

Photochemical Nitration by Tetranitromethane Part XXXI.† The Photochemical Reaction of 1,2,3,4-Tetramethylbenzene and Tetranitromethane

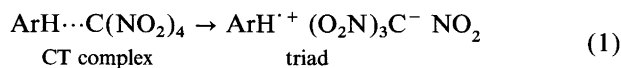
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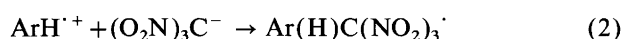
Butts, C. P., Ebersson, L., Fulton, K. L., Hartshorn, M. P., Jamieson, G. B. and Robinson, W. T., 1996. Photochemical Nitration by Tetranitromethane Part XXXI. The Photochemical Reaction of 1,2,3,4-Tetramethylbenzene and Tetranitromethane. – Acta Chem. Scand. 50: 735–744. © Acta Chemica

Photolysis of the 1,2,3,4-tetramethylbenzene–tetranitromethane charge-transfer complex yields the triad of 1,2,3,4-tetramethylbenzene radical cation, nitrogen dioxide and trinitromethanide ion. Recombination of this triad gives predominantly the epimeric 1,2,3,4-tetramethyl-3-nitro-6-trinitromethylcyclohexa-1,4-dienes **8** and **9**, 1,2,3,4-tetramethyl-*r*-5-nitro-*t*-6-trinitromethylcyclohexa-1,3-diene (**10**) and its nitro–alkene cycloaddition product, nitro cycloadduct **11**, the ‘double adduct’ 1,2,3,4-tetramethyl- *c*-2,*c*-5-dinitro-*t*-6-trinitromethylcyclohex-3-en-*r*-1-ol **12**, 2,3,4,5-tetramethyl-1-nitrobenzene (**13**), and the two products of elimination or rearrangement of labile intermediate adducts, 2,3,4,5-tetramethyl-1-trinitromethylbenzene (**7**) and 2,3,4-trimethyl-1-nitromethylbenzene (**14**). Adducts **8**–**12**, and 2,3,4,5-tetramethyl-1-trinitromethylbenzene (**7**) are formed by initial attack of trinitromethanide ion at a non-methylated ring position in the radical cation of 1,2,3,4-tetramethylbenzene (**6**), while 2,3,4-trimethyl-1-nitromethylbenzene (**14**) arises from initial attack of trinitromethanide ion *ipso* to a 1-(4-)-methyl group in the radical cation **6**⁺. Adduct formation is substantially suppressed in the photolysis of the 1,2,3,4-tetramethylbenzene–tetranitromethane charge-transfer complex in 1,1,1,3,3,3-hexafluoro-2-propanol, only the adduct elimination product 2,3,4,5-tetramethyl-1-trinitromethylbenzene (**7**) being formed in addition to the major product, 2,3,4,5-tetramethyl-1-nitrobenzene (**13**). X-Ray crystal structure determinations are reported for 2,3,4,5-tetramethyl-1-trinitromethylbenzene (**7**) and adduct **9**.

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 shown² to occur by recombination of a triad consisting of ArH⁺, trinitromethanide ion, and nitrogen dioxide.



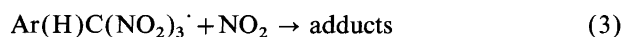
The first chemical step which occurs, leading to the formation of adducts, is reaction between ArH⁺ and trinitromethanide ion [eqn. (2)]



† Part XXX, see Ref. 1.

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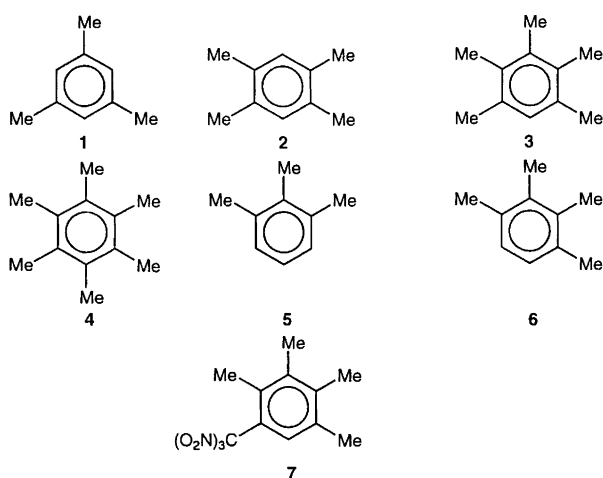
to give a carbon radical which then reacts with nitrogen dioxide to give adducts [eqn. (3)]:²



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**), and 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 a preliminary report, of 1,2,3,4-tetramethylbenzene **6**.⁶

We now report the results of the complete study of the photochemical reaction of 1,2,3,4-tetramethylbenzene (**6**) with tetranitromethane, which in dichloromethane gave mainly adducts (total 58–79%) and substantial amounts of 2,3,4,5-tetramethyl-1-trinitromethylbenzene

(7), a product of secondary elimination reaction(s) of adduct(s). A discussion of the relevance of this type of reaction to the classical electrophilic nitration reactions may be found in Ref. 2 (cf. also Ref. 3).

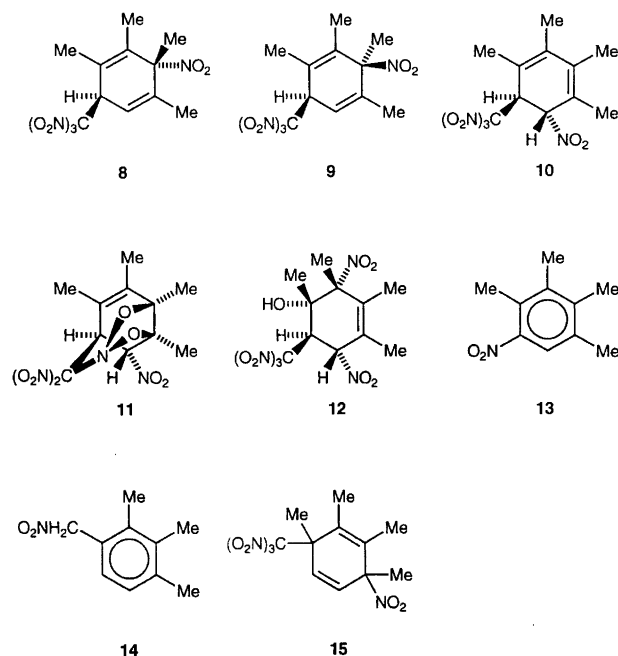


Results

General. The photochemical experiments were performed with filtered light (cut-off at 435 nm, 5 cm water IR filter, from a 300 W 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 $\leq 0^\circ\text{C}$. The crude product mixtures were stored at -78°C and were analysed (^1H NMR spectroscopy, see Experimental section; Tables 1 and 2) as soon as possible.

Photochemistry in dichloromethane at 20°C and the identification of adducts 8–12. A solution of

1,2,3,4-tetramethylbenzene **6** (0.47 mol dm^{-3}) and tetranitromethane (0.94 mol dm^{-3}) in dichloromethane was irradiated at 20°C . The composition of the mixture was monitored by withdrawing samples for NMR spectral analysis (Table 1).



