubility of **14**, particularly at temperatures lower than ambient. Consequently no serious attempt could be made at detecting the presence of labile adducts in the reaction mixtures. The reactions which were possible in dichloromethane or acetonitrile resulted in the formation of substantial amounts of pentamethylbenzyl nitrate **(39)** and pentamethylphenylnitromethane **(40)**, with lesser amounts of pentamethyl-(2',2',2'-trinitroethyl)benzene **(37)**. In contrast, in HFP the major product of the slow reaction was **37** (67%).

In the light of the discussion of the photolysis reactions of the CT complex of **13** with tetranitromethane above, it appears possible that the reactions of hexamethylbenzene also proceed via labile nitro–trinitromethyl adducts, which on rearrangement yield the observed products. If the progression of increased lability of adducts with increasing methyl substitution evident in the tetramethyl adducts **33** and **34**, and the pentamethyl adducts **18** and **19** extends to adducts from hexamethylbenzene **14**, these

1130

adducts would be extremely unstable. Unfortunately there is no direct experimental approach to testing this hypothesis, but it may be significant that the product 37 is formed in high yield in the photolysis reaction in HFP, in contrast to the reactions in dichloromethane or acetonitrile.

The reactions of pentamethylbenzene 13 and hexamethylbenzene 14 with excess nitrogen dioxide in dichloromethane at 20 °C. These reactions gave essentially the same product composition either in the dark or on irradiation with filtered light ($\lambda_{cut-off}$ 435 nm). For 13, 2,3,4,5-tetramethylphenylnitromethane (26) (ca. 35%) and two isomeric benzyl nitrates 31 and 32 (total ca. 56%) were formed, while 14 gave pentamethylphenylnitromethane (40) (ca. 38%) and pentamethylbenzyl nitrate (39) (ca. 54%).

The reactions of hexamethylbenzene (14) with excess nitrogen dioxide in acetonitrile at 20 °C. As in dichloromethane, these reactions gave essentially the same product composition either in the dark or on irradiation with filtered light ($\lambda_{cut-off}$ 435 nm). Apart from pentamethylbenzyl nitrate 39 (ca. 16%) and the mono- and bisnitromethyl compounds 40 (ca. 63%) and 43 (ca. 10%), the N-nitrosoacetamide 47 (ca. 3%) and its precursor 49 (ca. 1%) were formed. It is clear therefore that neither tetranitromethane nor irradiation is necessary for the formation of the N-nitrosoacetamide 47 or its presumed precursor 49.

Results of EPR spectroscopic examination of the photolysis of hexamethylbenzene (14) and tetranitromethane. The reactivity of 14⁺ is high,[12] and only in HFP–trifluoroacetic acid (0.4 mol dm⁻³) at 22 or 0 °C was it possible to detect 14⁺ from the irradiation of the 14-tetranitromethane CT complex. Again, the disfavouring of the 14⁺-trinitromethanide reaction by protonation of the anion of the triad leads to the predominance of slower reactions, thus allowing for the accumulation of a low concentration of 14⁺.

Experimental

Melting points are uncorrected. Infrared spectra were recorded on a Perkin Elmer 1600 series FTIR spectrometer; ^{1}H 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 and hexamethylbenzene were purchased from Aldrich and pentamethylbenzene from Tokyo Kasei Kogyo. Dichloromethane (AR) and acetonitrile (HiPerSolv) were from BDH and 1,1,1,3,3,3-hexafluoropropan-2-ol from Sigma.

WARNING. While we did not experience any incidents in working with tetranitromethane, it should be

noted that its mixtures with hydrocarbons are detonative within certain concentration limits and that due care should be taken in handling mixtures of tetranitromethane and organic molecules.[22]

General procedure for the photonitration of pentamethylbenzene (13) with tetranitromethane. A solution of 13 (500 mg, 0.42 mol dm⁻³) and tetranitromethane (0.84 mol dm⁻³) in dichloromethane (at 20, −20, −50 or −78 °C) or acetonitrile (20 or −20 °C) was irradiated with filtered light ($\lambda_{cut-off}$ 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 and 2).

Photochemistry in dichloromethane at −78 °C and the identification of adducts 18 and 19. Reaction of 13–tetranitromethane in dichloromethane at −78 °C, as above, for 3 h gave a product which was shown by ^{1}H NMR spectra to be a mixture of adduct 18 (15%), adduct 19 (1%), aromatic compounds 20–32 (total 79%), and unidentified aromatic products (5%) (Table 1). HPLC allowed the separation of the unstable adduct 18, but adduct 19 was not isolated by this means and its identification is only tentative.

