

Photochemical Nitration by Tetranitromethane. Part XXVI.† Adduct Formation in the Photochemical Reaction of 1,2,3-Trimethylbenzene: the Formation of 'Double' Adducts Including Nitronic Esters

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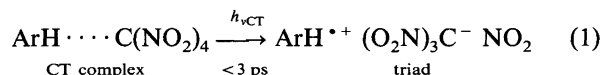
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The photolysis of the charge-transfer complex of 1,2,3-trimethylbenzene and tetranitromethane gives a complex mixture of products, most of which arise by initial attack of trinitromethanide ion on the unsubstituted ring positions at C4(C6) and C5 of the radical cation of 1,2,3-trimethylbenzene. The products 7–19 are adducts resulting directly or indirectly from the addition of the elements of tetranitromethane to 1,2,3-trimethylbenzene, and the trinitromethyl aromatic compounds 22–25 are formed by eliminations from intermediate adducts. Six adducts are simple 'single' adducts, nitro-trinitromethyl adducts 7, 8, 10–12, while nitro cycloadduct 9 is formed by cycloaddition of nitro-trinitromethyl adduct 8. The remaining addition products are 'double' adducts, formed by secondary addition reactions initiated by attack of nitrogen dioxide on the buta-1,3-diene system of 'single' adducts, and include trinitro-trinitromethyl compounds 13 and 15, the hydroxy-dinitro-trinitromethyl compound 14, and a group of four nitronic esters 16–19 formed by nitro-denitrocyclization of initially formed hydroxy-trinitromethyl and nitro-trinitromethyl 'single' adducts. Minor amounts of other products are formed including two nitrodienones 21 and 22, and the rearrangement product, 4,5,6-trimethyl-2-nitrophenol (28), and the 2,3,4-trimethyl- and 3,4,5-trimethylnitrobenzenes 26 and 27.

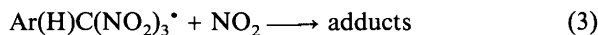
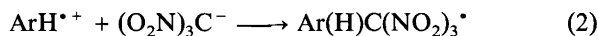
The modes of formation of the above products are discussed, and X-ray crystal structure determinations are reported for compounds 9, 13, 14, 18, 19, 22 and 29.

The photochemical addition of tetranitromethane (TNM) to aromatic compounds (ArH) by excitation of the ArH–TNM charge-transfer (CT) complex by light matching the wavelength of the CT band has been shown^{2,3} to occur by recombination of a triad consisting of ArH^{•+}, the trinitromethanide ion, and nitrogen dioxide [eqn. (1)].⁴



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)].^{2,3}



Although no adducts were reported from the photochemical reactions of mononuclear ArH, such as 1,3,5-trimethylbenzene (1), 1,2,4,5-tetramethylbenzene (2), pentamethylbenzene (3) and hexamethylbenzene (4) with tetranitromethane,⁵ adducts and products of their further transformation were formed in low yields in the analogous reactions of benzene⁶ and in yields of > 60% from 1,2,3,4-tetramethylbenzene (5).⁷

We now report the results of the photochemical reaction of 1,2,3-trimethylbenzene (6) with tetranitromethane,

† Part XXV, see Ref. 1.

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Table 1. Overview of yields of products from the photolysis of 1,2,3-trimethylbenzene (0.52 mol dm⁻³) and tetranitromethane (1.04 mol dm⁻³) in dichloromethane.

Yield (%)		7	10	11	12	8	9	13	14	15	16	17	18	19	20	21	28	22	23	24	25	26	27	30	31
20 °C																									
1	7.3	3.8	9.3	1.9	5.7	1.7	0.3	3.2	1.0	2.7	1.1	4.5	3.6	1.1	0.3	0.5	31.4	10.2	2.8	2.8	2.8	3.3	0.5	-	
4	9.0	5.3	10.0	3.1	4.4	3.2	1.5	4.2	2.7	3.6	1.5	6.7	4.1	0.5	0.6	0.1	23.6	9.5	1.0	0.0	0.0	2.4	0.7	-	
8	7.9	3.9	9.7	3.4	2.6	2.8	2.6	3.7	3.1	3.7	1.4	6.6	4.4	-	0.6	-	26.8	10.8	0.5	0.3	3.2	0.7	-		
-20 °C																									
1	3.4	4.2	4.8	3.4	4.4	-	-	-	-	-	-	-	-	1.3	2.1	0.3	2.8	40.7	4.6	4.7	4.8	3.0	0.9	-	
4	3.1	3.3	3.8	4.2	5.1	-	-	-	-	trace	-	-	-	1.5	2.0	0.8	0.7	45.8	13.4	1.8	2.1	2.4	1.0	-	
8	3.4	4.6	4.3	4.5	5.4	-	-	-	-	0.7	-	-	-	1.8	2.0	1.0	0.5	40.8	17.0	0.8	0.9	3.0	1.1	-	
-50 °C																									
1	2.8	2.0	4.7	4.2	3.5	-	-	-	-	-	-	-	-	-	2.2	2.0	2.9	48.8	2.5	6.1	5.7	2.8	0.8	-	
4	5.1	4.6	5.8	7.3	6.4	-	-	-	-	-	-	-	-	-	2.8	4.2	1.9	31.3	12.0	3.2	3.0	3.2	0.9	-	
8	4.9	4.4	6.7	7.6	6.5	-	-	-	-	-	-	-	-	-	2.7	9.1	1.0	28.2	12.0	1.9	2.5	3.0	0.9	-	

Table 2. Overview of yields of products from the photolysis of 1,2,3-trimethylbenzene (0.52 mol dm⁻³) and tetranitromethane (1.04 mol dm⁻³) in acetonitrile.

Yield (%)		7	10	11	12	8	9	13	14	15	16	17	18	19	20	21	28	22	23	24	25	26	27	30	31
20 °C																									
1	4.8	1.8	5.2	1.0	2.3	0.8	-	-	-	0.8	-	2.7	2.2	1.4	0.2	0.5	57.5	8.5	1.8	1.6	3.7	1.5	-	-	
4	6.1	1.9	5.6	1.7	1.2	1.1	-	-	-	0.7	-	4.1	2.3	1.1	2.1	-	55.1	5.7	0.7	0.7	5.8	1.9	0.6	-	
8	4.0	1.5	3.2	1.5	1.0	2.6	-	-	-	1.0	-	5.7	2.4	0.4	1.4	8.9	53.8	6.0	0.6	0.6	2.8	0.9	0.2	0.2	
-20 °C																									
1	3.2	2.1	5.4	2.7	2.9	-	-	-	-	trace	-	-	-	1.2	2.6	0.8	3.7	48.8	1.8	4.7	4.5	4.6	2.2	-	
4	3.1	1.3	4.8	2.3	2.3	-	-	-	-	0.4	-	-	-	1.3	2.2	1.8	3.3	54.1	7.1	1.6	1.5	4.2	2.0	-	
8	2.3	1.6	3.1	2.1	2.0	-	-	-	-	0.2	-	-	-	0.7	2.1	1.7	1.4	62.8	11.6	0.9	0.9	3.6	1.8	-	
-50 °C																									
1	2.8	2.0	5.3	5.9	2.2	-	-	-	-	-	-	-	-	-	2.6	9.5	7.2	12.3	2.0	14.7	14.1	10.7	3.3	-	
4	3.4	2.8	5.6	7.4	3.7	-	-	-	-	-	-	-	-	-	5.3	7.7	7.6	19.5	6.0	5.6	5.3	9.7	4.3	-	
8	3.6	4.4	5.9	6.2	5.6	-	-	-	-	0.6	-	-	-	-	4.9	0.7	7.5	26.4	9.6	2.8	2.8	9.7	4.4	-	

which in dichloromethane at 20 °C gives 'single' adducts (30%) arising by simple addition of the elements of tetranitromethane to the aromatic compound (6), 'double' adducts (25%) arising by further addition reactions of 'single' adducts involving the NO₂ formed, and trinitromethyl substitution compounds (total 38%), which are products of rearrangement/elimination from intermediate 'single' adducts.

Results

General. The photochemical experiments were performed with filtered light (cut-off 435 nm, 5 cm water IR filter, 300 W 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 -20 or -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 identification of adducts. A solution of 1,2,3-trimethylbenzene (0.52 mol dm⁻³) and tetranitromethane (1.04 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) contained the 'single' adducts **7** (8%), **8** (3%) and its cycloadduct **9** (3%), **10** (4%), **11** (10%) and **12** (3%), 'double' adducts **13** (3%), **14** (4%), **15** (3%), **16** (4%), **17** (1%), **18** (7%) and **19** (4%), nitro-dienones **20** (trace), and **21** (1%), trinitromethyl-substituted aromatic compounds **22** (27%), **23** (11%), **24** (0.5%), **25** (trace), and nitroaromatic compounds **26** (3%) and **27** (1%). The components of the mixture were separated partially by HPLC on a cyanopropyl column using hexane-dichloromethane mixtures as the eluting solvents. The order of elution of materials from the HPLC column is given in the Experimental section, but

here for simplicity the evidence for structural assignments will be presented for groups of products.

(A) 'Single' adducts **7**, **10**, **11** and **12**. These adducts were obtained only in small amounts and, in the cases of adducts **7** and **10**, in admixture with traces (ca. 5%) of impurities. Attempts to grow crystals suitable for X-ray crystallography failed, and the identification of these adducts is based therefore substantially on a consideration of their NMR spectra and their conversion into either 3,4,5-trimethyl-1-trinitromethylbenzene **22** (from adducts **7** and **11**), or 2,3,4-trimethyl-1-trinitromethylbenzene **23** (from adducts **10** and **12**) on treatment with 2,6-di-*tert*-butyl-4-methylpyridine in dichloromethane. The symmetrical structures of adducts **7** and **11** were revealed by the relative simplicity of their ¹H and ¹³C NMR spectra, and the assignment of stereochemistry to these compounds was based on the elution order from the HPLC column, *trans*-1,4-nitro-trinitromethyl adducts being eluted ahead of their *cis*-1,4-isomers.⁸ The ¹H and ¹³C NMR spectra of the epimeric 1,2,3-trimethyl-3-nitro-6-trinitromethylcyclohexa-1,4-dienes **10** and **12** were consistent with the structures assigned, the stereochemistry again being related to the elution order from the HPLC column.⁸

(B) 'Single' adduct **8** and its cycloaddition product **9**. Adduct **8** was isolated only in admixture with adducts **7** and **10** and traces of its related nitrocycloadduct **9**. The assignment of its structure **8** is based on a consideration of its ¹H NMR spectra, including the results of nuclear Overhauser experiments, and its conversion (half-life 19.5 h) in ²H-chloroform solution in the dark at 22 °C into the nitrocycloadduct **9**, the structure of which was established by single-crystal X-ray analysis. A perspective drawing of the nitrocycloadduct **9**, C₁₀H₁₂N₄O₈, m.p. 163 °C (decomp.) is presented in Fig. 1, and corresponding atomic coordinates are given in Table 3. In **9**, N(3) is clearly trigonal pyramidal and bond length dif-

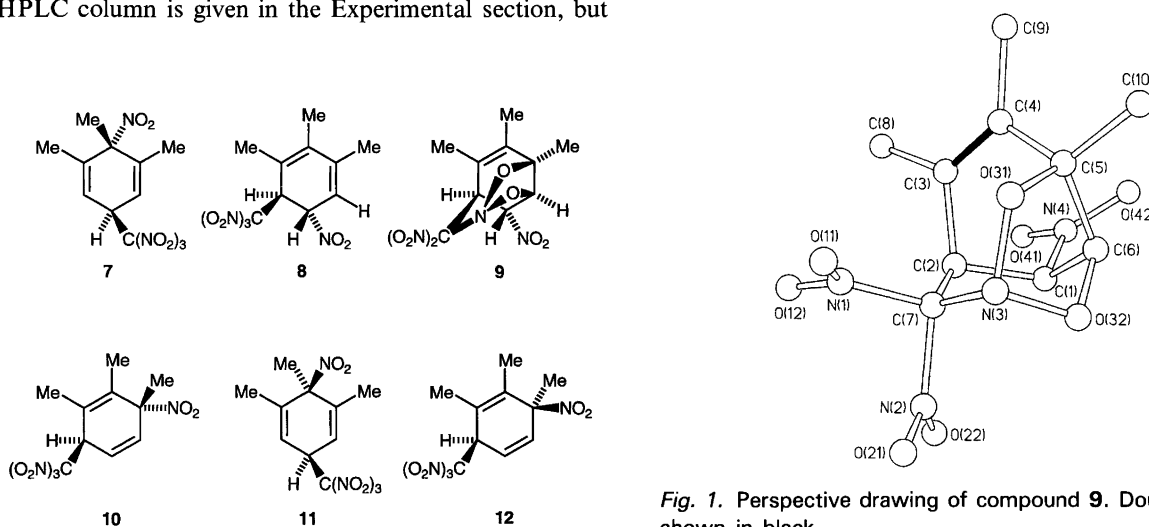


Fig. 1. Perspective drawing of compound **9**. Double bond is shown in black.