The final solution (after 8 h) after work-up contained the epimeric 1,2,3,4-tetramethyl-3-nitro-6-trinitromethylcyclohexa-1,4-dienes **8** (9%) and **9** (8%), 1,2,3,4-tetramethyl-*r*-5-nitro-*t*-6-trinitromethylcyclohexa-1,3-diene (**10**) (1%) and its cycloadduct **11** (20%), the 'double adduct' **12** (2%), unidentified adducts (total 19%), 2,3,4,5-tetramethyl-1-trinitromethylbenzene (**7**) (25%), 2,3,4,5-tetramethyl-1-nitrobenzene (**13**) (3%), 2,3,4-tri-

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

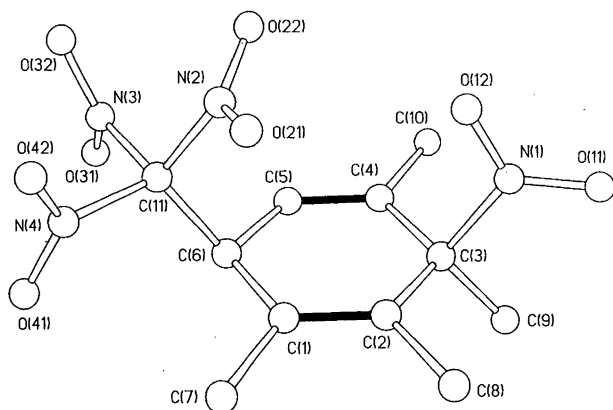
t/h	Yield (%)						Total adducts	7	13	14	Total aromatics
	8	9	10	11	12	15					
At 20°C											
2	17.1	11.0	12.0	12.9	2.2	2.2	76.5	16.4	1.6	1.7	23.5
4	15.9	11.6	7.0	16.8	2.2	1.0	69.7	17.1	2.4	1.5	30.3
8	8.9	7.6	1.3	19.6	2.3	–	58.3	25.1	2.6	3.2	41.6
At -20°C											
2	13.2	10.5	17.2	Trace	4.6	4.6	75.2	14.0	1.7	Trace	24.7
4	15.2	11.7	18.6	1.7	4.3	7.6	79.5	11.7	1.2	1.5	20.5
6	13.2	10.8	19.0	2.0	2.9	4.6	70.5	16.7	1.9	1.2	29.7
At -50°C											
2	10.9	9.2	12.0	2.9	3.2	7.1	65.7	22.1	2.8	3.7	34.3
4	8.3	10.7	9.8	2.8	2.1	6.5	63.2	24.1	2.0	6.5	36.8
6	10.6	10.1	10.1	1.4	3.6	6.8	67.3	19.5	2.2	5.1	32.7
8	10.3	9.9	11.9	1.7	3.3	6.5	62.8	24.7	1.9	3.1	37.2

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

t/h	Yield (%)						Total adducts	7	13	14	Total aromatics
	8	9	10	11	12	15					
At 20 °C											
2	13.4	5.3	2.4	3.9	–	–	34.5	5.9	12.8	35.7	65.5
4	9.9	4.7	1.9	1.9	–	–	36.8	3.9	18.8	29.2	63.2
6	10.1	5.8	4.4	Trace	–	–	38.7	6.3	11.9	31.3	61.2
At –20 °C											
2	9.0	6.0	6.0	–	–	3.7	47.1	7.3	9.0	24.1	52.7
4	8.8	6.3	5.9	–	–	2.6	43.3	8.0	8.8	29.1	56.6
8	7.2	6.0	4.3	–	–	–	35.7	12.3	8.4	35.3	64.3

methyl-1-nitromethylbenzene (**14**) (3%), and unidentified aromatic compounds (total 10%). The adducts **8–12** were separated partially by HPLC on a cyanopropyl column using hexane–dichloromethane mixtures as the eluting solvents. The order of elution of materials from the HPLC column are given in the Experimental section, but here for simplicity the evidence for structural assignments will be presented largely for pairs of compounds.

(A) *The epimeric 1,2,3,4-tetramethyl-3-nitro-6-trinitromethylcyclohexa-1,4-dienes 8 and 9.* Although adduct **9** was obtained in a pure state from the HPLC column, its epimer was eluted in admixture with the isomeric adduct **10** and was isolated only in low yield after adduct **10** was allowed to undergo nitro–alkene cycloaddition to give the cycloadduct **11**. The structure of 1,2,3,4-tetramethyl-*r*-3-nitro-*c*-6-trinitromethylcyclohexa-1,4-diene (**9**), $\text{C}_{11}\text{H}_{14}\text{N}_4\text{O}_8$, m.p. 93 °C (decomp.) was determined by single crystal X-ray analysis; a perspective drawing is presented in Fig. 1, and corresponding atomic coordinates are given in Table 3. In the solid state the alicyclic ring of adduct **9** exists in a flattened boat conformation with the C(3)–NO₂ and C(6)–C(NO₂)₃ groups in flagpole orientations [torsional angles: C(1)–C(2)–C(3)–C(4) 6.3(5)°, C(4)–C(5)–

**Fig. 1.** Perspective drawing of compound **9**. Double bonds are shown in black.**Table 3.** Fractional coordinates for atoms in 1,2,3,4-tetramethyl-*r*-3-nitro-*c*-6-trinitromethylcyclohexa-1,4-diene (**9**).

Atom	$10^4 X/a$	$10^4 Y/b$	$10^4 Z/c$	$10^3 U/\text{\AA}^2$ ^a
O(11)	–3021(3)	–650(2)	2409(1)	61(1)
O(12)	–2049(3)	329(2)	1915(1)	39(1)
O(21)	–2719(3)	1232(2)	1031(1)	37(1)
O(22)	–204(3)	660(2)	1163(1)	40(1)
O(31)	128(3)	–1954(2)	452(1)	42(1)
O(32)	589(3)	123(3)	418(1)	42(1)
O(41)	–3273(3)	–996(2)	76(1)	33(1)
O(42)	–2880(3)	1050(2)	226(1)	39(1)
N(1)	–2676(3)	–601(3)	2063(1)	30(1)
N(2)	–1531(4)	589(3)	977(1)	29(1)
N(3)	–188(3)	–812(3)	509(1)	30(1)
N(4)	–2778(3)	–104(3)	294(1)	28(1)
C(1)	–4108(4)	–1365(3)	1062(1)	20(1)
C(2)	–4313(3)	–1356(3)	1457(1)	19(1)
C(3)	–3040(4)	–1817(3)	1775(1)	22(1)
C(4)	–1458(4)	–2151(3)	1619(1)	24(1)
C(5)	–1268(4)	–2152(3)	1229(1)	23(1)
C(6)	–2514(4)	–1702(3)	906(1)	20(1)
C(7)	–5490(3)	–1088(3)	748(1)	31(1)
C(8)	–5914(3)	–977(3)	1613(1)	32(1)
C(9)	–3675(4)	–2901(3)	2030(1)	32(1)
C(10)	–103(3)	2515(3)	1928(1)	37(1)
C(11)	–1798(4)	–534(3)	685(1)	21(1)

The equivalent isotropic temperature factor in Tables 3–4 is defined as one-third of orthogonalized U_{ij} tensor in \AA^2 .