Trans- *1,2,3,4,6-pentamethyl-3-nitro-6-trinitromethylcyclohexa-1,4-diene (18),* isolated as an impure (95%) oil. IR: ν_{max} (liquid film) 1616, 1596, 1576, 1550 cm⁻¹. ^{1}H NMR (CDCl₃) δ 1.69 (q, $J_{2-Me,1-Me}$ 1.5 Hz, 2-Me), 1.74 (br s, 1-, 3-, and 4-Me), 1.97 (s, 6-Me), 6.21 (q, $J_{H5,4-Me}$ 1.5 Hz, H5). Results of nuclear Overhauser experiments are given in Table 9. The ^{13}C NMR spectrum was not obtainable because of the instability of adduct 18 in solution.

Cis-*1,2,3,4,6-pentamethyl-3-nitro-6-trinitromethylcyclohexa-1,4-diene (19),* only seen as a minor component in complex mixtures. ^{1}H NMR (CDCl₃) δ 6.33 (q, $J_{H5,4-Me}$ 1.5 Hz, H5); the remainder of the spectrum was obscured by signals due to other compounds.

Photochemistry in dichloromethane at 20 °C and the identification of aromatic products 20–30. Reaction of 13–tetranitromethane in dichloromethane at 20 °C, as above, for 3 h gave a product which was shown by ^{1}H NMR spectra to be a mixture of aromatic compounds 20–32, 35 and 36 (In Table 1, the yields of compounds 24 and 28 could not be assessed individually from ^{1}H NMR spectra because of signal coincidences.) Chromatography on a silica gel Chromatotron plate allowed the separation of compounds 20–30 in the order of elution below, the benzyl nitrates 31 and 32 and benzyl nitrites 35 and 36 being presumably hydrolysed to give the related benzyl alcohols 29 and 30.

2,3,4,6-Tetramethyl-1-(2',2',2'-trinitroethyl)benzene (20) as an oil, which could not be induced to crystallize. (Insufficient for elemental analysis. Found: M^+ 297.0959;

Table 9. Nuclear Overhauser effects for compounds isolated.

Compound	Irradiated at δ (ppm)	Enhancement(s) (%) at δ (ppm)
18	1.74	1.97 (0.9); 6.21 (6.7)
	1.97	1.69 (0.8); 1.74 (0.6); 6.21 (4.2)
	6.21	1.69 (0.8); 1.74 (0.6); 1.97 (0.7)
20	2.10	4.74 (1.9)
	2.16	4.74 (1.5); 6.88 (3.8)
	2.25	6.88 (3.8)
	4.74	2.10 (1.9); 2.16 (1.5)
	6.88	2.16 (0.6); 2.25 (0.6)
21	2.09	4.45 (1.8)
	2.23	6.74 (4.2)
	4.45	2.09 (1.6); 6.74 (5.4)
	6.74	2.23 (0.6); 4.45 (0.7)
25	2.28	6.95 (2.9)
	2.30	5.61 (1.4)
	2.35	5.61 (1.3); 6.95 (2.7)
	5.61	2.30 (1.2); 2.35 (0.8)
	6.95	2.28 (0.4); 2.35 (0.4)
30	2.31	6.92 (2.9)
	2.39	4.76 (1.7)
	2.41	4.76 (1.7); 6.92 (2.8)
	4.76	2.39 (1.4); 2.41 (1.0)
	6.92	2.31 (0.6); 2.41 (0.4)
37	2.12	4.82 (3.6)
	4.82	2.12 (2.1)
38	5.78	2.27 (1.2)
40	2.31	5.67 (2.8)
	5.67	2.31 (1.3)
41	2.19	2.32 (2.1)
	2.32	2.19 (2.0); 4.64 (5.2)
	4.64	2.32 (3.7)
42	2.34	5.72 (1.8)
	2.36	5.70 (2.0)
	5.70	2.36 (1.9)
	5.72	2.34 (2.3)
43	2.37	5.82 (1.9)
	5.82	2.37 (2.4)
44	2.30	5.80 (1.6)
	2.39	4.84 (1.5)
	4.84	2.39 (1.5); 5.80 (2.8)
	5.80	2.30 (1.1); 4.84 (2.5)
47	2.17	2.73 (0.7); 4.99 (3.9)
	2.73	2.17 (0.3)
	4.99	2.17 (2.3)
49	2.00	6.03 (2.7)
	2.37	4.46 (4.3); 6.03 (1.0)
	4.46	2.27 (2.4); 6.03 (2.1)
	6.03	2.00 (1.2); 2.27 (0.3); 4.46 (1.1)