Table 3. Fractional coordinates for atoms in nitro cycloadduct (**9**).^a

Atom	10 ⁴ X/a	10 ⁴ Y/b	10 ⁴ Z/c	10 ³ U/Å ²
O(11)	7001(2)	5670(3)	2565(1)	29(1)
O(12)	5547(2)	3401(4)	2579(1)	34(1)
O(21)	8471(2)	2574(4)	3664(1)	30(1)
O(22)	7680(2)	-246(4)	4258(1)	28(1)
O(31)	8634(2)	4229(3)	1635(1)	14(1)
O(32)	9656(2)	1687(3)	2240(1)	16(1)
O(41)	6435(2)	-2612(3)	1063(1)	24(1)
O(42)	8117(2)	-1938(3)	582(1)	28(1)
N(1)	6627(2)	3995(4)	2522(1)	19(1)
N(2)	7949(2)	1465(4)	3187(1)	19(1)
N(3)	8817(2)	3301(4)	2315(1)	15(1)
N(4)	7472(2)	-1708(4)	1059(1)	19(1)
C(1)	8022(3)	-509(4)	1699(1)	14(1)
C(2)	6926(3)	839(4)	1866(1)	14(1)
C(3)	6285(3)	1781(4)	1143(2)	14(1)
C(4)	7082(3)	2520(4)	734(1)	13(1)
C(5)	8532(3)	2654(4)	1076(1)	15(1)
C(6)	9078(3)	845(4)	1540(1)	14(1)
C(7)	7577(3)	2357(4)	2415(1)	15(1)
C(8)	4820(3)	1624(5)	947(2)	20(1)
C(9)	6646(3)	3352(5)	-12(2)	18(1)
C(10)	9434(3)	3271(5)	576(2)	19(1)

^aThe equivalent isotropic temperature factor in Tables 3–9 is defined as one-third of orthogonalized U_{ij} tensor (in Å²).

ferences [C(7)–N(1) 1.532(4) Å, C(7)–N(2) 1.553(4) Å, C(7)–N(3) 1.490(4) Å] are similar to those observed earlier^{7–9} for analogous heterocyclic cage structures. The spectroscopic data for the nitrocycloadduct **9** were in accord with the established structure. The stereochemistry of the *r*-5-nitro-*t*-6-trinitromethyl system in adduct **8** is established by the observed torsional angle in nitrocycloadduct **9**, C(7)–C(2)–C(1)–N(4) = 169.3(2)°. The heterocyclic structure in nitrocycloadduct **9** is clearly formed by thermal cycloaddition of a nitro group of the trinitromethyl group with the C3–C4 alkene system in the nitro-trinitromethyl precursor **8**.

(C) 'Double' adducts, trinitro-trinitromethyl adducts **13** and **15**. The structure of trinitro-trinitromethyl adduct **13** was determined by single-crystal X-ray analysis. A perspective drawing of 1,2,3-trimethyl-*r*-3,*c*-4,*c*-6-trinitro-*t*-5-trinitromethylcyclohex-1-ene (**13**), C₁₀H₁₂N₆O₁₂, m.p. 73°C (decomp.), is presented in Fig. 2, and corresponding atomic coordinates are given in Table 4. In the solid state the alicyclic ring of **13** exists in close to a 'pure' boat conformation [torsional angles: C(1)–C(2)–C(3)–C(4) – 43.1(4)°; C(2)–C(1)–C(6)–C(5) 34.4(4)°; C(3)–C(4)–C(5)–C(6) – 21.8(4)°], with the nitro groups at C(3) and C(6) in the flagpole orientations. The planes of these nitro groups are essentially parallel to each other [torsional angles: C(4)–C(3)–N(1)–O(12) – 2.3(4)°; C(5)–C(6)–N(3)–O(31) 31.0(4)°]. The remaining stereochemistry of the trinitro-trinitromethyl adduct **13** is defined by the torsional angles: C(10)–C(5)–C(6)–N(3) – 126.0(3)°; C(10)–C(5)–C(4)–N(2) 82.8(3)°; N(1)–C(3)–C(4)–N(2) 62.8(3)°. The spectroscopic data for **13** were in accord

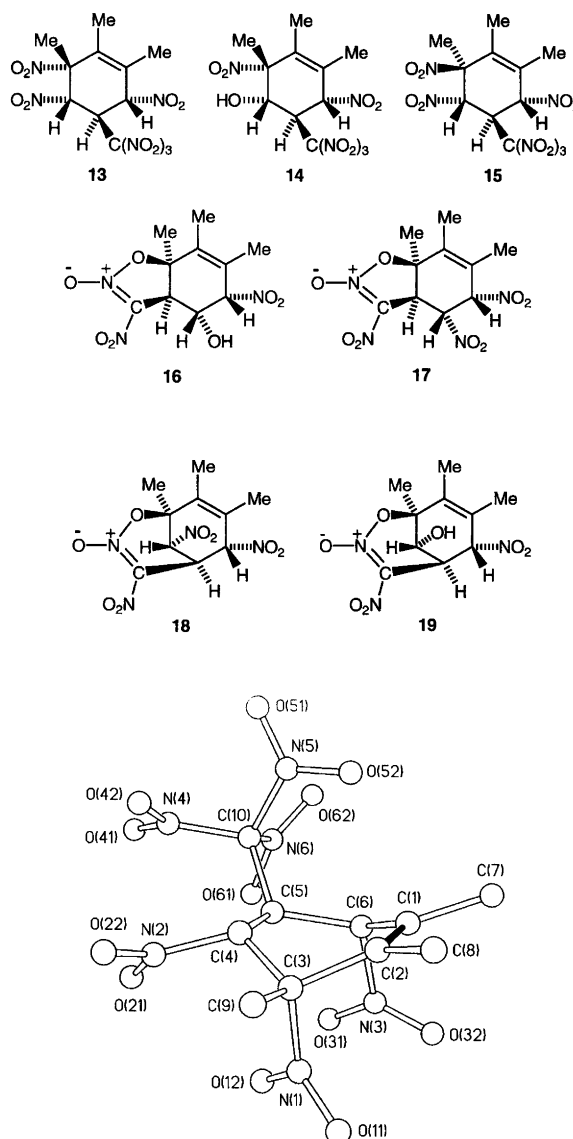


Fig. 2. Perspective drawing of compound **13**.

with the established structure. Notable among these data was the chemical shift observed for H5 (δ 6.62), remarkably deshielded for a proton *ipso* to a trinitromethyl group. A consideration of the established X-ray structure for **13** reveals the origin of this marked deshielding, H5 being 'sandwiched' between oxygen atoms, O(12), O(21), O(31) and O(61), of four proximate nitro functions.

The second trinitro-trinitromethyl adduct could not be induced to crystallize and was assigned structure **15**, epimeric with **13** at C3, on the basis of its NMR spectra. The connectivity in the structure was established by a combination of nuclear Overhauser experiments and long-range reverse-detected heteronuclear correlation spectra (HMBC, HMQC), which pointed to the presence of three nitro groups one of which was geminal to a methyl group, in addition to a trinitromethyl group. Spectroscopic data which were most informative about the

Table 4. Fractional coordinates for atoms in 1,2,3-trimethyl-*r*-3,*c*-4,*c*-6-trinitro-*t*-5-trinitromethylcyclohex-1-ene (**13**).

Atom	10 ⁴ X/a	10 ⁴ Y/b	10 ⁴ Z/c	10 ³ U/Å ²
O(11)	-126(3)	6513(2)	4394(2)	69(1)
O(12)	1820(2)	6430(2)	4112(2)	39(1)
O(21)	2819(3)	5671(2)	2383(2)	45(1)
O(22)	858(3)	4958(2)	1463(2)	51(1)
O(31)	3353(2)	8137(2)	4177(2)	37(1)
O(32)	1557(3)	8802(2)	4412(2)	55(1)
O(41)	3864(3)	6865(2)	487(2)	62(1)
O(42)	1720(2)	6336(2)	-106(2)	38(1)
O(51)	1135(3)	8199(2)	-995(2)	55(1)
O(52)	83(2)	8639(2)	162(2)	38(1)
O(61)	4391(2)	8216(2)	2178(2)	40(1)
O(62)	3185(2)	9242(2)	859(2)	44(1)
N(1)	553(3)	6516(2)	3775(2)	35(1)
N(2)	1542(3)	5670(2)	1894(2)	32(1)
N(3)	2141(3)	8415(2)	3827(2)	31(1)
N(4)	2653(3)	6903(2)	396(2)	35(1)
N(5)	1004(3)	8231(2)	-52(2)	30(1)
N(6)	3369(3)	8472(2)	1361(3)	32(1)
C(1)	-270(3)	8376(2)	2306(3)	26(1)
C(2)	-1018(3)	7582(2)	2268(3)	27(1)
C(3)	-284(3)	6604(2)	2455(3)	25(1)
C(4)	715(3)	6607(2)	1762(3)	22(1)
C(5)	1761(3)	7456(2)	1998(3)	20(1)
C(6)	1268(3)	8330(2)	2513(2)	22(1)
C(7)	-897(3)	9375(2)	2164(3)	43(1)
C(8)	-2557(3)	7605(3)	2060(3)	41(1)
C(9)	-1273(2)	5753(2)	2180(3)	39(1)
C(10)	2146(3)	7749(2)	947(3)	23(1)

stereochemistry of adduct **15** were the combination of a W-coupling between H4 and H6 ($J_{H4,H6}$ 3.9 Hz), the coupling constants $J_{H4,H5}$ 4.9 Hz and $J_{H5,H6}$ 1.0 Hz, and the absence of a significant nuclear Overhauser enhancement of H4 (δ 5.92) on irradiation of the 3-Me resonance at δ 1.74. These data point to a structure for **15** in which the alicyclic ring exists in a flattened skew boat (C1 and C2, sp^2), with the substituents at C3 and C4 eclipsed. In this conformation the C5–C(NO₂)₃ bond is close to *anti*-coplanar with the C4–NO₂ and C6–NO₂ bonds.

(D) 'Double' adduct, hydroxy-dinitro-trinitromethyl adduct **14**. The structure of the hydroxy-dinitro-trinitromethyl adduct **14** was determined for its diethyl etherate by single-crystal X-ray analysis. A perspective drawing of 2,3,4-trimethyl-*c*-2,*c*-5-dinitro-*t*-6-trinitromethylcyclohex-3-en-*r*-1-ol (**14**), C₁₄H₂₃N₅O₁₂ (**14**-diethyl etherate), m.p. 65 °C, is presented in Fig. 3, and the corresponding atomic coordinates are given in Table 5. Although the structure of **14** is identical with that of the trinitro-trinitromethyl adduct **13** except for the replacement of the 4-NO₂ group in adduct **13** by a hydroxy function in adduct **14**, the conformation of the alicyclic ring differs. While **13** exists in the solid state with the alicyclic ring in close to a 'pure' boat conformation, the ring conformation for adduct **14** is that of a slightly distorted half-chair. The spectroscopic data for adduct **14** were consistent with the established structure. The coupling constant $J_{H1,H6}$ 10.8 Hz is consistent with the torsional angle

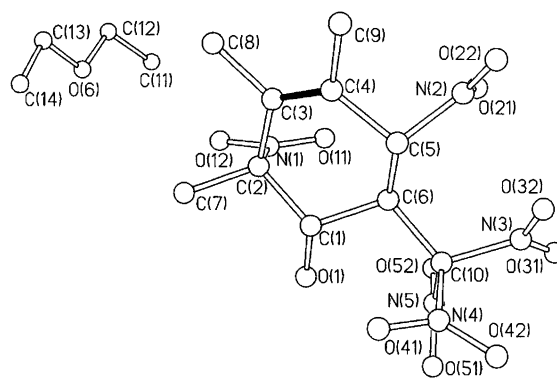


Fig. 3. Perspective drawing of compound **14**.

Table 5. Fractional coordinates for atoms in 2,3,4-trimethyl-*c*-2,*c*-5-dinitro-*t*-trinitromethylcyclohex-3-en-*r*-1-ol (**14**) diethyl etherate.