C(6)–C(1) –6.0(5)°, C(8)–C(2)–C(3)–N(1) –63.6(3)°, C(8)–C(2)–C(3)–C(9) 52.6(4)°, C(7)–C(1)–C(6)–C(11) 66.2(4)°, and the plane of the C(3)–NO₂ group is close to eclipsed with the C(3)–C(9) bond [torsional angle: C(9)–C(3)–N(1)–O(11) –4.7(4)°]. The spectroscopic data for adduct **9** were in accord with the established structure.

The structural assignment to adduct **8**, which could not be induced to yield crystalline material, is based on the close similarity between the spectroscopic data for the epimers **8** and **9**. In particular, the connectivity was established by nuclear Overhauser experiments, and the spectroscopic assignments were confirmed by reverse detected heteronuclear correlation spectra (HMBC,

HMQC). The relative stereochemistry of the two epimers **8** and **9** is consistent with the observed order of elution of *r*-1-nitro-*t*-4-trinitromethyl and *r*-1-nitro-*c*-4-trinitromethyl adducts from the cyanopropyl HPLC column.⁸

(B) *1,2,3,4-Tetramethyl-r-5-nitro-t-6-trinitromethylcyclohexa-1,3-diene (10) and its cycloadduct 11*. The labile adduct **10** could be isolated only in admixture with adduct **8**, above. Thus, its structural assignment rests substantially on its facile thermal nitro-alkene cycloaddition (see below) to give the nitro cycloadduct **11**, the single-crystal X-ray structure determination of which has been reported earlier.⁶ The kinetic plot for this cycloaddition reaction in [²H]-chloroform at 22 °C is given in Fig. 2. The spectroscopic data for the nitro cycloadduct **11** were in accord with the established structure.⁶

(C) *1,2,3,4-Tetramethyl-c-2,c-5-dinitro-t-6-trinitromethylcyclohex-3-en-r-1-ol (12)*. This 'double adduct' was isolated only in low yield and the waxy solid, although pure, could not be induced to crystallize. The accurate mass of the parent ion in the mass spectrum (C.I.) of 'double adduct' **12** indicated a molecular formula C₁₁H₁₅N₅O₁₁. The connectivity in the structure of adduct **12** was established by a consideration of the results of nuclear Overhauser experiments and reverse detected heteronuclear correlation spectra (HMBC, HMQC). The stereochemistry of adduct **12** was assigned tentatively on the basis of its likely mode of formation and by analogy with the structures of 'double adducts' formed in the photolysis of the charge transfer complex of 1,2,3-trimethylbenzene (**5**) and tetranitromethane.⁵ 'Double adduct' **12** is seen as being formed by addition of nitrogen dioxide to 1,2,3,4-tetramethyl-*t*-6-trinitromethylcyclohexa-2,4-dien-*r*-1-ol **16** (Scheme 1). Attack of nitrogen dioxide at the unsubstituted carbon atom of

the 1,3-butadiene system in **16** and *trans* to the bulky trinitromethyl group would give the delocalized carbon radical **17**. The radical coupling of nitrogen dioxide with the delocalized carbon radical occurs *vicinal* and *syn* to the hydroxyl group, a regiochemical and stereochemical outcome seen earlier for an analogous 'double adduct'.⁵

Photochemistry in acetonitrile at 20 °C and the identification of the aromatic products 7, 13 and 14. Photolysis of the charge-transfer complex of 1,2,3,4-tetramethylbenzene (**6**) and tetranitromethane in acetonitrile at 20 °C for 6 h gave a mixture (Table 2) of adducts **8**, **9** and **11** (total 20%), unidentified adducts (18%), 2,3,4,5-tetramethyl-1-trinitromethylbenzene (**7**) (6%), 2,3,4,5-tetramethyl-1-nitrobenzene (**13**) (12%), 2,3,4-trimethyl-1-nitromethylbenzene (**14**) (31%), and unidentified aromatic compounds (total 13%). The aromatic compounds were separated by chromatography on a silica gel Chromatotron plate using pentane and pentane-ether mixtures as the eluting solvents.

The structure of the first compound eluted, 2,3,4,5-tetramethyl-1-trinitromethylbenzene (**7**), C₁₁H₁₃N₃O₆, m.p. 76–77 °C, was determined by single crystal X-ray analysis; a perspective drawing is presented in Fig. 3, and corresponding atomic coordinates are given in Table 4. Unfortunately all crystals of the trinitromethyl compound **7** were twinned, with the twin fraction approximately equal. Notwithstanding this deficiency the structure of trinitromethyl aromatic compound **7** is certain, and the spectroscopic data for the compound are in accord with this structure.

2,3,4,5-Tetramethyl-1-nitrobenzene (**13**) was the second compound eluted, and was shown to be identical with an authentic sample.⁹

The third compound eluted, 2,3,4-trimethyl-1-

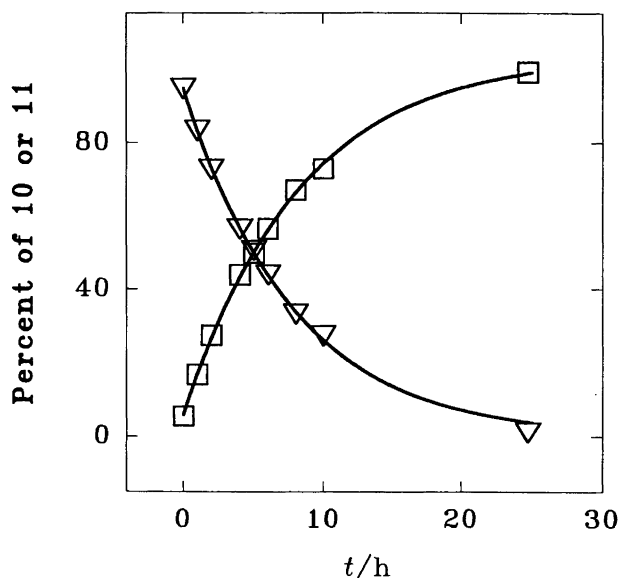
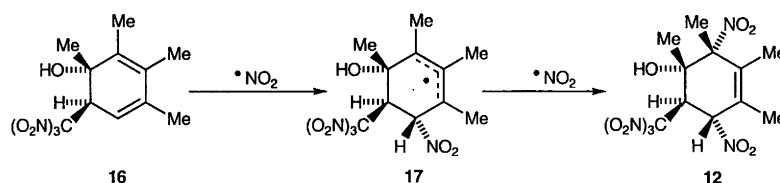


Fig. 2. Kinetics of nitroalkene cycloaddition of adduct **10** to give nitro cycloadduct **11** in [²H]-chloroform at 22 °C. The curves correspond to the best-fitting first-order kinetics expressions to the data, *k* for disappearance of **10** being 0.129(3) h⁻¹.