$C_{12}H_{15}N_3O_6$ requires 297.0961.) IR: v_{max} (liquid film) 1616, 1601, 1580 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 2.10 (s, 2-Me), 2.14 (s, 3-Me), 2.16 (s, 6-Me), 2.25 (s, 4-Me), 4.74 [br s, CH$_2$C(NO$_2$)$_3$], 6.88 (s, H5). Nuclear Overhauser experiments, see Table 9. ^{13}C NMR (CDCl$_3$) δ 16.1 (3-Me), 16.7 (2-Me), 20.1 (6-Me), 20.7 (4-Me), 34.8 [CH$_2$C(NO$_2$)$_3$], 123.5 (C1), 130.6 (C5), 134.2 (C3), 135.1 (C6), 136.9 (C2), 137.8 (C4), resonance for C(NO$_2$)$_3$ not observed. The above assignments were confirmed by reverse detected heteronuclear correlation spectra (HMBC, HMQC).

2,3,4,5-Tetramethyl-1-(2',2',2'-trinitroethyl)benzene (21) as an oil, which could not be induced to crystallize. (Insufficient for elemental analysis. Found: M^+ 297.0960. $C_{12}H_{15}N_3O_6$ requires 297.0961.) IR: v_{max} (liquid film) 1609, 1576 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 2.09 (s, 2-Me), 2.19, 2.20 (both s, 3-Me, 4-Me), 2.23 (s, 5-Me), 4.45 [br s, CH$_2$C(NO$_2$)$_3$], 6.74 (s, H6). Nuclear Overhauser experiments, see Table 9. ^{13}C NMR (CDCl$_3$) δ 16.1 (2-Me), 16.2 and 16.7 (3-Me, 4-Me), 20.7 (5-Me), 37.2 [CH$_2$C(NO$_2$)$_3$], 121.9 (C1), 128.6 (C6), 134.2 (C2), 134.8 (C5), 136.6 (C3), 136.9 (C4), resonance for C(NO$_2$)$_3$ not observed. The above assignments were confirmed by reverse detected heteronuclear correlation spectra (HMBC, HMQC).

2,3,4,5,6,2',3',4',6'-Nonamethyldiphenylmethane (22), identical with an authentic sample.[23]
2,3,4,5,6,2',3',4',5'-Nonamethyldiphenylmethane (23), identical with an authentic sample.[23]
2,3,4,5,6-Pentamethylnitrobenzene (24), identical with an authentic sample.[24]
2,3,4,6-Tetramethylphenylnitromethane (25), as an oil which could not be induced to crystallize. (Insufficient for elemental analysis. Found: M^+ 193.1102. $C_{11}H_{15}NO_2$ requires 193.1103.) IR: v_{max} (liquid film) 1541 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 2.19 (s, 3-Me), 2.28 (s, 4-Me), 2.30 (s, 2-Me), 2.35 (s, 6-Me), 5.61 (s, CH$_2$NO$_2$), 6.95 (s, H5). Nuclear Overhauser experiments, see Table 9. ^{13}C NMR (CDCl$_3$) δ 16.0 (3-Me), 16.2 (2-Me), 19.8 (6-Me), 20.9 (4-Me), 74.4 (CH$_2$NO$_2$), 124.8 (C1), 130.0 (C5), 133.6 (C3), 135.5 (C6), 137.2 (C2), 138.6 (C4). The above assignments were confirmed by reverse detected heteronuclear correlation spectra (HMBC, HMQC).

2,3,4,5-Tetramethylphenylnitromethane (26), identical with an authentic sample.[7]
2,3,4,5-Tetramethylbenzaldehyde (27), identical with an authentic sample.[9]
2,3,4,5,6-Pentamethylbenzoic acid (28), identical with an authentic sample.
2,3,4,5-Tetramethylbenzyl alcohol (29), identical with an authentic sample.[9]
2,3,4,6-Tetramethylbenzyl alcohol (30), isolated only in admixture with 2,3,4,5-tetramethylbenzyl alcohol (29). ^{1}H NMR (CDCl$_3$) δ 2.23 (s, 3-Me), 2.31 (s, 4-Me), 2.39 (s, 2-Me), 2.41 (s, 6-Me), 4.76 (s, CH$_2$OH), 6.92 (s, H5).