Atom	10 ⁴ X/a	10 ⁴ Y/b	10 ⁴ Z/c	10 ³ U/Å ²
O(1)	2012(3)	1611(3)	6366(3)	22(1)
O(6)	7026(3)	1330(3)	2320(4)	28(1)
O(11)	2701(1)	-310(4)	5120(4)	41(1)
O(12)	4035(4)	532(5)	5605(4)	55(2)
O(21)	1127(4)	-2330(4)	5900(4)	38(1)
O(22)	1116(3)	-2975(4)	7609(4)	38(1)
O(31)	-862(3)	-552(3)	5182(4)	33(1)
O(32)	-314(3)	-1298(3)	6911(4)	29(1)
O(41)	879(3)	1252(4)	8285(4)	30(1)
O(42)	-615(3)	863(3)	7506(4)	32(1)
O(51)	-109(3)	1958(4)	5639(4)	32(1)
O(52)	461(3)	776(4)	4608(4)	32(1)
N(1)	3331(4)	155(4)	5838(5)	28(1)
N(2)	1280(4)	-2254(4)	6975(5)	27(1)
N(3)	-304(4)	-618(4)	6150(4)	22(1)
N(4)	228(4)	844(4)	7534(4)	24(1)
N(5)	262(4)	1095(5)	5491(4)	27(1)
C(1)	2261(4)	690(4)	7114(5)	22(1)
C(2)	3261(4)	283(5)	7124(5)	23(1)
C(3)	3466(4)	-846(5)	7680(5)	25(2)
C(4)	2804(4)	-1451(5)	7985(5)	22(1)
C(5)	1739(4)	-1182(5)	7569(5)	22(1)
C(6)	1497(4)	-218(5)	6725(5)	19(1)
C(7)	3981(4)	1132(5)	7741(6)	29(1)
C(8)	4505(4)	-1199(5)	8010(6)	27(2)
C(9)	3051(5)	-2452(5)	8763(6)	31(2)
C(10)	481(4)	261(5)	6508(5)	19(1)
C(11)	6239(5)	843(6)	328(6)	36(2)
C(12)	7042(5)	571(5)	1397(6)	35(2)
C(13)	7676(5)	1017(5)	3412(5)	33(2)
C(14)	7540(5)	1766(6)	4357(6)	35(2)

H(1)–C(1)–C(6)–H(6) – 173.8° found in the X-ray crystal analysis. In addition, irradiation at δ 4.09 (H1) resulted in nuclear Overhauser enhancements of both δ 1.94 (2-Me) and δ 5.25 (*syn*-axial H5), but not at δ 4.99 (H6), consistent with the established stereochemistry and ring conformation.

(E) 'Double' adducts, nitronic esters **16–19**. The structures of the nitronic esters **18** and **19** were determined by single-crystal X-ray analysis. A perspective drawing of

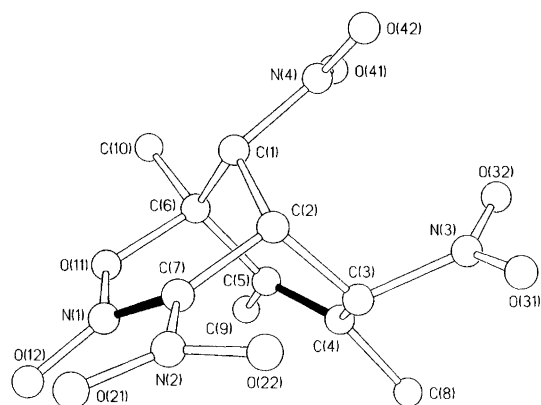


Fig. 4. Perspective drawing of compound 18.

the trinitro nitronic ester **18**, $C_{10}H_{12}N_4O_8$, m.p. 131–132.5°C, is presented in Fig. 4, and corresponding atomic coordinates are given in Table 6. Similar information is presented for the hydroxydinitro nitronic ester **19**, $C_{10}H_{13}N_3O_7$, m.p. 129°C, in Fig. 5 and Table 7. The two structures are closely similar with the most significant difference being in the orientation of the plane of the N(3)-nitro group, which presumably reflects the replacements of the C(1)–NO₂ in the trinitro nitronic ester **18** by the C(1)–OH in the hydroxydinitro nitronic ester **19**. In both structures the plane of the N(2)-nitro group is close to eclipsed with the N(1)–C(7) bond [torsional angles: N(1)–C(7)–N(2)–O(21) = 20.7(6)° for **18**; –24.4(2)° for **19**]. The spectroscopic data for **18** and **19** were in accord with the established structures.

The hydroxydinitro nitronic ester **16** and the trinitro nitronic ester **17** were assigned structures isomeric with

Table 6. Fractional coordinates for atoms in trinitro nitronic ester **18**.

Atom	10 ⁴ X/a	10 ⁴ Y/b	10 ⁴ Z/c	10 ³ U/Å ²
O(11)	907(5)	2191(2)	1869(1)	17(1)
O(12)	3552(5)	2811(2)	2237(1)	22(1)
O(21)	3347(5)	4544(2)	2415(1)	28(1)
O(22)	1881(5)	5262(2)	1798(1)	25(1)
O(31)	–809(6)	5284(2)	638(1)	34(1)
O(32)	–2463(5)	4089(2)	403(1)	28(1)
O(41)	–4483(5)	2572(2)	1023(1)	31(1)
O(42)	–4778(4)	3929(2)	1330(1)	24(1)
N(1)	1998(6)	2987(3)	1991(1)	18(1)
N(2)	2254(6)	4571(3)	2042(1)	21(1)
N(3)	–1103(6)	4471(3)	641(1)	22(1)
N(4)	–3874(6)	3194(3)	1286(1)	21(1)
C(1)	–1939(7)	3092(3)	1593(2)	15(1)
C(2)	–515(7)	3877(3)	1506(2)	14(1)
C(3)	341(7)	3894(3)	964(2)	16(1)
C(4)	715(7)	2991(3)	732(2)	16(1)
C(5)	281(7)	2233(3)	977(2)	14(1)
C(6)	–774(7)	2222(3)	1482(2)	15(1)
C(7)	1234(7)	3765(3)	1854(2)	13(1)
C(8)	1794(6)	3052(3)	237(2)	19(1)
C(9)	904(8)	1308(3)	779(2)	24(1)
C(10)	–1949(8)	1376(3)	1626(2)	24(1)

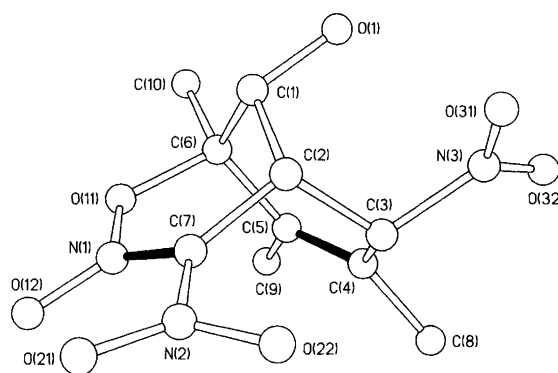


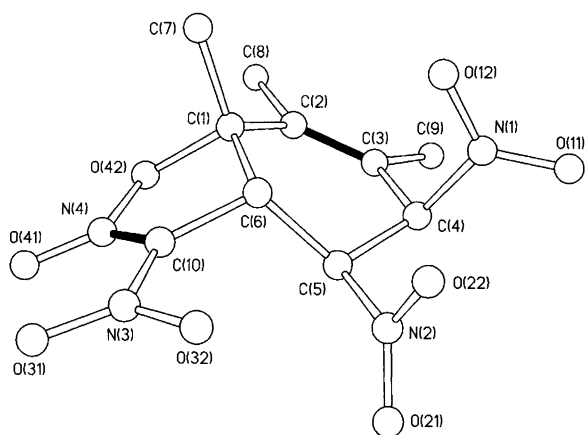
Fig. 5. Perspective drawing of compound 19.

Table 7. Fractional coordinates for atoms in trinitro nitronic ester **19**.

Atom	10 ⁴ X/a	10 ⁴ Y/b	10 ⁴ Z/c	10 ³ U/Å ²
O(1)	7433(1)	6909(1)	6835(1)	16(1)
O(11)	8456(1)	10482(1)	8190(1)	16(1)
O(12)	10236(1)	11051(1)	9151(1)	20(1)
O(21)	12072(1)	8818(2)	9498(1)	30(1)
O(22)	11163(1)	6437(2)	9514(1)	25(1)
O(31)	8611(1)	3959(1)	7786(1)	24(1)
O(32)	6625(1)	4137(2)	8212(1)	25(1)
N(1)	9612(2)	9924(2)	8740(1)	15(1)
N(2)	11138(2)	7883(2)	9301(1)	18(1)
N(3)	7760(2)	4640(2)	8181(1)	17(1)
C(1)	8312(2)	7997(2)	7353(1)	13(1)
C(2)	9146(2)	7140(2)	8156(1)	13(1)
C(3)	8183(2)	6204(2)	8704(1)	14(1)
C(4)	6999(2)	7164(2)	8927(1)	14(1)
C(5)	6707(2)	8606(2)	8532(1)	14(1)
C(6)	7472(2)	9253(2)	7777(1)	13(1)
C(7)	9908(2)	8387(2)	8744(1)	14(1)
C(8)	6248(2)	6491(2)	9678(1)	20(1)
C(9)	5626(2)	9690(2)	8816(1)	21(1)
C(10)	6619(2)	10227(2)	7050(1)	18(1)

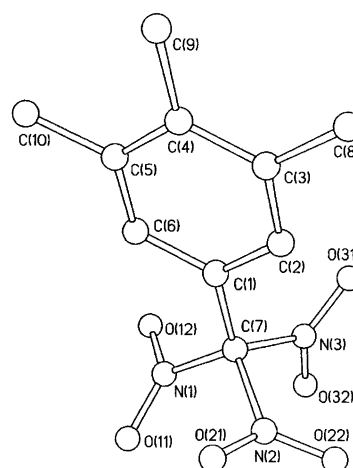
the nitronic esters **19** and **18**, respectively, above. Of the two nitronic esters, **16** and **17**, only the trinitro nitronic ester **17** gave a crystal of barely acceptable quality for attempted structure determination by single-crystal X-ray analysis. The structure of **17** was indicated by the preliminary results of a single-crystal X-ray analysis.[†] Owing to apparent disorder in the crystal involving solvent molecules, it was not possible to refine the data to a satisfactory *R* factor, but for our purpose the important features of the structure were secured. A perspective drawing of **17** is presented in Fig. 6. The spectroscopic data for **17** were in accord with the established structure. In particular, the *anti*-orientation of H(5)–C(5)–C(6)–H(6) was reflected in the coupling constant (J_{H_5, H_6} 11.7 Hz), and the *gauche* relationship of H(4) and H(5) in the coupling constant (J_{H_4, H_5} 3.5 Hz).

[†] Crystal data for a poor-quality crystal of trinitro nitronic ester **17**, $C_{10}H_{12}N_4O_8 \cdot X$ -solvate, m.p. 127°C (decomp.), $a = 8.119(3)$, $b = 9.623(2)$, $c = 10.903(2)$ Å, $\alpha = 73.501(9)$, $\beta = 74.40(1)$, $\gamma = 68.46(2)^\circ$, $V = 746.6(3)$ Å³.

Fig. 6. Perspective drawing of compound **17**.

Although it did not prove possible to obtain crystalline samples of the hydroxydinitro nitronic ester **16**, the structure of this 'double' adduct appears to be securely established from its spectroscopic data, which are closely similar to those for **17**, except for those features affected by the hydroxy/nitro replacement at C(5).[†] The connectivity in **16** was established by nuclear Overhauser experiments and the observed coupling constants. For **16**, the crucial coupling constants, $J_{H5,H6}$ 10.3 Hz, $J_{H4,H5}$ 4.4 Hz, are closely similar to those given above for **17**. The general upfield shift of all resonances in the ¹H NMR spectrum of **16**, relative to those for **17**, are as expected for the replacement of the 5-NO₂ (in **17**) by the 5-OH (in **16**).

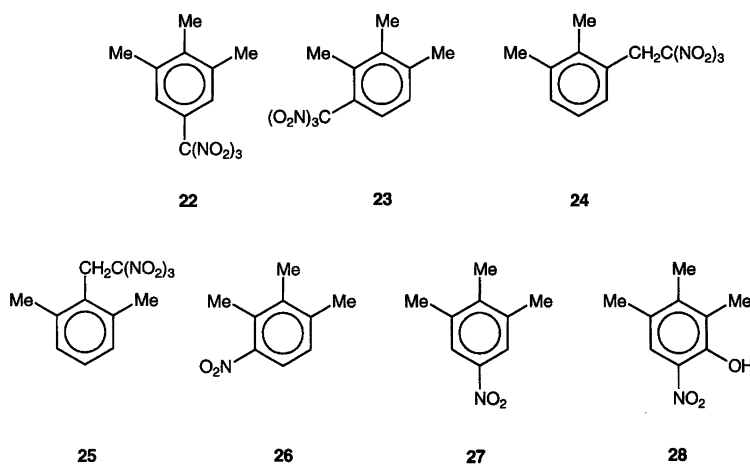
(F) *Aromatic products.* The two ring-substituted trinitromethyl aromatic compounds **22** and **23** were isolated by chromatography. The structure of the major isomer was determined by single-crystal X-ray analysis. A perspective drawing of 3,4,5-trimethyl-1-trinitromethylbenzene

Fig. 7. Perspective drawing of compound **22**.