Scheme 1

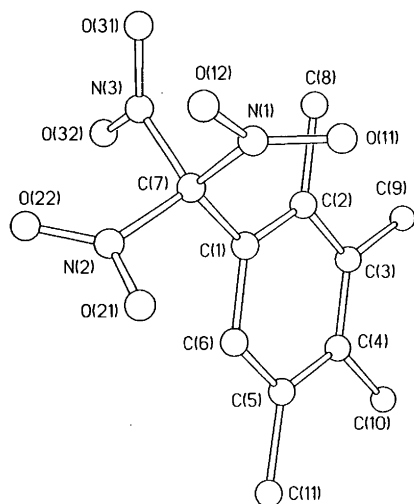


Fig. 3. Perspective drawing of compound 7.

nitromethylbenzene (**14**), was recovered only in low yield. The mass spectrum of compound **14** pointed to a molecular formula $C_{10}H_{13}NO_2$ and nuclear Overhauser experiments, combined with a consideration of reverse detected heteronuclear correlation spectra (HMBC, HMQC), confirmed the connectivity of the structure assigned.

Photochemistry in dichloromethane at -20 and -50 °C. The compositions of the product mixtures obtained in these photolyses are given in Table 1. At these lower temperatures the relative yields of products remained essentially constant with reaction time, in contrast to the photolysis at 20 °C where (a) the yields of adducts **8** and **9** decreased with time as the yield of 2,3,4,5-tetramethyl-1-trinitromethylbenzene (**7**) increased, (b) the yield of the precursor, 1,2,3,4-tetramethyl-*r*-5-nitro-*tert*-6-trinitromethylcyclohexa-1,3-diene (**10**) decreased with time as its thermally induced conversion occurred into the nitro cycloadduct **11** (see below), and (c) the labile 1,2,3,6-tetramethyl-3-nitro-6-trinitromethylcyclohexa-1,4-diene (**15**) [partial 1H NMR spectrum ($CDCl_3$) δ 6.48 (d, $J_{H,H} = 10.3$ Hz, H4 or H5), 6.00 (d, $J_{H,H} = 10.3$ Hz, H5 or H4)] rearranged to give 2,3,4-trimethyl-1-nitromethylbenzene (**14**) (cf. Ref. 10).

Photochemistry in acetonitrile at -20 °C. The compositions of the reaction mixtures obtained in this photolysis

Table 4. Fractional coordinates for atoms in 2,3,4,5-tetramethyl-1-trinitromethylbenzene (**7**).

Atom	$10^4 X/a$	$10^4 Y/b$	$10^4 Z/c$	$10^3 U/\text{Å}^2a$
Molecule 1				
O(11)	-3833(8)	5899(5)	2233(6)	55(2)
O(12)	-4273(9)	7142(5)	2456(6)	60(2)
O(21)	-1619(8)	7402(4)	2931(6)	51(2)
O(22)	-2542(8)	7721(4)	4139(6)	50(2)
O(31)	-5302(8)	6694(5)	4014(7)	64(3)
O(32)	-3724(9)	6420(5)	4953(6)	57(2)
N(1)	-3789(9)	6498(6)	2645(7)	44(2)
N(2)	-2341(9)	7280(5)	3560(6)	38(2)
N(3)	-4135(10)	6531(5)	4228(8)	48(3)
C(1)	-2147(9)	5780(5)	3649(7)	27(2)
C(2)	-2680(10)	5017(6)	3771(7)	35(2)
C(3)	-1758(11)	4368(5)	3862(7)	36(3)
C(4)	-374(11)	4494(6)	3836(7)	41(3)
C(5)	146(10)	5261(6)	3724(7)	35(3)
C(6)	-727(10)	5885(6)	3645(7)	37(3)
C(7)	-3057(11)	6472(6)	3529(7)	37(3)
C(8)	-4184(10)	4851(6)	3828(8)	39(3)
C(9)	-2327(14)	3543(6)	4005(9)	55(3)
C(10)	602(12)	3794(7)	3934(9)	54(3)
C(11)	1661(10)	5412(7)	3696(9)	49(3)
Molecule 2				
O(11')	3412(9)	3606(5)	2660(6)	55(2)
O(12')	3523(8)	2571(5)	1860(6)	57(2)
O(21')	2889(9)	3496(5)	-149(6)	64(3)
O(22')	4609(8)	2830(5)	331(6)	55(2)
O(31')	5673(7)	4364(5)	579(5)	46(2)
O(32')	5800(7)	4092(4)	1932(5)	49(2)
N(1')	3551(9)	3289(5)	1976(7)	40(2)
N(2')	3727(10)	3322(6)	382(7)	48(3)
N(3')	5232(8)	4120(5)	1257(6)	31(2)
C(1')	2743(9)	4516(5)	1230(7)	29(2)
C(2')	1339(10)	4388(6)	1249(7)	35(2)
C(3')	494(10)	5028(7)	1283(7)	38(3)
C(4')	1005(10)	5821(6)	1257(7)	38(3)
C(5')	2399(10)	5940(6)	1235(7)	31(2)
C(6')	3237(10)	5292(6)	1215(7)	32(2)
C(7')	3733(9)	3839(6)	1203(7)	36(3)
C(8')	746(10)	3560(7)	1264(9)	50(3)
C(9')	-1036(10)	4907(8)	1281(10)	56(3)
C(10')	55(12)	6534(7)	1281(9)	55(3)
C(11')	3009(11)	6760(6)	1223(8)	45(3)

are given in Table 2. An interesting feature of these results is the disappearance over time of the labile adduct **15**; this increased lability in acetonitrile, such that rearrangement occurred even at -20 °C, is probably a reflection of the known greater rearrangement rates

of analogous adducts in acetonitrile relative to dichloromethane.¹⁰

*Thermal nitro-alkene cycloaddition in 1,2,3,4-tetramethyl-*r*-5-nitro-*t*-6-trinitromethylcyclohexa-1,3-diene (10) to give the nitro cycloadduct 11.* Although the cycloaddition precursor, 1,2,3,4-tetramethyl-*r*-5-nitro-*t*-6-trinitromethylcyclohexa-1,3-diene (10) [partial ¹H NMR spectrum (CDCl₃) δ 5.03 (br s, H6), 5.11 (br s, H5)], could be obtained only in admixture with 1,2,3,4-tetramethyl-*r*-3-nitro-*t*-6-trinitromethylcyclohexa-1,4-diene (8), the latter adduct was essentially inert in [²H]-chloroform at 22 °C for a period of 25 h in the dark. Accordingly, it was possible to monitor the ¹H NMR spectrum of the mixture of adducts 8 and 10 in [²H]-chloroform in the dark and follow the conversion of the precursor 10 into the nitro cycloadduct 11 (Fig. 2). The rate constant of disappearance of 10 was 0.13 h⁻¹.