Nuclear Overhauser experiments, see Table 9. ^{13}C NMR (CDCl3) δ 15.7 (2-Me and 3-Me), 19.4 (6-Me), 20.7 (4-Me), 59.6 (CH$_2$OH), 129.6 (C5), 133.2 (C3), 133.9 (C6), 134.2 (C1), 136.0 and 136.3 (C2 and C4). The above assignments were confirmed by reverse detected heteronuclear correlation spectra (HMBC, HMQC).

The labile benzyl nitrates 31 and 32 and benzyl nitrites 35 and 36 were identified from the ^{1}H NMR (CDCl$_3$) signal assigned to the CH$_2$–O–X function in each case, where X = NO$_2$ or NO: 31 (δ 5.56,[9] s), 32 (δ 5.42,[9] s), 35 [δ 5.73, br s (cf. Ref. 7)], 36 [δ 5.65, br s (cf. Ref. 7)].

Photochemistry in acetonitrile. Reaction of 13–tetranitromethane in acetonitrile at either 20 or −20 °C for 3 h gave products which were shown by ^{1}H NMR spectra to be mixtures of predominantly 2,3,4,5-tetramethylphenylnitromethane (26) and minor amounts of compounds 20–23, 25, 27 and 29–32.

Photochemistry in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) at 20 °C. Reaction of 13–tetranitromethane in HFP at 20 °C, as above, for 24 h gave a product which was shown by ^{1}H NMR spectra to be a mixture of predominantly 2,3,4,5,6-pentamethylnitrobenzene (24) (68%), 2,3,4,5-tetramethyl-1-(2′,2′,2′-trinitroethyl)benzene (21) (8%), 2,3,4,5-tetramethylphenylnitromethane (26) (11%), and minor amounts of compounds 20, 23, 25–27, 29 and 30 (total 8%). The reaction was slow, only a low conversion (ca. 17%) occurring in 3 h.

Photochemistry in dichloromethane at 20 °C containing trifluoroacetic acid (0.7 M). Reaction of 13–tetranitromethane in dichloromethane containing trifluoroacetic acid (0.7 M) at 20 °C, as above, for 3 h resulted in a low conversion (ca. 26%) into the 2′,2′,2′-trinitroethyl compounds 20 (20%) and 21 (5%), nonamethyldiphenylmethanes 22 (9%) and 23 (31%), 2,3,4,5-tetramethylphenylnitromethane 26 (18%), and minor amounts of compounds 25, 27, 29–32 (total 7%) and unidentified aromatic compounds (total 10%) (Table 3).

Nitration of pentamethylbenzene (13) with nitrogen dioxide in dichloromethane at 20 °C. A solution of 13 (0.42 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 ^{1}H NMR spectral analysis (Table 4). After 3 h the products formed were shown to be predominantly 2,3,4,5-tetramethylphenylnitromethane (26) (39%), the benzyl nitrates 31 (14%) and 32 (39%) small amounts of aromatic compounds 22, 23, 25, 27, 29 and 30 (total 7%), and unidentified aromatic compounds (total 1%).

Photochemical nitration of pentamethylbenzene (13) with nitrogen dioxide in dichloromethane at 20 °C. A solution

of 13 (0.42 mol dm^{-3}) in dichloromethane saturated with nitrogen dioxide was irradiated with filtered light (λ$_{cut-off}$ 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 (Table 4). After 3 h the products formed were shown to be similar to those of the 'dark' reaction above, i.e. predominantly 2,3,4,5-tetramethylphenylnitromethane (26) (32%), the benzyl nitrates 31 (13%) and 32 (48%) and small amounts of aromatic compounds 22, 23, 25, 27, 29 and 30 (total 6%), and unidentified aromatic compounds (total 2%).

Eliminative rearrangement of trans-1,2,3,4,6-pentamethyl-3-nitro-6-trinitromethyl-cyclohexa-1,4-diene (18) in [$^2H_2$]dichloromethane at 22 °C. A solution of adduct 18 in [$^2H_2$]dichloromethane was stored at 22 °C and its ^{1}H NMR spectrum monitored at appropriate time intervals. Already after 2 min significant rearrangement (26%) of the adduct mixture had occurred, and the rearrangement was complete after 1 h (for rate constants, see Fig. 2). At that time the major rearrangement products were 2,3,4,5-tetramethyl-1-(2′,2′,2′-trinitroethyl)benzene (21) (11%), 2,3,4,5-tetramethylphenylnitromethane (26) (49%), 2,3,4,5-tetramethylbenzyl nitrate (32) (9%) and 2,3,4,5-tetramethylbenzyl nitrite (35) (26%).