(**22**), C₁₀H₁₁N₃O₆, m.p. 91 °C, is presented in Fig. 7, and corresponding atomic coordinates are given in Table 8. In the solid state the trinitromethyl group is orientated such that the C(7)–N(1) bond is eclipsed with the plane of the benzene ring [torsional angle: C(6)–C(1)–C(7)–N(1) – 1.6(3)°], and consequently the remaining nitro functions are close to being perfectly staggered with respect to the benzene ring. The spectroscopic data for **22** were in accord with the established structure.

The isomeric compound **23** could be isolated only in admixture with **22**, but its structure was established from a consideration of its spectroscopic data and comparison with similar data for its isomer **22**.

The isomeric side-chain trinitromethyl aromatic compounds **24** and **25** could be isolated only in low yields, and even then compound **25** was obtained only in admixture with its isomer **24**. The structure of the unsymmetrical 2,3,-dimethyl-1-(2',2',2'-trinitroethyl)benzene **24** rests on an accurately measured mass spectrum giving



[†] For convenience, the numbering system used for compounds **16** and **17** is that given in Fig. 6 for compound **17**.

Table 8. Fractional coordinates for atoms in 3,4,5-trimethyl-1-trinitromethylbenzene (**22**).

Atom	$10^4 X/a$	$10^4 Y/b$	$10^4 Z/c$	$10^3 U/\text{\AA}^2$
O(11)	7886(2)	-1447(3)	4961(1)	53(1)
O(12)	8550(2)	1247(3)	4818(1)	36(1)
O(21)	6450(2)	-2932(3)	3592(1)	48(1)
O(22)	4688(2)	-1166(3)	3588(1)	46(1)
O(31)	5821(2)	2721(3)	3292(1)	52(1)
O(32)	5590(2)	1828(3)	4474(1)	44(1)
N(1)	7872(2)	-74(3)	4596(1)	30(1)
N(2)	5928(2)	-1502(3)	3649(1)	29(1)
N(3)	6040(2)	1715(3)	3852(2)	31(1)
C(1)	7806(3)	139(3)	3114(2)	22(1)
C(2)	7085(3)	156(3)	2327(2)	23(1)
C(3)	7803(3)	170(3)	1693(2)	24(1)
C(4)	9290(3)	142(3)	1840(2)	26(1)
C(5)	10015(3)	115(3)	2628(2)	25(1)
C(6)	9272(3)	111(3)	3259(2)	24(1)
C(7)	6975(3)	75(3)	3772(2)	24(1)
C(8)	6980(3)	240(4)	854(2)	35(1)
C(9)	10077(3)	127(4)	1148(2)	36(1)
C(10)	11607(3)	84(4)	2815(2)	35(1)

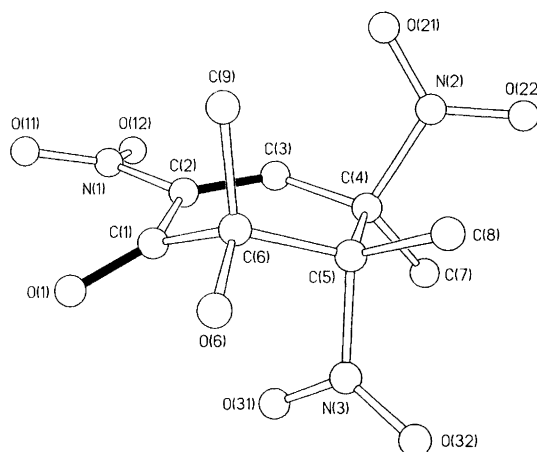


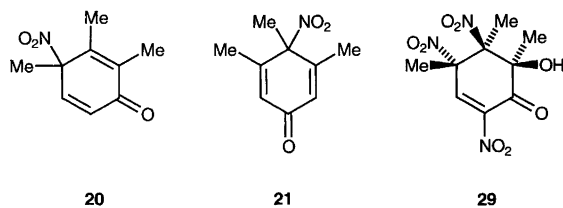
Fig. 8. Perspective drawing of compound **29**.

the molecular formula $C_{10}H_{11}N_3O_6$, and the 1H NMR spectrum, which revealed two methyl signals at δ 2.29 and 2.33, and a signal due to the $CH_2-C(NO_2)_3$ at δ 5.52. For isomer **25**, as expected from the structure, the signals due to the two methyl groups appeared at δ 2.41 and the signal due to the $CH_2-C(NO_2)_3$ at δ 5.57.

The remaining aromatic compounds, substituted nitrobenzenes **26** (Ref. 10) and **27** (Ref. 10), and the nitrophenol **28** (Ref. 11), were identified by comparison of their spectroscopic data with those for authentic materials. Nitrobenzenes **26** and **27** were present among the products throughout the photolysis reaction, but the nitrophenol **28**, while present in the early stages was absent from the product mixture finally isolated.

(G) Nitroketones **20**, **21** and **29**. The nitroketones **20**¹² and **21**¹³ were present in small quantities in the product mixture prior to separation, and were partially separated by HPLC. Compound **20** was obtained only in admixture with the nitro-trinitromethyl adduct **12**, but a small amount of nitrodienone **21** was obtained in a pure state. These compounds were identified by comparison with authentic samples and literature data.

The hydroxytrinitroketone **29** was not present in the product mixture prior to HPLC separation, but did appear in low yield among the materials eluted from the cyanopropyl HPLC column. The structure of **29** was de-



termined by single-crystal X-ray analysis. A perspective drawing of *t*-6-hydroxy-4,5,6-trimethyl-2,*r*-4,*t*-5-trinitrocyclohex-2-enone (**29**), $C_9H_{11}N_3O_8$, m.p. 121–123°C, is presented in Fig. 8, and the corresponding atomic coordinates are given in Table 9. In the solid state the alicyclic ring of the hydroxytrinitroketone **29** exists in a flattened [C(1) sp^2] skew boat form [torsional angles: C(3)–C(2)–C(1)–C(6) 26.9(2); C(2)–C(3)–C(4)–C(5) –8.1(2)°]. The orientations of the planes of the three nitro groups relative to their surroundings are indicated by the following torsional angles: O(12)–N(1)–C(2)–C(3) 19.7(2)°; O(22)–N(2)–C(4)–C(7) –31.0(2)°; O(32)–N(3)–C(5)–C(8) –4.4(2)°. The substituents around the C(4)–C(5) bond are imperfectly staggered [torsional angles: C(7)–C(4)–C(5)–C(8) 86.1(2)°; N(2)–C(4)–C(5)–N(3) –148.5(1)°], and the C(6)–O(6) bond is close to eclipsed with the C(1)–O(1) bond, which coupled with a

Table 9. Fractional coordinates for atoms in *t*-6-hydroxy-4,5,6-trimethyl-2,*r*-4,*t*-5-trinitrocyclohex-2-enone (**29**).

Atom	$10^4 X/a$	$10^4 Y/b$	$10^4 Z/c$	$10^3 U/\text{\AA}^2$
O(1)	4824(2)	108(1)	1672(2)	24(1)
O(6)	6662(2)	-1052(1)	1573(2)	21(1)
O(11)	1033(2)	559(1)	1030(2)	33(1)
O(12)	-457(2)	314(1)	3017(2)	28(1)
O(21)	230(2)	-1946(1)	1995(2)	28(1)
O(22)	151(2)	-2528(1)	4105(2)	33(1)
O(31)	6157(2)	-637(1)	4880(2)	24(1)
O(32)	7650(2)	-1569(1)	5223(2)	32(1)
N(1)	798(2)	216(1)	2196(2)	20(1)
N(2)	1368(2)	-2026(1)	3302(2)	20(1)
N(3)	6303(2)	-1220(1)	4572(2)	20(1)
C(1)	3966(3)	-373(1)	1995(2)	16(1)
C(2)	2082(3)	-359(1)	2588(2)	14(1)
C(3)	1505(3)	-842(1)	3438(2)	16(1)
C(4)	2711(3)	-1441(1)	3974(2)	16(1)
C(5)	4640(3)	-1511(1)	3245(2)	16(1)
C(6)	4678(2)	-1065(1)	1725(2)	16(1)
C(7)	3066(3)	-1492(1)	5847(2)	21(1)
C(8)	5193(3)	-2214(1)	2945(2)	21(1)
C(9)	3371(3)	-1324(1)	146(2)	19(1)

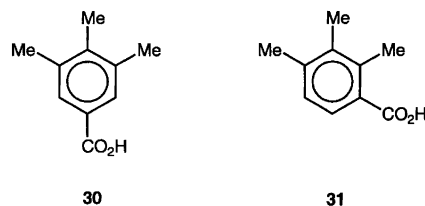
O(1)···O(6) distance of 2.697 Å is probably indicative of intramolecular hydrogen bonding in the solid state.

Photochemistry in dichloromethane at -20 and -50°C. Reaction of 1,2,3-trimethylbenzene (0.52 mol dm⁻³) and tetranitromethane (1.04 mol dm⁻³) in dichloromethane, as above, was carried out at -20 and -50°C (Table 1). Notable at lower reaction temperatures was the partial (-20°C) or complete (-50°C) suppression of the formation of 'double' adducts **13**–**19**, and the prevention of the thermal intramolecular cycloaddition of the nitro-trinitromethyl adduct **8** to give the nitro cycloadduct **9**.

Photochemistry in acetonitrile at 20, -20 and -50°C. Reaction of 1,2,3-trimethylbenzene (0.52 mol dm⁻³) and tetranitromethane (1.04 mol dm⁻³) in acetonitrile, as above, was carried out at 20, -20 and -50°C. The composition of the mixture was monitored by withdrawing samples for NMR spectral analysis (Table 2). In acetonitrile a similar pattern of reactivity is evident except that 'double' adducts **13**–**15** and **17** were not seen at any reaction temperature, and traces of the two carboxylic acids **30** and **31** were formed at 20°C.

Photochemistry in dichloromethane at 20°C in the presence of trifluoroacetic acid. Reaction of 1,2,3-trimethylbenzene (0.52 mol dm⁻³) and tetranitromethane (1.04 mol dm⁻³) in dichloromethane, as above except for the addition of trifluoroacetic acid (1.04 mol dm⁻³), was carried out at 20°C. The composition of the mixture was monitored by withdrawing samples for NMR spectral analysis (Table 10). The products formed after 8 h were 3,4,5-trimethyl-1-trinitromethylbenzene (**22**) (62%), 2,3,4-trimethyl-1-trinitromethylbenzene (**23**) (11%), 3,4,5-trimethylbenzoic acid (**30**) (5%), 2,3,4-trimethylbenzoic acid (**31**) (2%) and some unidentified material (20%). The two carboxylic acids **30**¹⁴ and **31**¹⁵ were isolated by HPLC and identified by comparison with literature data.

A similar reaction to the above, but with trifluoroacetic acid (2.08 mol dm⁻³) gave a mixture of 3,4,5-trimethyl-



1-trinitromethylbenzene (**22**) (20%), 2,3,4-trimethyl-1-trinitromethylbenzene (**23**) (11.5%), 3,4,5-trimethylbenzoic acid (**30**) (10%), 2,3,4-trimethylbenzoic acid (**31**) (4.5%), and some unidentified material (34%) (Table 10).

Discussion

The reactivity of trinitromethanide ion with the radical cation of 1,2,3-trimethylbenzene. From the results reported above it is clear that in the photolysis of the charge-transfer complex of tetranitromethane (1.04 mol dm⁻³) and 1,2,3-trimethylbenzene (0.52 mol dm⁻³) the reactivity of the radical cation of 1,2,3-trimethylbenzene towards trinitromethanide ion is high. Even in the presence of trifluoroacetic acid (1.04 mol dm⁻³) the trinitromethyl aromatic compounds **22** and **23** were formed in high yield (total ca. 86% after 1 h; Table 10) indicating that coupling of trinitromethanide ion with the radical cation of 1,2,3-trimethylbenzene was more than competitive with protonation of trinitromethanide ion. Even at a higher trifluoroacetic acid concentration (2.08 mol dm⁻³) trinitromethyl aromatic products **22** and **23** predominated (total 63% after 1 h) over the products **26** and **27** (total 10.5%) of the slower radical coupling of the radical cation with nitrogen dioxide. These preparative results are consistent with the absence of detectable EPR signals on irradiation at λ > 435 nm of 1,2,3-trimethylbenzene in dichloromethane solution at -60°C in the presence of (i) tetranitromethane, (ii) tetranitromethane and trifluoroacetic acid, or (iii) trifluoroacetic acid.³

The general pattern of products formed on photolysis of the charge transfer complex of tetranitromethane with 1,2,3-trimethylbenzene. The complete details of yields of reaction products in dichloromethane and acetonitrile solution at 20, -20 and -50°C are given in Tables 1 and 2, and a summary in terms of 'product type' are given in Table 11. Here the term 'single' adducts refers to those products formed by a single addition of the elements of tetranitromethane to 1,2,3-trimethylbenzene, while the term 'double' adducts refers to products derived by some form of extramolecular addition to initially formed 'single' adducts. The details of these processes will be discussed below.