Photochemistry in 1,1,1,3,3,3-hexafluoro-2-propanol at 20 °C. The photolysis of the 1,2,3,4-tetramethylbenzene-tetranitromethane charge-transfer complex in 1,1,1,3,3,3-hexafluoro-2-propanol for 8 h at 20 °C gave a conversion (c. 55%) into a mixture of 2,3,4,5-tetramethyl-1-trinitromethylbenzene 7 (16%), 2,3,4,5-tetramethyl-1-nitrobenzene 13 (72%), and some unidentified aromatic compounds (total 12%). No adducts or 2,3,4-trimethyl-1-nitromethylbenzene (14) were detected during the photolysis.

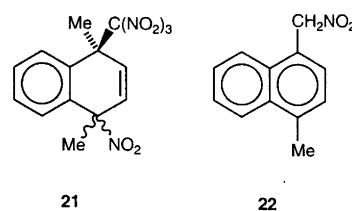
Photochemistry in dichloromethane containing trifluoroacetic acid (0.7 M) at 20 °C. Photolysis under these reaction conditions for 8 h resulted in a conversion (ca. 79%) into a complex mixture including 2,3,4,5-tetramethyl-1-trinitromethylbenzene 7 (20%), 2,3,4,5-tetramethyl-1-nitrobenzene 13 (42%), and a number of unidentified compounds (total 38%).

Discussion

The regiochemistry of attack of trinitromethanide ion on the radical cation of 1,2,3,4-tetramethylbenzene in dichloromethane. Brief (2 h) photolysis of the charge-transfer complex of 1,2,3,4-tetramethylbenzene (6) with tetranitromethane in dichloromethane at 20 °C gave products 7–12 (total 72%) which result from attack of trinitromethanide ion at C5 of 6^{•+}, and products 14 and 15 (total 4%) which result from attack of trinitromethanide ion at C1 of 6^{•+}. Reaction of trinitromethanide ion at C5 of the radical cation 6^{•+} would give the delocalized carbon radical 18 (Scheme 2). Radical coupling at C4 of this delocalized carbon radical with nitrogen dioxide, with C–N bond formation would give adducts 8 and 9, while analogous radical coupling at C6 would give adduct 10, which is the precursor of the nitro cycloadduct 11. 1,2,3,4-Tetramethyl-*t*-6-trinitromethylcyclohexa-2,4-dien-*r*-1-ol 16, presumed to be the precursor of the ‘double adduct’ 12 (Scheme 1), could be formed by

radical coupling of nitrogen dioxide at C2 in the delocalized carbon radical 18 with C–ONO bond formation followed by hydrolysis in the reaction mixture. Although the formation of some 2,3,4,5-tetramethyl-1-trinitromethylbenzene 7 at 20 °C by loss of nitrous acid from adducts 8–10 cannot be excluded, the high initial yields of the trinitromethyl aromatic compound 7, even at –50 °C where there is no evidence of reactivity in adducts 8–10, point to a facile photochemically initiated loss of nitrous acid from adduct 19; this adduct 19 would arise by radical coupling of nitrogen dioxide with C–N bond formation at C2 in the delocalized carbon radical 18.

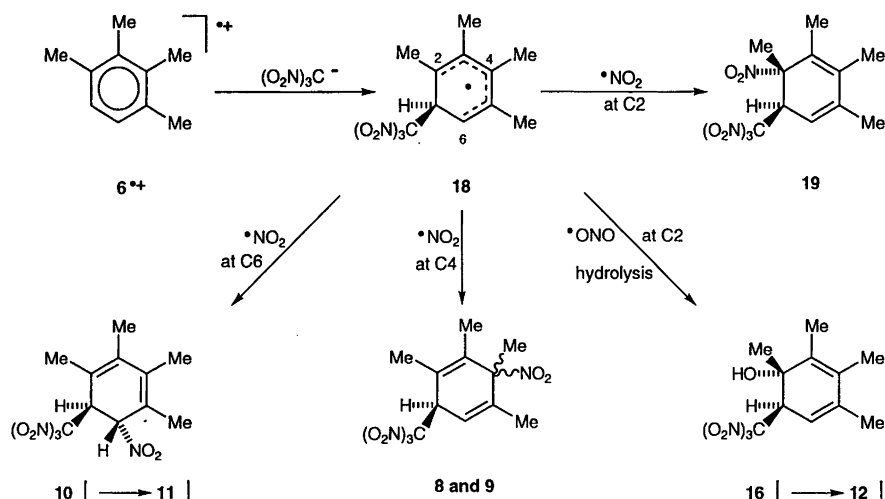
Reaction of trinitromethanide ion at C1 of radical cation 6^{•+} would yield the delocalized carbon radical 20 (Scheme 3). Subsequent radical coupling with nitrogen dioxide at C4, with C–N bond formation, would give the labile adduct 15.



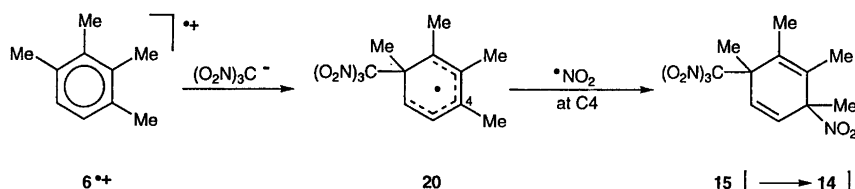
By analogy with the known rearrangement of 1,4-dimethyl-1-nitro-4-trinitromethyl-1,4-dihydronaphthalenes 21 to give 4-methyl-1-nitromethylnaphthalene 22,¹⁰ thermal rearrangement of adduct 15 would represent one route to 2,3,4-trimethyl-1-nitromethylbenzene 14; however, this established rearrangement mechanism¹⁰ does not account for the yields of the nitromethyl compound 14 at low reaction temperatures.

The regiochemistry of attack of trinitromethanide ion on the radical cation of 1,2,3,4-tetramethylbenzene in acetonitrile. Brief (2 h) photolysis of the charge transfer complex of 1,2,3,4-tetramethylbenzene 6 with tetranitromethane in acetonitrile at 20 °C gave products 7–11 (total 31%) which result from attack of trinitromethanide ion at C5 of 6^{•+}, and products 14 and 15 (total 36%) which result from attack of trinitromethanide ion at C1 of 6^{•+}. In acetonitrile the rearrangement of 1,4-dimethyl-1-nitro-4-trinitromethyl-1,4-dihydronaphthalenes (21) to give 4-methyl-1-nitromethylnaphthalene (22) is known to be more facile than in dichloromethane;¹⁰ this is in accord with the rearrangement of adduct 15 even at –20 °C to give the nitromethyl aromatic compound 14.