General procedure for the photonitration of hexamethylbenzene (14) with tetranitromethane. A solution of 14 (500 mg, 0.39 mol dm^{-3}) and tetranitromethane (0.78 mol dm^{-3}) in dichloromethane (at 20 or −20 °C) or acetonitrile (20 °C) was irradiated with filtered light (λ$_{cut-off}$ 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 5 and 6).

Photochemistry in dichloromethane at −20 °C and the identification of aromatic products (37–45). Reaction of 14–tetranitromethane in dichloromethane at −20 °C, as above, for 8 h gave a product which was shown by ^{1}H NMR spectra to be a mixture of pentamethyl(2′,2′,2′-trinitroethyl)benzene (37) (10%), pentamethylbenzyl nitrite (38) (6%), pentamethylbenzyl nitrate (39) (42%), pentamethylphenylnitromethane (40) (40%), and small amounts of compounds 41–45 (Table 4). The components of this mixture were separated by HPLC to give in elution order:

Pentamethyl-(2′,2′,2′-trinitroethyl)benzene (37), identical with authentic material.[7] ^{1}H NMR (CDCl$_3$) δ 2.12 (s, 2-Me, 6-Me), 2.20 (s, 3-Me, 5-Me), 2.24 (s, 4-Me), 4.82 [br s, CH$_2$C(NO$_2$)$_3$]. Nuclear Overhauser experiments, see Table 9. ^{13}C NMR (CDCl$_3$) δ 17.0 (3-Me, 4-Me, 5-Me), 17.1 (2-Me, 6-Me), 35.1 [CH$_2$C(NO$_2$)$_3$], 123.1 (C1), 133.8, 133.9 (C2, C3), 136.6 (C4), resonance for C(NO$_2$)$_3$ not observed. The above assignments were

confirmed by reverse-detected heteronuclear correlation spectra (HMBC, HMQC).

Pentamethylbenzyl nitrite (**38**), identical with authentic material.[7] ^{1}H NMR (CDCl$_3$) δ 2.23 (s, 3-Me, 5-Me), 2.26 (s, 4-Me), 2.27 (s, 2-Me, 6-Me), 5.78 (br s, CH$_2$ONO). Results of nuclear Overhauser experiment are shown in Table 9.

Pentamethylbenzyl nitrate (**39**), identical with authentic material.[7]

Pentamethylphenylnitromethane (**40**), identical with authentic material.[25] ^{1}H NMR (CDCl$_3$) δ 2.25 (s, 3-Me, 5-Me), 2.27 (s, 4-Me), 2.31 (s, 2-Me, 6-Me), 5.67 (s, CH$_2$NO$_2$). Nuclear Overhauser results are shown in Table 9. ^{13}C NMR (CDCl$_3$) δ 16.6 (2-Me, 6-Me), 16.8 (3-Me, 5-Me), 17.2 (4-Me), 74.8 (CH$_2$NO$_2$), 124.6 (C1), 133.2 (C3, C5), 134.1 (C2, C6), 137.3 (C4). The above assignments were confirmed by reverse-detected heteronuclear correlation spectra (HMBC, HMQC).

Bis(pentamethylbenzyl) ether (**41**),[7] m.p. 168 °C (decomp.) (insufficient for elemental analysis. Found: M^+ 338.2603. C$_{24}$H$_{34}$O requires 338.2610). IR: ν_{max} (KBr) 1088, 1042 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 2.19 (s, 3-Me, 5-Me), 2.21 (s, 4-Me), 2.32 (s, 2-Me, 6-Me), 4.64 (s, CH$_2$–O–). For nuclear Overhauser experiments, see Table 9. ^{13}C NMR (CDCl$_3$) δ 16.2 (2-Me, 6-Me), 16.6 (3-Me, 5-Me), 16.9 (4-Me), 67.4 (CH$_2$-O-), 131.6 (C1), 132.3 (C3, C5), 133.4 (C2, C6), 134.7 (C4). The above assignments were confirmed by reverse detected heteronuclear correlation spectra (HMBC, HMQC).

3,4,5,6-Tetramethyl-2-nitromethylbenzyl nitrate (**42**), m.p. 79–82 °C. (Insufficient for elemental analysis. Found: M^+ 268.10545. C$_{12}$H$_{16}$N$_2$O$_5$ requires 268.1059.) IR: ν_{max} (KBr) 1628, 1541, 1279, 858 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 2.29 (s, 4-Me, 5-Me), 2.34 (s, 3-Me), 2.36 (s, 6-Me), 5.70 (s, CH$_2$-ONO$_2$), 5.72 (s, CH$_2$NO$_2$). For nuclear Overhauser experiments, see Table 9. ^{13}C NMR (CDCl$_3$) δ 16.6 (4-Me or 5-Me), 16.7 (6-Me), 17.2 (3-Me), 17.3 (5-Me or 4-Me), 70.1 (CH$_2$ONO$_2$), 74.1 (CH$_2$NO$_2$), 126.4 (C2), 127.2 (C1), 135.4 (C3), 135.8 (C6), 138.4, 138.6 (C4, C5).