Some general features of the results summarized in Table 11 are worthy of comment. First, it is clear that the incidence of the formation of 'double' adducts is markedly temperature dependent in both dichloromethane and

Table 10. Overview of yields of products from the photolysis of 1,2,3-trimethylbenzene (0.52 mol dm⁻³) and tetranitromethane (1.04 mol dm⁻³) at 20 °C in dichloromethane containing trifluoroacetic acid

t/h	Yield (%)						Unidentified
	22	23	30	31	26	27	
Trifluoroacetic acid (1.04 mol dm ⁻³)							
1	71.4	14.3	—	—	—	—	14.3
4	63.9	12.0	1.9	trace	—	—	22.2
8	62.2	10.5	5.0	2.1	—	—	20.2
Trifluoroacetic acid (2.08 mol dm ⁻³)							
1	50.0	13.2	—	—	7.9	2.6	26.3
4	28.4	9.7	5.8	5.0	9.1	6.8	35.2
8	20.1	11.6	9.8	4.5	11.2	8.8	34.0

Table 11. Yields of product types from the photolysis of 1,2,3-trimethylbenzene and tetranitromethane.

t/h	Yield (%)				Identified aromatics
	'Single' adducts	'Double' adducts	Total adducts	Dienones etc.	
Dichloromethane at 20 °C					
1	29.7	16.4	47.1	1.9	51.0
4	35.0	24.3	60.7	1.2	38.1
8	30.3	25.5	57.1	0.6	39.3
Dichloromethane at -20 °C					
1	20.2	1.3	36.1	5.2	58.7
4	19.5	1.5	33.0	3.5	63.0
8	22.2	2.5	32.9	3.5	63.6
Dichloromethane at -50 °C					
1	17.2	—	26.1	7.1	66.8
4	29.2	—	37.5	8.9	53.6
8	30.1	—	38.7	12.8	48.5
Acetonitrile at 20 °C					
1	15.9	5.7	23.3	2.1	74.6
4	17.6	7.1	26.4	3.2	70.4
8	15.1	10.0	26.6	2.0	71.4
Acetonitrile at -20 °C					
1	16.3	1.2	27.1	7.1	65.8
4	13.8	1.7	22.2	7.3	70.5
8	11.1	0.9	13.2	5.2	81.6
Acetonitrile at -50 °C					
1	18.2	—	23.6	19.3	57.1
4	22.9	—	29.0	20.6	50.4
8	25.7	0.6	31.2	13.1	55.7

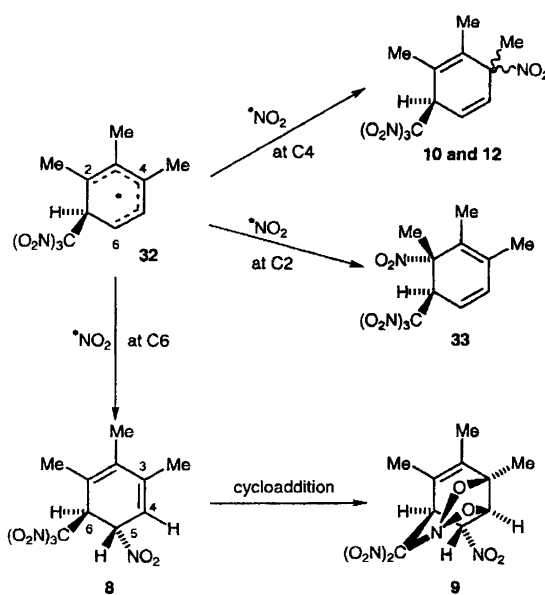
^aIncluding 4,5,6-trimethyl-2-nitrophenol **28**.

acetonitrile, implying a thermal addition process subsequent to the initial photochemical addition of the elements of tetranitromethane to 1,2,3-trimethylbenzene to form 'single' adducts. These thermal additions appear to be initiated by attack, with C–N bond formation, of the somewhat electrophilic nitrogen dioxide (freely available in the photolysis of ArH–tetranitromethane solutions)¹⁶ on 5-trinitromethyl-6-X-cyclohexa-1,3-dienes (where X = OH or NO₂). Consistent with this conclusion is the observation that the 'double' adducts formed at lower reaction temperatures are those derived from 5-trinitromethyl-6-hydroxycyclohexa-1,3-dienes, where the electron availability in the diene system might be expected to be higher than in the corresponding 5-trinitromethyl-6-nitro derivatives.

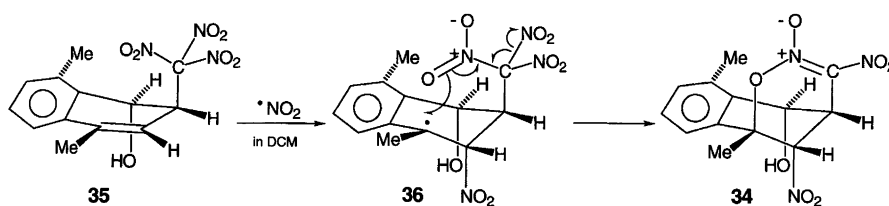
A number of trends in yields of product 'types' with reaction temperature and solvent are evident in Tables 1, 2 and 11. In dichloromethane the yields (at 1 h reaction time) of the ring-substituted trinitromethyl aromatic compounds **22** and **23** increase steadily with decreasing reaction temperature [41.6% (20 °C), 51.3% (-50 °C)].

Correspondingly the yields of the side-chain trinitromethyl compounds **24** and **25**, which are probably derived by photochemically promoted decomposition of nitro–trinitromethyl adducts, also rise with decreasing reaction temperature [5.6% (20 °C), 11.8% (-50 °C)]. In contrast, in acetonitrile the yields of ring-substituted trinitromethyl aromatic compounds **22** and **23** decrease markedly with lower reaction temperatures [66.0% (20 °C), 14.3% (-50 °C)]; and the yields of the side-chain trinitromethyl compounds **24** and **25** rise appreciably [3.4% (20 °C), 28.8% (-50 °C)]. Only in acetonitrile at lower reaction temperatures do the combined yields of the mononitro aromatic compounds **26** and **27** become appreciable [14.0% at -50 °C]. In both dichloromethane and acetonitrile solution the trend appears to be towards higher yields of the two dienones **20** and **21**, and rearrangement product **28** with lower reaction temperatures.

*Some consequences of initial trinitromethanide ion attack at C4 of the radical cation of 1,2,3-trimethylbenzene: the formation of 'single' adducts **8**, **10** and **12**, and cycloadduct **9**.* Attack of trinitromethanide ion at C4 of the radical cation of 1,2,3-trimethylbenzene would give the delocalized carbon radical **32** (Scheme 1). Subsequent coupling of this neutral radical **32** with nitrogen dioxide at C4 would yield the epimeric 1,2,3-trimethyl-3-nitro-6-trinitromethylcyclohexa-1,4-dienes **10** and **12**, which appear to be relatively stable species. In the radical coupling of nitrogen dioxide at C6 in **32**, only the *trans* isomer **8** is formed because of the extensive shielding of the *syn*-face of the system by the bulky trinitromethyl group, itself forced from the plane of the carbon ring system by steric interaction with the adjacent methyl group.



Scheme 1.



Scheme 2.

No products were detected which could be definitively associated with radical coupling of nitrogen dioxide at C2 in **32**, but it seems possible that 2,3,4-trimethyl-1-trinitromethylbenzene (**23**), isolated from reactions even at -50°C , is formed by photochemical decomposition of the highly sterically compressed adduct **33**.

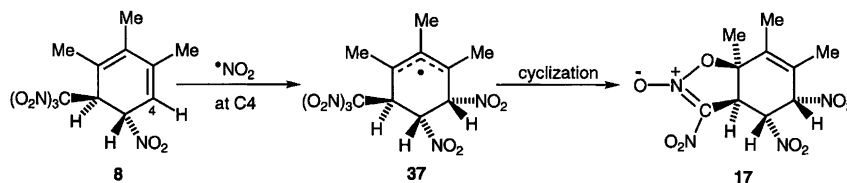
The 5-nitro-6-trinitromethylcyclohexa-1,3-diene **8** undergoes internal cycloaddition of a nitro group of the trinitromethyl function with 3,4-alkene system to give the nitrocycloadduct **9**. This cycloaddition is clearly in competition with the formation of the nitronic ester **17**, the formation of which is initiated by attack of nitrogen dioxide at C4 of **8**.

Some consequences of initial trinitromethanide ion attack at C4 of the radical cation of 1,2,3-trimethylbenzene: the formation of nitronic esters 16 and 17. Although no direct evidence has been obtained on the mode of formation of the nitronic ester **17** from **8**, its genesis is closely analogous to the quantitative formation of nitronic ester **34** on reaction of the hydroxytrinitromethyl alkene **35** with nitrogen dioxide in dichloromethane solution in the absence of light (Scheme 2).¹ Formally, the attack of nitrogen dioxide on an alkene system gives a carbon radical **36** which interacts with the proximate trinitromethyl group leading to cyclization and extrusion of a molecule of nitrogen dioxide from the former trinitromethyl group, yielding the nitro nitronic ester **34**. In the present situation, attack of nitrogen dioxide at C4 of the methylated buta-1,3-diene system of **8** would give the delocalized car-

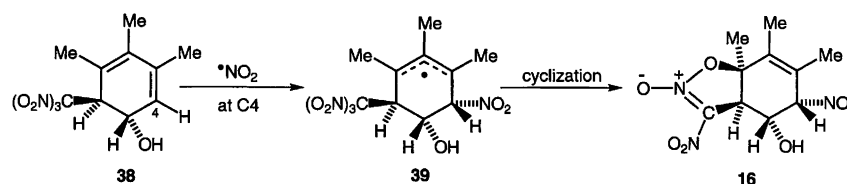
bon radical **37** (Scheme 3). Cyclization and extrusion of a molecule of nitrogen dioxide from this radical **37** would yield the trinitro nitronic ester **17**.

Although the 5-hydroxy-6-trinitromethylcyclohexa-1,3-diene **38** was not detected in the present study, it is clear that **16** is likely to have been formed via **39** by the analogous reaction pathway given in Scheme 4. The attack by NO_2 *cis* to the hydroxy group is presumably aided by hydrogen bonding.¹⁷ The inherently higher reactivity towards NO_2 of the buta-1,3-diene system in the hydroxy precursor **38**, compared with that of the nitro precursor **8**, accounts for the observation that **16** is formed even at low reaction temperatures.

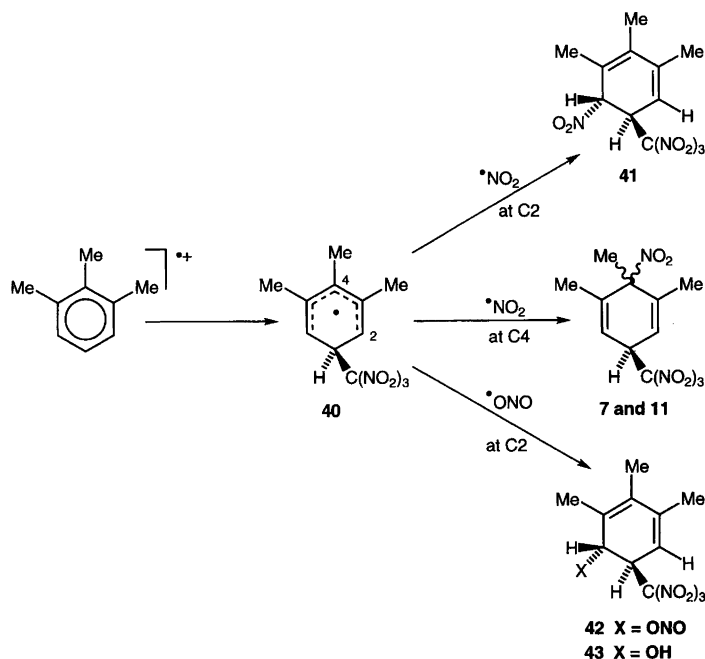
Some consequences of initial trinitromethanide ion attack at C5 of the radical cation of 1,2,3-trimethylbenzene: the formation of 'single' adducts 7 and 11. Attack of trinitromethanide ion at C5 in the radical cation of 1,2,3-trimethylbenzene would give the delocalized carbon radical **40** (Scheme 5). Subsequent coupling **40** with nitrogen dioxide at C4 would yield the epimeric 2,3,4-trimethyl-3-nitro-6-trinitromethylcyclohexa-1,4-dienes **7** and **11**, which were found to be relatively labile, decomposing on attempted crystallization to give the 3,4,5-trimethyl-1-trinitromethylbenzene **22**. Although it is clear that coupling of nitrogen dioxide occurs also at C2(C6), and with initial C- NO_2 and C-ONO bond formation yielding adducts **41** and **42**, respectively, neither of these adducts nor the hydroxy adduct **43** formed on hydrolysis of the nitrite ester **42** was isolated from the photolysis reactions. As



Scheme 3.