The photolyses of the charge transfer complex of 1,2,3,4-tetramethylbenzene (6) and tetranitromethane in 1,1,1,3,3,3-hexafluoro-2-propanol, and in dichloromethane containing trifluoroacetic acid (0.7 M). The photolysis of the charge transfer complex of 1,2,3,4-tetramethylbenzene (6) and tetranitromethane in 1,1,1,3,3,3-hexafluoro-2-propanol at 20 °C for 8 h resulted in a lower conversion (55%, compared with 88% in dichloromethane) into a mixture mainly of 2,3,4,5-tetramethyl-1-trinitromethylbenzene (7) (16%), 2,3,4,5-tetramethyl-1-nitrobenzene



Scheme 2



Scheme 3

(13) (72%), but no adducts were detected. Although 1,1,1,3,3,3-hexafluoro-2-propanol is known to exert extreme deactivation of nucleophilic attack on radical cations,¹¹ it is therefore clear in the case of the present substrate that trinitromethanide ion, generated along with the radical cation $6^{\bullet+}$ and nitrogen dioxide in the triad within the solvent cage, retains some nucleophilic reactivity towards the radical cation. Notwithstanding that limited reactivity, the major reaction pathway involves the radical coupling of nitrogen dioxide with the radical cation $6^{\bullet+}$ to give 2,3,4,5-tetramethyl-1-nitrobenzene (13), a reaction not impeded by the properties of the solvent.

The photolysis in dichloromethane containing trifluoroacetic acid (0.7 M) gave a more complex mixture of products. Nonetheless the yield of 2,3,4,5-tetramethyl-1-trinitromethylbenzene (7) (20%), and the absence of adducts, reveals the reduced reactivity of the trinitromethanide ion due to some protonation by the trifluoroacetic acid present; 2,3,4,5-tetramethyl-1-nitrobenzene (13) (42%) was the other identifiable product.

The fact that the transient products of photoprotonation have been detected in the laser flash photolysis at 248 nm of certain aromatic compounds, like mesitylene or hexamethylbenzene,¹² in HFP suggests that other pathways to 7 might be feasible in this medium. Protonation of 6 in the 2-position, followed by reaction of trinitromethanide or nitroform at the center of positive charge in the 5-position, would yield a nitroform adduct which upon oxidation might give 7. However, before this

mechanism can be considered, it must first be established that photoprotonation can be induced in the wavelength region used here, $\lambda > 435$ nm, where the CT complex is the photoactive species.

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 and 1,2,3,4-tetramethylbenzene were purchased from Aldrich. Dichloromethane (AR) and acetonitrile (HiPerSolv) were from BDH.

WARNING. While we did not experience any incidents in working with tetranitromethane, it should be noted that its mixtures with hydrocarbons are detonative within certain concentration limits and that due care should be taken in handling mixtures of tetranitromethane and organic compounds.¹³

General procedure for the photonitration of 1,2,3,4-tetramethylbenzene (6) with tetranitromethane. A solution of 6 (500 mg, 0.47 mol dm^{-3}) and tetranitromethane (0.94 mol dm^{-3}) in dichloromethane (at

20, -20 or -50 °C) or acetonitrile (20 or -20 °C) was irradiated with filtered light ($\lambda_{\text{cut-off}}$ at 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). Photolyses were performed, as above, but in 1,1,1,3,3,3-hexafluoro-2-propanol at 20 °C, or dichloromethane containing trifluoroacetic acid (0.7 M) also at 20 °C.

Photochemistry in dichloromethane at 20 °C and the identification of the adducts 8–12. Reaction of 1,2,3,4-tetramethylbenzene-tetranitromethane in dichloromethane at 20 °C, as above, for 8 h gave a conversion (ca. 88%) into a mixture (^1H NMR; Table 1) of adducts **8–12** (total 40%), unidentified adducts (total 19%), 2,3,4,5-tetramethyl-1-trinitromethylbenzene (**7**) (25%), 2,3,4,5-tetramethyl-1-nitrobenzene (**13**) (3%), 2,3,4-trimethyl-1-nitromethylbenzene (**14**) (3%) and unidentified aromatic compounds (total 10%). 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 the aromatic compounds **7**, **13** and **14**; these compounds were obtained subsequently by chromatography on a silica gel Chromatotron plate of a product mixture obtained by photolysis of 1,2,3,4-tetramethylbenzene-tetranitromethane in acetonitrile at 20 °C (see below).

The second material eluted was a mixture of 1,2,3,4-tetramethyl-*r*-3-nitro-*tert*-6-trinitromethylcyclohexa-1,4-diene (**8**) and 1,2,3,4-tetramethyl-*r*-5-nitro-*t*-6-trinitromethylcyclohexa-1,3-diene (**10**). In solution the latter diene (**10**) underwent thermal nitro-alkene cycloaddition to give the markedly more polar cycloadduct **11**, below, and allowed the subsequent HPLC separation of the resulting mixture to give in low yield 1,2,3,4-tetramethyl-*r*-3-nitro-*t*-6-trinitromethylcyclohexa-1,4-diene (**8**) (insufficient for elemental analysis. Parent ion not visible in mass spectrum. Found: $M^+ - \text{NO}_2$, 283.0805. $\text{C}_{11}\text{H}_{13}\text{N}_4\text{O}_8 - \text{NO}_2$ requires 283.0804). IR: ν_{max} (liquid film) 1605, 1551 cm^{-1} . ^1H NMR (CDCl_3) δ 1.70 (br s, 2-Me), 1.72 (s, 3-Me), 1.76 (dd, $J_{\text{Me,H5}}$ 1.5 Hz, $J_{\text{Me,H6}}$ 1.5 Hz, 4-Me), 1.78 (br s, 1-Me), 4.87 (br s, H6), 5.93 (dq, $J_{\text{H5,H6}}$ 3.4 Hz, $J_{\text{H5,4-Me}}$ 1.5 Hz, H5). Nuclear Overhauser experiments gave the following results: irradiation at δ 1.76 gave an enhancement at δ 5.95 (4.1%); irradiation at δ 1.78 gave enhancements at δ 1.70 (0.9%) and at δ 4.87 (3.1%); irradiation at δ 4.87 gave an enhancement at δ 5.95 (1.7%); irradiation at δ 5.95 gave enhancements at δ 1.76 (0.7%) and at δ 4.87 (1.9%). ^{13}C NMR (CDCl_3) δ 14.5 (2-Me), 16.6 (1-Me), 17.8 (4-Me), 23.2 (3-Me), 47.9 (C6), 91.8 (C3), 117.2 (C5), 121.8 (C1), 135.5 (C2), 141.0 (C4), a resonance for $\text{C}(\text{NO}_2)_3$ was not detected; the assignments above were confirmed by reverse detected heteronuclear correlation spectra (HMBC, HMQC).