1,2-Bis(nitromethyl)-3,4,5,6-tetramethylbenzene (**43**), identical with authentic material.[26] ^{1}H NMR (CDCl$_3$) δ 2.29 (s, 4-Me, 5-Me), 2.37 (s, 3-Me, 6-Me), 5.82 (s, CH$_2$NO$_2$). For nuclear Overhauser experiments, see Table 9.

3,4,5,6-Tetramethyl-2-nitromethylbenzyl alcohol (**44**), as an oil which could not be induced to crystallize (insufficient for elemental analysis. Found: M^+ 223.1203. C$_{12}$H$_{17}$NO$_3$ requires 223.1208). IR: ν_{max} (liquid film) 3383, 1551 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 2.27, 2.28 (s, 4-Me, 5-Me), 2.30 (s, 3-Me), 2.39 (s, 6-Me), 4.84 (s, CH$_2$OH), 5.80 (s, CH$_2$NO$_2$). For nuclear Overhauser experiments, see Table 9. ^{13}C NMR (CDCl$_3$) δ 16.3 (6-Me), 16.4, 17.0, 17.2 (3-Me, 4-Me, 5-Me), 59.8 (CH$_2$OH), 74.5 (CH$_2$NO$_2$), 125.4 (C2), 134.0 (C6), 134.9

(C3), 135.8 (C1), 136.3 (C4), 138.3 (C5). The above assignments were confirmed by reverse-detected heteronuclear correlation spectra (HMBC, HMQC).

Pentamethylbenzyl alcohol (**45**), identical with authentic material.[7] This compound was isolated in higher yield than that present in the mixture prior to HPLC separation, and may be formed by hydrolysis of either/both of the benzyl esters **38** and **39** during chromatography.

Photochemistry in acetonitrile at 20 °C and the identification of aromatic products (**47–49**). Reaction of **14**-tetranitromethane in acetonitrile at 20 °C, as above, for 8 h gave a product which was shown by ^{1}H NMR spectra to be a mixture of compounds **37** (9%), **39** (21%), **40** (40%), **43** (10%), and small amounts of compounds **38**, **41**, **42**, **44**, **45** and **47–49** (Table 5). The components of this mixture were separated by HPLC to give the additional compounds (**47–49**) in elution order:

N-Nitroso-N-(pentamethylbenzyl)acetamide (**47**), as an oil which could not be induced to crystallize. (Insufficient for elemental analysis. Found: M^+ 248.1526. C$_{14}$H$_{20}$N$_2$O$_2$ requires 248.1525. M^+–NO 218.1534. C$_{14}$H$_{20}$NO requires 218.1545.) IR: ν_{max} (liquid film) 1719, 1504, 1121 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 2.17 (s, 2'-Me, 6'-Me), 2.20 (s, 3'-Me, 5'-Me), 2.21 (s, 4'-Me), 2.73 (s, CH$_3$-C=O), 4.99 (s, CH$_2$). For nuclear Overhauser experiments, see Table 9. ^{13}C NMR (CDCl$_3$) δ 16.7 (2'-Me, 4'-Me, 6'-Me), 16.9 (3'-Me, 5'-Me), 20.3 (CH$_3$-C=O), 39.7 (CH$_2$), 128.3 (C2', C6'), 132.9 (C1', C3', C5'), 134.8 (C4'), 174.5 (CH$_3$-C=O). The above assignments were confirmed by reverse detected heteronuclear correlation spectra (HMBC, HMQC).

Pentamethylbenzyl acetate (**48**), identical with an authentic sample.[14]

N-(Pentamethylbenzyl)acetamide (**49**), identical with an authentic sample.[15] IR: ν_{max} (KBr) 3304, 1643, 1537, 1385 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 2.00 (s, 1-Me), 2.24 (s, 3'-Me, 4'-Me, 5'-Me), 2.27 (s, 2'-Me, 6'-Me), 4.46 (d, $J_{methylene,NH}$ 4.4 Hz, CH$_2$), 6.03 (br s, N–H). For nuclear Overhauser experiments, see Table 9. ^{13}C NMR (CDCl$_3$) δ 16.3 (2'-Me, 6'-Me), 16.7 (3'-Me, 5'-Me), 16.9 (4'-Me), 22.4 (1-Me), 39.6 (CH$_2$), 130.4 (C1'), 132.9, 133.0 (C2', C3', C5', C6'), 135.0 (C4'), 170.8 (C2). The above assignments were confirmed by reverse detected heteronuclear correlation spectra (HMBC, HMQC).