Scheme 4.



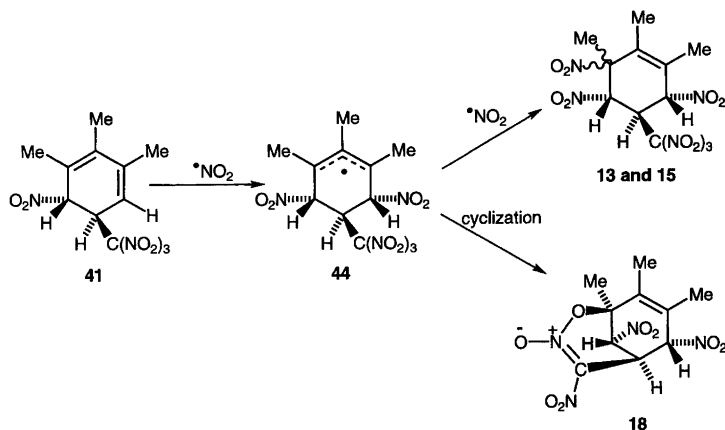
Scheme 5.

will be seen in the next section these adducts, **41** and **43**, are intermediates in the formation of 'double' adducts **13**, **14** and **18**, and the two nitronic esters **18** and **19**.

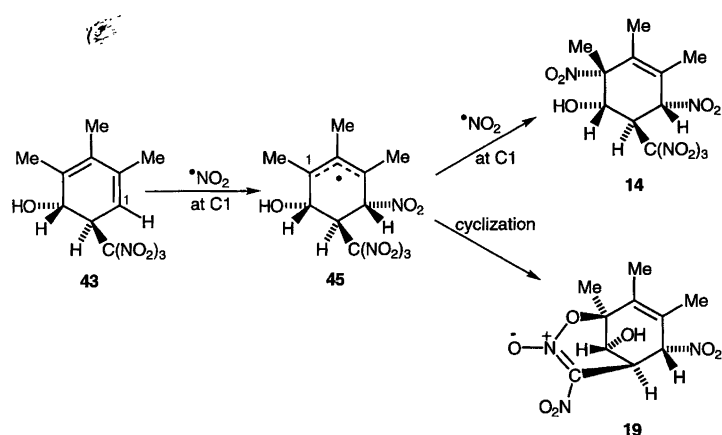
Some consequences of initial trinitromethanide ion attack at C5 of the radical cation of 1,2,3-trimethylbenzene: the formation of 'double' adducts **13** and **15**, and trinitro nitronic ester **18**. Reaction of 2,3,4-trimethyl-5-nitro-6-trinitromethylcyclohexa-1,3-diene (**41**) with nitrogen dioxide at C1 would give the carbon radical **44**, the stereochemistry of which is determined by the entry of the nitrogen dioxide molecule *anti* to the bulky trinitromethyl group. Further coupling of this carbon radical with nitrogen dioxide at either terminus of the allylic system gives the epimeric trinitro-trinitromethyl adducts **13** and **15**. Alternatively, cyclization involving the trinitromethyl

group can occur with concomitant extrusion of nitrogen dioxide to give the trinitro nitronic ester **18**.

Some consequences of initial trinitromethanide ion attack at C5 of the radical cation of 1,2,3-trimethylbenzene: the formation of 'double' adduct **14** and hydroxy dinitro nitronic ester **19**. The modes of formation of 'double' adduct **14** and hydroxy dinitro nitronic ester **19** are closely analogous to those for the trinitro-trinitromethyl adducts **13** and **15**, and the trinitro nitronic ester **18**. Addition of nitrogen dioxide at C1 in the hydroxy-trinitromethyl adduct **43** (Scheme 7) would give the radical **45**, the stereochemistry of this addition being determined as for delocalized radical **44**, above. Subsequent attack of nitrogen dioxide at C1 in this allylic radical **45** occurs *vicinal* and *syn* to the hydroxyl group in the system, in keeping with



Scheme 6.



Scheme 7.

earlier observations of the stereochemistry of the C5-addition of nitrogen dioxide to 6-hydroxy-6-methylcyclohexa-2,4-dienone system.¹⁸ The alternative reaction pathway for further reaction of the allylic radical **45** results from cyclization involving the trinitromethyl group and extrusion of nitrogen dioxide from that functional group to give the hydroxy dinitro nitronic ester **19**.

Experimental

Melting points are uncorrected. Infrared spectra were recorded on a Perkin Elmer 1600 series FTIR spectrometer; ¹H NMR spectra were recorded on a Varian Unity 300 spectrometer with SiMe₄ as an internal standard. Tetranitromethane and 1,2,3-trimethylbenzene were purchased from Aldrich. Dichloromethane (AR) and acetonitrile (HiPerSolv) were from BDH. EPR spectra were recorded by the Upgrade version ESP 3220-200SH of a Bruker ER-200D spectrometer. Photolyses were performed at -60 °C in the photolysis cavity (ER 4104 OR), using unfiltered light from the 50 W high-pressure Hg lamp from Bruker (ER 202).

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.¹⁹

General procedure for the photonitration of 1,2,3-trimethylbenzene (6) with tetranitromethane. A solution of 1,2,3-trimethylbenzene (**6**) (500 mg, 0.52 mol dm⁻³) and tetranitromethane (1.04 mol dm⁻³) in dichloromethane (at 20, -20 °C or -50 °C) or acetonitrile (20, -20 or -50 °C) was irradiated with filtered light ($\lambda_{\text{cut-off}} = 435$ 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).

Reaction in dichloromethane at 20 °C and the identification of the products. Reaction of 1,2,3-trimethylbenzene-tetranitromethane in dichloromethane at 20 °C, as above, for 8 h gave a product which was shown by ¹H NMR spectra to be a mixture (Table 1) of adducts **7–19** (total 56%), nitro dienones (**20**) (trace) and (**21**) (0.5%), 3,4,5-trimethyl-1-trinitromethylbenzene (**22**) (27%), 2,3,4-trimethyl-1-trinitromethylbenzene (**23**) (11%), minor amounts of the 2',2',2'-trinitroethyl compounds **24** and **25**, 2,3,4-trimethyl-1-nitrobenzene (**26**) (3%), 3,4,5-trimethyl-1-nitrobenzene (**27**) (1%). 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 **22**, **23** and **26–28**, which was separated into its components by chromatography on a silica gel Chromatotron plate (see below).

1,5,6-Trimethyl-t-6-nitro-r-3-trinitromethylcyclohexa-1,4-diene (7) as an impure oil [decomposed to give 3,4,5-trimethyl-1-trinitromethylbenzene (**22**) on attempted crystallization]. IR: ν_{max} (liquid film) 1613, 1586, 1550 cm⁻¹. ¹H NMR (CDCl₃): δ 1.77 (s, 6-Me), 1.82 (br s, 1-Me, 5-Me), 4.74 (br s, H3), 5.82 (d, $J_{\text{H2,H3}} = J_{\text{H4,H3}}$ 3.4 Hz, H2, H4). ¹³C NMR (CDCl₃): δ 18.5 (1-Me, 5-Me), 22.5 (6-Me), 43.2 (C3), 117.2 (C2, C4), 140.9 (C1, C5), resonances for C(NO₂)₃ and C3 not observed in a weak spectrum. The above assignments were confirmed by long-range reverse-detected heteronuclear correlation spectra (HMBC, HMQC).

5-Nitro-6-trinitromethylcyclohexa-1,3-diene (8) isolated only in admixture with adducts (**7**) and (**10**), and traces of nitro cycloadduct (**9**). ¹H NMR (CDCl₃) δ 1.78 (br s, 3-Me), 1.82 (br s, 2-Me), 1.90 (br s, 1-Me), 5.11 (br s, H4), 5.36 (d, $J_{\text{H5,H6}}$ 6.8 Hz, H5), 5.60 (d, $J_{\text{H6,H5}}$ 6.8 Hz, H6). Nuclear Overhauser experiments gave the following results: irradiation at δ 1.78 gave an enhancement at δ 5.11 (5.0%); irradiation at δ 1.90 gave an enhancement at δ 5.60 (5.3%); irradiation at δ 5.11 gave enhancements at δ 1.78 (0.5%) and at δ 5.36 (2.5%); irradiation at δ

5.36 gave enhancements at δ 5.11 (1.3%) and at δ 5.60 (2.6%); irradiation at δ 5.60 gave enhancements at δ 1.90 (0.3%) and at δ 5.36 (4.8%). The structure of the nitro-trinitromethyl adduct (**8**) was further confirmed by its thermal cycloaddition in ^2H -chloroform to give the nitro cycloadduct (**9**), the structure of which is established below.

1,2,3-Trimethyl-r-3-nitro-t-6-trinitromethylcyclohexa-1,4-diene (**10**) isolated as an oil containing an impurity (5%). IR: ν_{max} (liquid film) 1615, 1603, 1575, 1551 cm^{-1} . ^1H NMR (CDCl_3) δ 1.74 (s, 3-Me), 1.75 (q, $J_{2\text{-Me},1\text{-Me}}$ 1.0 Hz, 2-Me), 1.81 (q, $J_{1\text{-Me},2\text{-Me}}$ 1.0 Hz, 1-Me), 4.89 (br s, H6), 6.19–6.27 (m, H4, H5). Nuclear Overhauser experiments gave the following results: irradiation at δ 1.74 gave an enhancement at δ 6.21 (2.0%); irradiation at δ 1.81 gave an enhancement at δ 4.89 (2.9%); irradiation at δ 4.89 gave enhancements at δ 1.81 (0.9%) and at δ 6.24 (3.9%); irradiation at δ 6.21 gave an enhancement at δ 1.74 (0.4%); irradiation at δ 6.24 gave an enhancement at δ 4.89 (5.4%). ^{13}C NMR (CDCl_3) δ 15.3 (2-Me), 17.2 (1-Me), 25.4 (3-Me), 47.6 (C6), 88.8 (C3), 121.7 (C4), 123.2 (C1), 135.4 (C2), 135.5 (C5), the resonance for $\text{C}(\text{NO}_2)_3$ was not observed. The above assignments were confirmed by long-range reverse-detected heteronuclear correlation spectra (HMBC, HMQC).

2,3-Dimethyl-1-(2',2',2'-trinitroethyl)benzene (**24**) isolated as an oil (insufficient for elemental analysis. Found: $M^+ \cdot$, 269.06463. $\text{C}_{10}\text{H}_{11}\text{N}_3\text{O}_6$ requires 269.06479). ^1H NMR (CDCl_3) δ 2.29 (s, 2- or 3-Me), 2.33 (s, 3- or 2-Me), 5.52 (s, CH_2), 7.13–7.24 (m, H4, H5, H6).

2,6-Dimethyl-1-(2',2',2'-trinitroethyl)benzene (**25**) isolated only in admixture with its isomer (**24**). ^1H NMR (CDCl_3) (by subtraction) δ 2.41 (s, 2- and 6-Me), 5.57 (s, CH_2), 7.06–7.37 (m, H4, H5, H6).

1,5,6-Trimethyl-c-6-nitro-r-3-trinitromethylcyclohexa-1,4-diene (**11**) m.p. 45°C (decomp.) (insufficient for elemental analysis; parent ion not visible in the mass spectrum under a variety of experimental conditions). IR: ν_{max} (liquid film) 1595, 1544 cm^{-1} . ^1H NMR (CDCl_3) δ 1.77 (s, 6-Me), 1.83 (br s, 1-Me, 5-Me), 4.61 (br s, H3), 5.75 (d, $J_{\text{H}_2,\text{H}_3} = J_{\text{H}_4,\text{H}_3}$ 2.4 Hz, H2, H4). Nuclear Overhauser experiments gave the following results: irradiation at δ 4.61 gave an enhancement at δ 5.75 (1.6%); irradiation at δ 5.75 gave enhancements at δ 1.83 (0.9%) and at δ 4.61 (3.8%). ^{13}C NMR (CDCl_3) δ 18.4 (1-Me, 5-Me), 21.9 (6-Me), 42.0 (C3), 90.0 (C6), 116.8 (C2, C4), 139.7 (C1, C5), the resonance for $\text{C}(\text{NO}_2)_3$ was not observed. The above assignments were confirmed by long range reverse detected heteronuclear correlation spectra (HMBC, HMQC).