*1,2,3,4-Tetramethyl-*r*-3-nitro-*c*-6-trinitromethylcyclohexa-1,4-diene (9)*, m.p. 93 °C (decomp.) (X-ray crystal structure determined, see below). IR: ν_{max} (KBr) 1618, 1578 cm^{-1} . ^1H NMR (CDCl_3) δ 1.74 (s, 3-Me), 1.76 (br s, 1-Me, 2-Me), 1.80 (dd, $J_{\text{4-Me,H5}}$ 1.5 Hz, $J_{\text{4-Me,H6}}$ 1.5 Hz, 4-Me), 4.81 (br s, H6), 5.93 (dq, $J_{\text{H5,H6}}$ 3.5 Hz, $J_{\text{H5,4-Me}}$ 1.5 Hz, H5). Nuclear Overhauser experiments gave the following results: irradiation at δ 1.76 gave an enhancement at δ 4.81 (4.5%); irradiation at δ 1.80 gave an enhancement at δ 5.93 (4.8%); irradiation at δ 4.81 gave enhancements at δ 5.93 (2.2%) and at δ 1.76 (0.6%); irradiation at δ 5.93 gave enhancements at δ 1.80 (0.7%) and at δ 4.81 (2.7%). ^{13}C NMR (CDCl_3) δ 15.6 and 17.0 (1-Me, 2-Me), 18.8 (4-Me), 22.5 (3-Me), 47.1 (C6), 90.95 (C3), 118.1 (C5), 122.7 (C1), 134.7 (C2), 134.7 (C2), a resonance for $\text{C}(\text{NO}_2)_3$ was not detected; the assignments above were confirmed by reverse detected heteronuclear correlation spectra (HMBC, HMQC).

Nitro cycloadduct 11, m.p. 137 °C (decomp.) (X-ray crystal structure determined⁶). IR: ν_{max} (KBr) 1591, 1558 cm^{-1} . ^1H NMR (CDCl_3) δ 1.51 (s, 3-Me), 1.74 (s, 6H, 1-Me, 2-Me), 1.84 (s, 4-Me), 4.57 (d, $J_{\text{H6,H5}}$ 3.9 Hz, H6), 5.41 (d, $J_{\text{H5,H6}}$ 3.9 Hz, H5). Nuclear Overhauser experiments gave the following results: irradiation at δ 1.51 gave enhancements at δ 1.74 (1.0%) and at δ 1.84 (2.2%); irradiation at δ 4.57 gave enhancements at δ 1.74 (0.4%) and at δ 5.41 (3.2%); irradiation at δ 5.41 gave enhancements at δ 1.84 (0.3%) and at δ 4.57 (2.8%). ^{13}C NMR (CDCl_3) δ 14.5 (2-Me), 17.8 (4-Me), 18.9 (3-Me), 20.1 (1-Me), 45.2 (C6), 85.4 (C5), 86.4 (C4), 88.3 (C3), 126.8 (C1), 142.1 (C2), a resonance for $\text{C}(\text{NO}_2)_2$ was not detected; the assignments above were confirmed by reverse detected heteronuclear correlation spectra (HMBC, HMQC).

*1,2,3,4-Tetramethyl-*c*-2,*c*-5-dinitro-*t*-6-trinitromethylcyclohex-3-en-*r*-1-ol (12)*, as a waxy solid (insufficient for elemental analysis. Found: M^+ 347.0840. $\text{C}_{11}\text{H}_{15}\text{N}_5\text{O}_{11}$ requires 347.0839). IR: ν_{max} (KBr) 1618, 1541 cm^{-1} . ^1H NMR (CDCl_3) δ 1.20 (br s, 1-Me), 1.88 (s, 2-Me), 2.02 (br s, 3-Me), 2.08 (br s, 4-Me), 5.01 (br s, OH), 5.02 (d, $J_{\text{H6,H5}}$ 5.9 Hz, H6), 5.56 (d, $J_{\text{H5,H6}}$ 5.9 Hz, H5). Nuclear Overhauser experiments gave the following results: irradiation at δ 1.20 gave an enhancement at δ 1.88 (1.7%); irradiation at δ 1.88 gave enhancements at δ 1.20 (2.0%) and at δ 2.02 (1.6%); irradiation at δ 2.02 gave an enhancement at δ 1.88 (0.4%); irradiation at δ 2.08 gave an enhancement at δ 5.56 (4.4%); irradiation at δ 5.02 gave enhancements at δ 1.20 (0.4%) and at δ 1.88 (0.5%); irradiation at δ 5.56 gave an enhancement at δ 2.08 (0.7%). ^{13}C NMR (CDCl_3) δ 17.0 (3-Me), 19.2 (4-Me), 20.2 (2-Me), 20.8 (1-Me), 48.9 (C6), 73.8 (C1), 87.9 (C5), 98.8 (C2), 127.5 (C4), 134.4 (C3), a resonance for $\text{C}(\text{NO}_2)_3$ was not detected; the assignments above were confirmed by reverse detected heteronuclear correlation spectra (HMBC, HMQC).

Photochemistry in acetonitrile at 20 °C and the identification of the aromatic products 7, 13 and 14. Reaction of 1,2,3,4-tetramethylbenzene–tetranitromethane in acetonitrile at 20 °C, as above, for 6 h gave a product which was shown by ^1H NMR spectra to be a mixture (Table 2) of adducts **8**, **9** and **11** (total 20%), unidentified adducts (18%), 2,3,4,5-tetramethyl-1-trinitromethylbenzene (**7**) (6%), 2,3,4,5-tetramethyl-1-nitrobenzene (**13**) (12%), 2,3,4-trimethyl-1-nitromethylbenzene (**14**) (31%), and unidentified aromatic compounds (total 13%). The aromatic compounds **7**, **13** and **14** were separated by chromatography on a silica gel Chromatotron plate using pentane and pentane–ether mixtures as the eluting solvents to give in elution order:

2,3,4,5-Tetramethyl-1-trinitromethylbenzene (7), m.p. 76–77 °C (X-ray crystal structure determined, see below). IR: ν_{max} (KBr) 1684, 1618, 1578 cm^{-1} . ^1H NMR (CDCl_3) δ 2.03 (s, 2-Me), 2.28 (s, 3-Me), 2.307, 2.313 (both s, 4-Me, 5-Me), 6.85 (s, H6). Nuclear Overhauser experiments gave the following results: irradiation at δ 2.03 gave an enhancement at δ 2.28 (1.9%); irradiation at δ 6.85 gave an enhancement at δ 2.31 (0.2%). ^{13}C NMR (CDCl_3) δ 16.4 (3-Me), 16.8 ((4-Me), 18.5 (2-Me), 21.0 (5-Me), 118.9 (C1), 128.0 (C6), 133.5 (C5), 135.2 (C3), 138.5 (C2), 142.5 (C4), a resonance for $\text{C}(\text{NO}_2)_3$ was not detected; the assignments above were confirmed by reverse detected heteronuclear correlation spectra (HMBC, HMQC).

2,3,4,5-Tetramethyl-1-nitrobenzene (13), identical with an authentic sample.⁹ ^1H NMR (CDCl_3) δ 2.25 (s, Me), 2.28 (s, Me), 2.31 (s, Me), 2.36 (s, Me), 7.43 (s, H6).