Photochemistry of hexamethylbenzene (**14**) *in 1,1,1,3,3,3-hexafluoro-propan-2-ol (HFP) at 20 °C.* A solution of **14** and tetranitromethane in HFP at 20 °C, as above, after 24 h gave a mixture of 2,3,4,5,6-pentamethyl-1-(2',2',2'-trinitroethyl)benzene **37** (67%) and 2,3,4,5,6-pentamethylphenylnitromethane **40** (11%), with small amounts of the dibenzyl ether **41** (3%), 2,3,4,5,6-pentamethylbenzyl alcohol **45** (5%) and unidentified aromatic compounds (total 14%) (Table 7).

Nitration of hexamethylbenzene (**14**) *with nitrogen dioxide in dichloromethane at 20 °C.* A solution of **14** (0.39 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 ^{1}H NMR spectral analysis (Table 8). After 8 h the products formed were shown to be predominantly 2,3,4,5,6-pentamethylbenzyl nitrate (**39**) (50%) and 2,3,4,5,6-pentamethylphenylnitromethane (**40**) (40%) and a small amount of 2,3,4,5,6-pentamethylbenzyl nitrite (**38**) (7%).

*Photochemical nitration of hexamethylbenzene (**14**) with nitrogen dioxide in dichloromethane at 20 °C.* A solution of **14** (0.39 mol dm^{-3}) in dichloromethane saturated with nitrogen dioxide was irradiated with filtered light of λ>435 nm for 8 h. 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 (Table 8). After 8 h the products formed were shown to be similar to those of the 'dark' reaction, i.e. predominantly 2,3,4,5,6-pentamethylbenzyl nitrate (**39**) (56%) and 2,3,4,5,6-pentamethylphenylnitromethane (**40**) (35%) and a small amount of 2,3,4,5,6-pentamethylbenzyl nitrite (**38**) (4%).

*Nitration of hexamethylbenzene (**14**) with nitrogen dioxide in acetonitrile at 20 °C.* A solution of **14** (0.39 mol dm^{-3}) in acetonitrile saturated with nitrogen dioxide was stored at 20 °C in the dark. After 1 h complete reaction of **14** had occurred, the excess nitrogen dioxide and solvent were removed under reduced pressure at ≤0 °C, and the product was composition determined by ^{1}H NMR spectral analysis. The products formed were shown to be predominantly 2,3,4,5,6-pentamethylbenzyl nitrate (**39**) (19%), 2,3,4,5,6-pentamethylphenylnitromethane (**40**) (63%), 1,2-bis(nitromethyl)-3,4,5,6-tetramethylbenzene (**43**) (9%) and the *N*-nitrosoacetamide (**47**) (4%).

*Photochemical nitration of hexamethylbenzene (**14**) with nitrogen dioxide in acetonitrile at 20 °C.* A solution of **14** (0.39 mol dm^{-3}) in acetonitrile saturated with nitrogen dioxide was irradiated with filtered light ($λ_{cut-off}$ <435 nm). After 1 h complete reaction of **14** had occurred, the excess nitrogen dioxide and solvent were removed under reduced pressure at ≤0 °C, and the product composition was determined by ^{1}H NMR spectral analysis. The products formed were shown to be predominantly 2,3,4,5,6-pentamethylbenzyl nitrate (**39**) (13%), 2,3,4,5,6-pentamethylphenylnitromethane (**40**) (63%), 1,2-bis(nitromethyl)-3,4,5,6-tetramethylbenzene (**43**) (11%) and the *N*-nitrosoacetamide (**47**) (2%).

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 a 50 W high-pressure Hg lamp from Bruker (ER 202) and the filter was from Schott, Germany

(cut-off at 430 nm). For experimetal details, see Refs. 1, 13 and 20.