1,2,3-Trimethyl-r-3-nitro-c-6-trinitromethylcyclohexa-1,4-diene (**12**) m.p. 72°C (decomp.) (insufficient for elemental analysis; parent ion not visible in mass spectrum under a

variety of experimental conditions). IR: ν_{max} (KBr) 1604, 1575, 1546 cm^{-1} . ^1H NMR (CDCl_3) δ 1.77 (s, 3-Me), 1.81 (q, $J_{1\text{-Me},2\text{-Me}}$ 1.0 Hz, 1-Me), 1.89 (q, $J_{2\text{-Me},1\text{-Me}}$ 1.0 Hz, 2-Me), 4.79 (br s, H6), 6.24 (dd, $J_{\text{H}_5,\text{H}_4}$ 10.3 Hz, $J_{\text{H}_5,\text{H}_6}$ 3.9 Hz, H5), 6.30 (dd, $J_{\text{H}_4,\text{H}_5}$ 10.3 Hz, $J_{\text{H}_4,\text{H}_6}$ 1.0 Hz, H4). Nuclear Overhauser experiments gave the following results: irradiation at δ 1.77 gave an enhancement at δ 6.30 (3.9%); irradiation at δ 1.81 gave an enhancement at δ 4.79 (3.4%); irradiation at δ 4.79 gave enhancements at δ 1.81 (0.4%) and at δ 6.24 (1.1%); irradiation at δ 6.24 gave an enhancement at δ 4.79 (1.8%); irradiation at δ 6.30 gave an enhancement at δ 1.77 (0.6%). ^{13}C NMR (CDCl_3) δ 16.2 (2-Me), 17.6 (1-Me), 25.6 (3-Me), 47.0 (C6), 86.7 (C3), 122.3 (C5), 124.1 (C1), 134.8 (C2), 134.9 (C4), the resonance for $\text{C}(\text{NO}_2)_3$ was not observed. The above assignments were confirmed by long range reverse detected heteronuclear correlation spectra (HMBC, HMQC).

2,3,4-Trimethyl-4-nitrocyclohexa-2,5-dien-1-one (**20**)¹² isolated only in admixture with adduct (**12**). ^1H NMR (CDCl_3) δ 1.88 (s, 4-Me), 1.95 (br s, 2-Me, 3-Me), 6.41 (d, $J_{\text{H}_6,\text{H}_5}$ 9.8 Hz, H6), 6.81 (d, $J_{\text{H}_5,\text{H}_6}$ 9.8 Hz, H5). A nuclear Overhauser experiment gave the following result: irradiation at δ 1.88 gave an enhancement at δ 6.81 (3.2%). The nitrodienone (**20**) was unstable in ^2H -chloroform solution and rearranged (half life *c.* 6 h) to give 4,5,6-trimethyl-2-nitrophenol (**28**), ^1H NMR (CDCl_3) δ 2.25 (s, 6-Me), 2.26 (s, 5-Me), 2.27 (s, 4-Me), 7.75 (s, H3), 10.98 (s, OH). ^{13}C NMR (CDCl_3) δ 12.1 (6-Me), 17.0 (5-Me), 20.1 (4-Me), 121.9 (C3), 126.8 (C6), 128.5 (C4), 131.0 (C1), 147.0 (C5), 152.0 (C2). The above assignments were confirmed by long-range reverse-detected heteronuclear correlation spectra (HMBC, HMQC).

Nitrocycloadduct (**9**) m.p. 163°C (decomp.) (X-ray crystal structure determined, see below). IR: ν_{max} (KBr) 1590, 1556 cm^{-1} . ^1H NMR (CDCl_3) δ 1.67 (s, 3-Me), 1.75 (q, $J_{2\text{-Me},1\text{-Me}}$ 1.4 Hz, 2-Me), 1.80 (q, $J_{1\text{-Me},2\text{-Me}}$ 1.4 Hz, 1-Me), 4.60 (dd, $J_{\text{H}_6,\text{H}_5}$ 4.4 Hz, $J_{\text{H}_6,\text{H}_4}$ 2.5 Hz, H6), 5.27 (dd, $J_{\text{H}_4,\text{H}_6}$ 2.5 Hz, $J_{\text{H}_4,\text{H}_5}$ 2.0 Hz, H4), 5.51 (dd, $J_{\text{H}_5,\text{H}_6}$ 4.4 Hz, $J_{\text{H}_5,\text{H}_4}$ 2.0 Hz, H5). Nuclear Overhauser experiments gave the following results: irradiation at δ 1.67 gave an enhancement at δ 5.27 (7.1%); irradiation at δ 1.80 gave an enhancement at δ 4.60 (3.2%); irradiation at δ 4.60 gave enhancements at δ 1.80 (0.2%) and at δ 5.51 (10.4%); irradiation at δ 5.27 gave enhancements at δ 1.67 (0.5%) and at δ 5.51 (2.0%); irradiation at δ 5.51 gave enhancements at δ 4.60 (2.3%) and at δ 5.27 (1.0%). ^{13}C NMR (CDCl_3) δ 14.1 (2-Me), 20.0 (1-Me), 21.7 (3-Me), 45.2 (C6), 79.7 (C5), 81.4 (C4), 87.4 (C3), 128.5 (C1), 140.1 (C2). The above assignments were confirmed by long-range reverse-detected heteronuclear correlation spectra (HMBC, HMQC).

3,4,5-Trimethyl-4-nitrocyclohexa-2,5-dien-1-one (**21**)¹³ isolated as an oil. IR: ν_{max} (liquid film) 1677, 1638, 1598, 1551 cm^{-1} . ^1H NMR (CDCl_3) δ 1.88 (s, 4-Me), 1.99 (d,

$J_{3\text{-Me,H2}} = J_{5\text{-Me,H6}}$ 1.5 Hz, 3-Me, 5-Me), 6.23 (br s, 152.0 (C2). The above assignments were confirmed by long-range reverse-detected heteronuclear correlation spectra (HMBC, HMQC).

Nitrocycloadduct (9) m.p. 163 °C (decomp.) (X-ray crystal structure determined, see below). IR: ν_{max} (KBr) 1590, 1556 cm^{-1} . ^1H NMR (CDCl_3) δ 1.67 (s, 3-Me), 1.75 (q, $J_{2\text{-Me,1-Me}}$ 1.4 Hz, 2-Me), 1.80 (q, $J_{1\text{-Me,2-Me}}$ 1.4 Hz, 1-Me), 4.60 (dd, $J_{\text{H6,H5}}$ 4.4 Hz, $J_{\text{H6,H4}}$ 2.5 Hz, H6), 5.27 (dd, $J_{\text{H4,H6}}$ 2.5 Hz, $J_{\text{H4,H5}}$ 2.0 Hz, H4), 5.51 (dd, $J_{\text{H5,H6}}$ 4.4 Hz, $J_{\text{H5,H4}}$ 2.0 Hz, H5). Nuclear Overhauser experiments gave the following results: irradiation at δ 1.67 gave an enhancement at δ 5.27 (7.1%); irradiation at δ 1.80 gave an enhancement at δ 4.60 (3.2%); irradiation at δ 4.60 gave enhancements at δ 1.80 (0.2%) and at δ 5.51 (10.4%); irradiation at δ 5.27 gave enhancements at δ 1.67 (0.5%) and at δ 5.51 (2.0%); irradiation at δ 5.51 gave enhancements at δ 4.60 (2.3%) and at δ 5.27 (1.0%). ^{13}C NMR (CDCl_3) δ 14.1 (2-Me), 20.0 (1-Me), 21.7 (3-Me), 45.2 (C6), 79.7 (C5), 81.4 (C4), 87.4 (C3), 128.5 (C1), 140.1 (C2). The above assignments were confirmed by long-range reverse-detected heteronuclear correlation spectra (HMBC, HMQC).

*3,4,5-Trimethyl-4-nitrocyclohexa-2,5-dien-1-one (21)*¹³ isolated as an oil. IR: ν_{max} (liquid film) 1677, 1638, 1598, 1551 cm^{-1} . ^1H NMR (CDCl_3) δ 1.88 (s, 4-Me), 1.99 (d, $J_{3\text{-Me,H2}} = J_{5\text{-Me,H6}}$ 1.5 Hz, 3-Me, 5-Me), 6.23 (br s, H2, H6).

1,2,3-Trimethyl-r-3,c-4,c-6-trinitro-t-5-trinitromethylcyclohex-1-ene (13) m.p. 73 °C (decomp.) (X-ray crystal structure determined, see below). IR: ν_{max} (KBr) 1605, 1566, 1529 cm^{-1} . ^1H NMR (CDCl_3) δ 2.03 (br s, 2-Me), 2.15 (br s, 1-Me), 2.19 (s, 3-Me), 5.01 (d, $J_{\text{H6,H5}}$ 6.8 Hz, H6), 5.10 (br s, H4), 6.62 (br d, $J_{\text{H5,H6}}$ 6.8 Hz, H5). Nuclear Overhauser experiments gave the following results: irradiation at δ 2.03 gave an enhancement at δ 2.19 (0.5%); irradiation at δ 2.19 gave enhancements at δ 2.03 (2.9%), at δ 5.01 (10.8%), and at δ 5.10 (5.9%); irradiation at δ 5.01 gave enhancements at δ 2.19 (0.5%) and at δ 6.62 (3.2%); irradiation at δ 5.10 gave an enhancement at δ 2.19 (0.3%); irradiation at δ 6.62 gave enhancements at δ 5.01 (0.9%) and at δ 5.10 (0.6%). ^{13}C NMR (CD_3CN) δ 15.6 (2-Me), 23.0 (1-Me), 24.3 (3-Me), 42.7 (C5), 82.7 (C4), 85.5 (C6), 87.8 (C3), 130.2 (C2), 132.5 (C1), the resonance for $\text{C}(\text{NO}_2)_3$ was not observed. The above assignments were confirmed by long-range reverse-detected heteronuclear correlation spectra (HMBC, HMQC).

t-6-Hydroxy-4,5,6-trimethyl-2,r-4,t-5-trinitrocyclohex-2-enone (29) m.p. 121–123 °C (X-ray crystal structure determined, see below). IR: ν_{max} (KBr) 3423, 1740, 1560, 1541 cm^{-1} . ^1H NMR (CDCl_3) δ 1.52 (s, 6-Me), 1.85 (s, 5-Me), 1.88 (s, 4-Me), 3.97 (br s, OH), 7.44 (s, H3). Nuclear Overhauser experiments gave the following results: irradiation at δ 1.52 gave an enhancement at δ 1.85

(0.8%); irradiation at δ 7.44 gave an enhancement at δ 1.88 (0.3%). ^1H NMR (CD_3CN) δ 1.54 (s, 6-Me), 1.84 (s, 5-Me), 1.91 (s, 4-Me), 4.92 (br s, OH), 7.70 (s, H3). Nuclear Overhauser experiments gave the following results: irradiation at δ 1.54 gave an enhancement at δ 1.84 (0.8%); irradiation at δ 1.84 gave an enhancement at δ 1.54 (1.2%); irradiation at δ 1.91 gave an enhancement at δ 7.70 (7.4%); irradiation at δ 7.70 gave an enhancement at δ 1.91 (0.2%). ^{13}C NMR (CD_3CN) δ 15.9 (5-Me), 23.5 (6-Me), 23.6 (4-Me), 79.2 (C6), 90.3 (C4), 99.7 (C5), 137.5 (C3), 147.0 (C2), 188.4 (C1).

2,3,4-Trimethyl-c-2,c-5-dinitro-t-6-trinitromethylcyclohex-3-en-r-1-ol (14) m.p. 65 °C (decomp.) (X-ray crystal structure determined for 14-diethyl etherate, see below). IR: ν_{max} (KBr) 3502, 1610, 1571, 1545 cm^{-1} . ^1H NMR (CDCl_3) δ 1.94 (s, 2-Me), 1.97 (br s, 4-Me), 2.05 (br s, 3-Me), 3.86 (d, $J_{\text{OH,H1}}$ 12.7 Hz, 1-OH), 4.09 (dd, $J_{\text{H1,OH}}$ 12.7 Hz, $J_{\text{H1,H6}}$ 10.8 Hz, H1), 4.99 (dd, $J_{\text{H6,H1}}$ 10.8 Hz, $J_{\text{H6,H5}}$ 6.3 Hz, H6), 5.25 (d, $J_{\text{H5,H6}}$ 6.3 Hz, H5). Nuclear Overhauser experiments gave the following results: irradiation at δ 1.97 gave an enhancement at δ 5.25 (4.2%); irradiation at δ 4.09 gave enhancements at δ 1.94 (0.8%) and at δ 5.25 (1.1%); irradiation at δ 5.25 gave an enhancement at δ 1.97 (0.5%). ^{13}C NMR (CDCl_3) δ 16.6 (3-Me), 18.7 (4-Me), 22.2 (2-Me), 45.4 (C6), 71.4 (C1), 87.8 (C5), 88.4 (C2), 127.0 (C4), 134.9 (C3), the resonance for $\text{C}(\text{NO}_2)_3$ was not observed. The above assignments were confirmed by long-range reverse-detected heteronuclear correlation spectra (HMBC, HMQC).