2,3,4-Trimethyl-1-nitromethylbenzene (14), an oil (Insufficient material for elemental analysis. Found: M^+ 179.0947. $\text{C}_{10}\text{H}_{13}\text{NO}_2$ requires 179.0946). IR: ν_{max} (CHCl_3) 1551 cm^{-1} . ^1H NMR (CDCl_3) δ 2.22 (s, 3-Me), 2.28 (s, 2-Me), 2.31 (s, 4-Me), 5.47 (s, $\text{C H}_2\text{-NO}_2$), 7.06 (d, $J_{\text{H5, H6}}$ 7.9 Hz, H5), 7.09 (d, $J_{\text{H6, H5}}$ 7.9 Hz, H6). Nuclear Overhauser experiments gave the following results: irradiation at δ 5.47 gave enhancements at δ 2.28 (0.7%) and at δ 7.09 (2.0%); irradiation at δ 2.31 gave an enhancement at δ 7.06 (3.3%). ^{13}C NMR (CDCl_3) δ 15.8 (2-Me, 3-Me), 21.0 (4-Me), 78.5 (CH_2NO_2), 126.1 (C1), 127.7 (C5), 128.9 (C6), 136.3 and 136.4 (C2 and C3), 138.9 (C4); the assignments above were confirmed by reverse detected heteronuclear correlation spectra (HMBC, HMQC).

*Thermal nitro–alkene cycloaddition in 1,2,3,4-tetramethyl-*r*-5-nitro-*t*-6-trinitromethylcyclohexa-1,3-diene (10) to give the nitro cycloadduct 11.* A mixture of 1,2,3,4-tetramethyl-*r*-3-nitro-*t*-6-trinitromethylcyclohexa-1,4-diene (**8**) and 1,2,3,4-tetramethyl-*r*-5-nitro-*t*-6-trinitromethylcyclohexa-1,3-diene (**10**), obtained by HPLC separation of the product of photolysis of 1,2,3,4-tetramethylbenzene–tetranitromethane at -20 °C in dichloromethane, was dissolved in [^2H]-chloroform. The solution was stored in the dark at 22 °C, and the ^1H

NMR spectrum of the solution was monitored at appropriate intervals. Under these conditions adduct **8** was unchanged, but adduct **10** [part ^1H NMR spectrum (CDCl_3) δ 5.03 (br s, H6), 5.11 (br s, H5)] underwent cycloaddition to give the nitro cycloadduct **11**; the kinetic plot for this reaction is given in Fig. 2.

Photolysis in 1,1,1,3,3,3-hexafluoro-2-propanol at 20 °C. Photolysis of the charge transfer complex of 1,2,3,4-tetramethylbenzene (**6**) and tetranitromethane in 1,1,1,3,3,3-hexafluoro-2-propanol for 8 h at 20 °C, as above, gave a conversion (ca. 55%) into a mixture of 2,3,4,5-tetramethyl-1-trinitromethylbenzene (**7**) (16%), 2,3,4,5-tetramethyl-1-nitrobenzene (**13**) (72%), and unidentified aromatic compounds (12%). At no time during the photolysis were adducts **8–12** or **15** or 2,3,4-trimethyl-1-nitromethylbenzene (**14**) detected in the reaction mixture.

Photolysis in dichloromethane containing trifluoroacetic acid (0.7 M) at 20 °C. Photolysis of the charge transfer complex of 1,2,3,4-tetramethylbenzene (**6**) and tetranitromethane in dichloromethane containing trifluoroacetic acid (0.7 M) for 8 h at 20 °C, as above, gave a conversion (ca. 79%) into a mixture of 2,3,4,5-tetramethyl-1-trinitromethylbenzene (**7**) (20%), 2,3,4,5-tetramethyl-1-nitrobenzene (**13**) (42%), and unidentified compounds (total 38%).

Crystallography. Crystal data, established from precession photographs and measured accurately, by means of a Siemens R3m/V four-circle diffractometer [molybdenum X-radiation, $\lambda(\text{Mo K}\alpha)$ 0.71069 Å, from a crystal monochromator] are given below. The space group was, in each case, determined unambiguously as a result of the structure analyses reported below, but initially indicated 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 25 accurately centred high-angle reflections were used.

Crystal data.

*1, 2, 3, 4-Tetramethyl-*r*-3-nitro-*c*-6-trinitromethylcyclohexa-1,4-diene (9)*, $\text{C}_{11}\text{H}_{14}\text{N}_4\text{O}_8$, M 330.26, monoclinic, space group $C2_c$, $a=8.317(1)$, $b=10.277(2)$, $c=33.100(2)$ Å, $\beta=94.90(1)^\circ$; $V=2818.8(7)$ Å³, $D_c=1.556$ g cm^{-3} , $Z=8$, $\mu(\text{Mo K}\alpha)$ 1.34 cm^{-1} . The crystal was colourless and of approximate dimensions 0.4 × 0.18 × 0.18 mm. Data were collected at 151(2) K out to a maximum Bragg angle $\theta=24^\circ$. Number of independent reflections measured 2234, 805 with $I>2\sigma(I)$. Absorption corrections were not applied; $g_1=0.0025$, $g_2=0.0000$; $R_{(\text{obs})}$ -factor=0.038, $wR_{(\text{all data})}=0.044$.

2,3,4,5-Tetramethyl-1-trinitromethylbenzene (7), $\text{C}_{11}\text{H}_{13}\text{N}_3\text{O}_6$, M 283.24, monoclinic, space group $P2_1/c$,

$a=9.846(5)$, $b=16.829(7)$, $c=15.585(8)$ Å, $\beta=90.25(3)^\circ$, $V=2582(2)$ Å³, $D_c=1.457$ g cm⁻³, $Z=8$, $\mu(\text{Mo K}\alpha)=1.20$ cm⁻¹. The crystal was yellow and of approximate dimensions $0.90 \times 0.57 \times 0.20$ mm. Data were collected at 166(2) K out to a maximum Bragg angle $\theta=22.5^\circ$. Number of independent reflections measured 3368, 2219 with $I > 2\sigma(I)$. Absorption corrections were not applied; $g_1=0.1934$, $g_2=2.5000$; $R_{(\text{obs})}$ -factor = 0.098, $wR_{(\text{all data})}=0.314$.

Structure determination. Full-matrix least-squares refinements (SHELXL-93).¹⁴ This program is based on intensities and uses all data. The observed threshold $I > 2\sigma(I)$ was used only for calculating $R_{(\text{obs})}$, 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.

For 2,3,4,5-tetramethyl-1-trinitromethylbenzene (7) all crystals examined were twinned, with the twin fraction approximately equal, such that the h , k , l and h , $-k$, $-l$ reflections coincided. The poor $R_{(\text{int})}$ probably arises from incompletely scanned reflections at higher angles.

Final Fourier syntheses show no significant residual electron density, and there were no abnormal discrepancies between observed and calculated structure factors.

Acknowledgements. Financial support (to L. E.) from the Swedish Natural Science Research Council and the Knut and Alice Wallenberg Foundation is gratefully acknowledged.

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Received November 7, 1995.