References

1. Butts, C. P., Eberson, L., Fulton, K. L., Hartshorn, M. P., Robinson, W. T. and Timmerman-Vaughan, D. J. *Acta Chem. Scand. Part XXXIII.* (A2891).
2. Eberson, L., Hartshorn, M. P. and Radner, F. *Acta Chem. Scand. 48* (1994) 937; and references cited therein.
3. Butts, C. P., Eberson, L., Hartshorn, M. P., Robinson, W. T., Timmerman-Vaughan, D. J. and Young, D. A. W. *Acta Chem. Scand. 50* (1996) 29.
4. Butts, C. P., Eberson, L., Hartshorn, M. P. and Robinson, W. T. *Aust. J. Chem. 48* (1995) 1989.
5. Butts, C. P., Calvert, J. L., Eberson, L., Hartshorn, M. P., Radner, F. and Robinson, W. T. *J. Chem. Soc., Perkin Trans. 2* (1994) 1485.
6. Butts, C. P., Eberson, L., Fulton, K. L., Hartshorn, M. P., Jamieson, G. B. and Robinson, W. T. *Acta Chem. Scand. Part XXXI. 50* (1996) 735.
7. Masnovi, J. M., Sankararaman, S. and Kochi, J. K. *J. Am. Chem. Soc. 111* (1989) 2263.
8. Calvert, J. L., Eberson, L., Hartshorn, M. P., Maclagan, R. G. A. R. and Robinson, W. T. *Aust. J. Chem. 47* (1994) 1211.
9. Suzuki, H. and Nakamura, K. *Bull. Chem. Soc. Jpn. 43* (1970) 473.
10. Lau, W. and Kochi, J. K. *J. Am. Chem. Soc. 106* (1984) 7100; Fritz, H. P. and Artes, R. O. *Electrochim. Acta 26* (1981) 417; Hulme, R. and Symons, M. C. R. *J. Chem. Soc. A* (1966) 446; Singer, L. S. and Lewis, I. C. *J. Am. Chem. Soc. 87* (1965).
11. Eberson, L. and Radner, F. *J. Chem. Soc., Chem. Commun.* (1991) 1233; *Acta Chem. Scand. 46* (1992) 630; Sebastiano, R., Korp, J. D. and Kochi, J. K. *J. Chem. Soc., Chem. Commun.* (1991) 1481.
12. Eberson, L., Hartshorn, M. P., Persson, O. and Svensson, J. O. *J. Chem. Soc., Perkin Trans. 2* (1995) 1253.
13. Eberson, L., Persson, O., Radner, F. and Hartshorn, M. P. *Res. Chem. Intermediat. 22* (1996) 799.
14. Baciocchi, E., Rol, C. and Mandolini, L. *J. Org. Chem. 42* (1977) 3682.
15. Suzuki, H. and Hanafusa, T. *Bull. Chem. Soc. Jpn. 46* (1973) 3607.
16. Bellamy, L. J. *Spectrochim. Acta 13* (1958) 60.
17. Elson, I. H. and Kochi, J. K. *J. Am. Chem. Soc. 95* (1973) 5060.
18. Eberson, L, Hartshorn, M. P. and Radner, F. *J. Chem. Soc., Perkin Trans. 2* (1992) 1799.
19. (a) Eberson, L., Hartshorn, M. P. and Persson, O. *Angew. Chem., Int. Ed. Engl. 34* (1995) 2268. (b) Eberson, L., Hartshorn, M. P. and Persson, O. *J. Chem. Soc., Chem. Commun.* (1995) 1131. (c) Eberson, L., Hartshorn, M. P. and Persson, O. *J. Chem. Soc., Perkin Trans. 2* (1995) 1735. (d) Eberson, L., Hartshorn, M. P. and Persson, O. *Acta Chem. Scand. 49* (1995) 640. (e) Eberson, L., Hartshorn, M. P. and Persson, O. *J. Chem. Soc., Perkin Trans. 2* (1996) 141. (f) Eberson, L. and Hartshorn, M. P. *J. Chem. Soc., Perkin Trans. 2* (1996) 151.
20. Eberson, L., Hartshorn, M. P., Radner, F. and Svensson, J. O. *J. Chem. Soc., Perkin Trans. 2* (1994) 1719.

21. Eberson, L., Hartshorn, M. P. and Persson, O. *J. Chem. Soc., Perkin Trans. 2* (1995) 409.
22. Tschinkel, J. G. *Ind. Eng. Chem. 48* (1965) 732.
23. Nyberg, K. *Chem. Scr. 5* (1974) 115.
24. Kim, F. K. and Kochi, J. K. *J. Org. Chem. 54* (1989) 1692.

25. Suzuki, H. *Bull. Chem. Soc. Jpn. 43* (1970) 879.
26. Mori, K., Yukitake, K. and Matsui, S. *Japan Kokai* 75 35, 123; *Chem. Abs. 83* (1975) 96715z.