1,2,3-Trimethyl-r-3,t-4,t-6-trinitro-t-5-trinitromethylcyclohex-1-ene (15) isolated only as an oil (insufficient for elemental analysis, parent ion not visible in mass spectrum under a variety of experimental conditions). IR: ν_{max} (liquid film) 1647, 1570 cm^{-1} . ^1H NMR (CDCl_3) δ 1.74 (s, 3-Me), 1.93 (br s, 2-Me), 1.96 (br s, 1-Me), 4.88 (dd, $J_{\text{H5,H4}}$ 4.9 Hz, $J_{\text{H5,H6}}$ 1.0 Hz, H5), 5.81 (dd, $J_{\text{H6,H4}}$ 3.9 Hz, $J_{\text{H6,H5}}$ 1.0 Hz, H6), 5.92 (dd, $J_{\text{H4,H5}}$ 4.9 Hz, $J_{\text{H4,H6}}$ 3.9 Hz, H4). Nuclear Overhauser experiments gave the following results: irradiation at δ 1.74 gave an enhancement at δ 1.93 (1.2%); irradiation at δ 1.93 gave an enhancement at δ 1.74 (1.3%); irradiation at δ 1.96 gave an enhancement at δ 5.81 (3.3%); irradiation at δ 4.88 gave enhancements at δ 5.81 (1.3%) and at δ 5.92 (3.6%); irradiation at δ 5.81 gave enhancements at δ 1.96 (0.7%) and at δ 4.88 (0.9%); irradiation at δ 5.92 gave enhancements at δ 1.74 (0.5%) and at δ 4.88 (1.6%). ^{13}C NMR (CDCl_3) δ 14.5 (2-Me), 17.7 (1-Me), 24.7 (3-Me), 46.7 (C5), 78.6 (C4), 81.1 (C3), 84.1 (C6), 124.1 (C1), 132.9 (C2), the resonance for $\text{C}(\text{NO}_2)_3$ was not observed. The above assignments were confirmed by long-range reverse-detected heteronuclear correlation spectra (HMBC, HMQC).

Hydroxydinitro nitronic ester (16) isolated only as an oil (insufficient for elemental analysis, parent ion not visible in mass spectrum under a variety of experimental con-

ditions). IR: ν_{\max} (liquid film) 3511, 1637, 1560 cm^{-1} . ^1H NMR (CDCl_3): δ 1.85 (s, 1-Me), 1.87 (br s, 2-Me), 1.93 (br s, 3-Me), 3.92 (br, OH), 4.31 (d, $J_{\text{H}_6, \text{H}_5}$ 10.3 Hz, H6), 4.40 (dd, $J_{\text{H}_5, \text{H}_6}$ 10.3 Hz, $J_{\text{H}_5, \text{H}_4}$ 4.4 Hz, H5), 5.23 (d, $J_{\text{H}_4, \text{H}_5}$ 4.4 Hz, H4). Nuclear Overhauser experiments gave the following results: irradiation at δ 1.85 gave an enhancement at δ 4.31 (5.8%); irradiation at δ 1.93 gave an enhancement at δ 5.23 (3.2%); irradiation at δ 4.31 gave an enhancement at δ 1.85 (0.78%); irradiation at δ 4.40 gave an enhancement at δ 5.23 (5.8%); irradiation at δ 5.23 gave enhancements at δ 1.93 (0.8%) and at δ 4.40 (3.5%). ^{13}C NMR (CDCl_3) δ 14.1 (2-Me), 18.3 (3-Me), 24.8 (1-Me), 48.6 (C6), 67.8 (C5), 85.3 (C1), 88.8 (C4), 124.8 (C3), 132.8 (C2), the resonance for =C-NO₂ was not observed. The above assignments were confirmed by long-range reverse-detected heteronuclear correlation spectra (HMBC, HMQC).

Trinitro nitronic ester (17) m.p. 127°C (decomp.) (preliminary X-ray crystal structure reported in the Results section). IR: ν_{\max} (solid film) 1639, 1564, 1512 cm^{-1} . ^1H NMR (CDCl_3) δ 1.91 (br s, 2-Me), 1.92 (s, 1-Me), 2.03 (br s, 3-Me), 5.12 (dd, $J_{\text{H}_5, \text{H}_6}$ 11.7 Hz, $J_{\text{H}_5, \text{H}_4}$ 3.5 Hz, H5), 5.16 (d, $J_{\text{H}_6, \text{H}_5}$ 11.7 Hz, H6), 5.52 (d, $J_{\text{H}_4, \text{H}_5}$ 3.5 Hz, H4). Nuclear Overhauser experiments gave the following results: irradiation at δ 1.92 gave an enhancement at δ 2.16 (5.3%); irradiation at δ 2.03 gave an enhancement at δ 5.52 (4.4%); irradiation at δ 5.12 gave an enhancement at δ 5.52 (3.1%); irradiation at δ 5.16 gave an enhancement at δ 1.91 (0.5%); irradiation at δ 5.52 gave enhancements at δ 2.03 (0.5%) and at δ 5.12 (2.4%). ^{13}C NMR (CDCl_3) δ 15.2 (2-Me), 18.3 (1-Me), 25.0 (3-Me), 44.9 (C4), 80.7 (C5), 84.2 (C6); these assignments were confirmed by long-range reverse-detected heteronuclear correlation spectra (HMBC, HMQC), but the remainder of the resonances were not detected in a weak spectrum.

Trinitro nitronic ester (18) m.p. 131–132.5°C (X-ray crystal structure determined, see below). IR: ν_{\max} (KBr) 1608, 1565, 1525 cm^{-1} . ^1H NMR (CDCl_3) δ 1.83 (s, 3-Me), 2.01 (br s, 2-Me), 2.09 (br s, 1-Me), 5.04 (br s, H6), 5.08 (d, $J_{\text{H}_4, \text{H}_5}$ 3.4 Hz, H4), 5.42 (dd, $J_{\text{H}_5, \text{H}_4}$ 3.4 Hz, $J_{\text{H}_5, \text{H}_6}$ 1.4 Hz, H5). ^1H NMR (CD_3CN) δ 1.88 (s, 3-Me), 2.22 (br s, 1-Me, 2-Me), 5.29 (dd, $J_{\text{H}_5, \text{H}_4}$ 4.0 Hz, $J_{\text{H}_5, \text{H}_6}$ 1.4 Hz, H5), 5.34 (br s, H6), 5.40 (d, $J_{\text{H}_4, \text{H}_5}$ 4.0 Hz, H4). Nuclear Overhauser experiments gave the following results: (in CDCl_3) irradiation at δ 1.83 gave an enhancement at δ 5.08 (5.9%) (in CD_3CN); irradiation at δ 1.88 gave an enhancement at δ 5.40 (8.9%); irradiation at δ 2.22 gave an enhancement at δ 5.34 (3.4%); irradiation at δ 5.34 gave an enhancement at δ 2.22 (0.45%), irradiation at δ 5.40 gave an enhancement at δ 1.88 (0.3%). ^{13}C NMR (CD_3CN) δ 14.1 (2-Me), 19.3 (1-Me), 21.3 (3-Me), 38.7 (C5), 78.9 (C4), 83.3 (C6), 84.0 (C3), 127.6 (C1), 133.5 (C2). The above assignments were confirmed by long-range reverse-detected heteronuclear correlation spectra (HMBC, HMQC).

Hydroxydinitro nitronic ester (19) m.p. 129°C (X-ray crystal structure determined, see below). IR: ν_{\max} (KBr) 3463, 1604, 1556, 1295 cm^{-1} . ^1H NMR (CDCl_3) δ 1.63 (s, 3-Me), 1.90 (br s, 2-Me), 2.01 (br s, 1-Me), 4.30 (d, $J_{\text{H}_4, \text{H}_5}$ 3.9 Hz, H4), 4.80 (dd, $J_{\text{H}_5, \text{H}_4}$ 3.9 Hz, $J_{\text{H}_5, \text{H}_6}$ 2.4 Hz, H5), 4.91 (br s, H6). Nuclear Overhauser experiments gave the following results: irradiation at δ 1.63 gave enhancements at δ 1.90 (2.3%) and at δ 4.30 (2.6%); irradiation at δ 1.90 gave an enhancement at δ 1.63 (1.0%); irradiation at δ 2.01 gave an enhancement at δ 4.91 (4.8%); irradiation at δ 4.30 gave enhancements at δ 1.63 (1.1%) and at δ 4.80 (3.2%); irradiation at δ 4.80 gave enhancements at δ 4.30 (3.0%) and at δ 4.91 (3.1%); irradiation at δ 4.91 gave an enhancement at δ 2.01 (1.1%). ^{13}C NMR (CDCl_3) δ 13.9 (2-Me), 19.5 (1-Me), 19.7 (3-Me), 40.1 (C5), 66.3 (C4), 82.4 (C6), 85.4 (C3), 126.3 (C1), 131.5 (C2). The above assignments were confirmed by long-range reverse-detected heteronuclear correlation spectra (HMBC, HMQC).

Chromatography on a silica gel Chromatotron plate of the mixture of compounds **22**, **23**, **26** and **27**, first eluted from the HPLC column, gave the following compounds in elution order:

3,4,5-Trimethyl-1-trinitromethylbenzene (22) m.p. 91°C (decomp.) (X-ray crystal structure determined, see below). IR: ν_{\max} (KBr) 1617, 1585 cm^{-1} . ^1H NMR (CDCl_3) δ 2.27 (s, 3H, 4-Me), 2.36 (s, 6H, 5-Me), 7.20 (s, 2H, H2, H6). ^{13}C NMR (CDCl_3) δ 15.9 (4-Me), 20.8 (3-Me, 5-Me), 119.0 (C1), 128.1 (C2, C6), 138.1 (C3, C5), 143.2 (C4), the resonance for C(NO₂)₃ was not observed. The above assignments were confirmed by long-range reverse-detected heteronuclear correlation spectra (HMBC, HMQC).

2,3,4-Trimethyl-1-trinitromethylbenzene (23) obtained only in admixture with 3,4,5-trimethyl-1-trinitromethylbenzene (**22**). ^1H NMR (CDCl_3) δ 2.04 (s, 2-Me), 2.26 (s, 3-Me), 2.40 (s, 4-Me), 6.99 (d, $J_{\text{H}_6, \text{H}_5}$ 8.3 Hz, H6), 7.19 (d, $J_{\text{H}_5, \text{H}_6}$ 8.3 Hz, H5). Nuclear Overhauser experiments gave the following results: irradiation at δ 2.04 gave an enhancement at δ 2.26 (0.8%); irradiation at δ 2.26 gave an enhancement at δ 2.04 (0.5%); irradiation at δ 2.40 gave an enhancement at δ 7.19 (2.7%); irradiation at δ 6.99 gave an enhancement at δ 7.19 (5.3%); irradiation at δ 7.19 gave enhancements at δ 2.40 (0.4%) and at δ 6.99 (4.9%). ^{13}C NMR (CDCl_3) δ 16.0 (3-Me), 18.5 (2-Me), 21.4 (4-Me), 119.8 (C1), 126.8 (C6), 128.2 (C5), 138.0 (C2), 138. & (C3), 143.7 (C4), the resonance for C(NO₂)₃ was not observed. The above assignments were confirmed by long-range reverse-detected heteronuclear correlation spectra (HMBC, HMQC).

4,5,6-Trimethyl-2-nitrophenol (28) isolated as an oil (ca. 95% pure). IR: ν_{\max} (liquid film) 3442, 1612, 1593, 1537 cm^{-1} . ^1H NMR (CDCl_3) δ 2.25 (s, 6-Me), 2.26 (s, 5-Me), 2.27 (s, 4-Me), 7.75 (s, H3), 10.98 (s, OH). ^{13}C NMR (CDCl_3) δ 12.1 (6-Me), 17.0 (5-Me), 20.1 (4-Me),

121.9 (C3), 126.8 (C6), 128.5 (C4), 131.0 (C1), 147.0 (C5), 152.0 (C2). The above assignments were confirmed by long-range reverse-detected heteronuclear correlation spectra (HMBC, HMQC).

2,3,4-Trimethyl-1-nitrobenzene (26) isolated as an oil (c. 95% pure) (Found: M^+ , 165.07890. $C_9H_{11}NO_2$ requires 165.07898). IR: ν_{\max} (liquid film) 1518 cm^{-1} . 1H NMR ($CDCl_3$) δ 2.26 (s, 3-Me), 2.35 (s, 4-Me), 2.39 (s, 2-Me), 7.09 (d, $J_{H5,H6}$ 8.4 Hz, H5), 7.51 (d, $J_{H6,H5}$ 8.4 Hz, H6). Nuclear Overhauser experiments gave the following results: irradiation at δ 2.35 gave an enhancement at δ 7.09 (2.0%); irradiation at δ 7.09 gave enhancements at δ 2.35 (0.2%) and δ 7.51 (5.3%); irradiation at δ 7.51 gave an enhancement at δ 7.09 (2.4%). ^{13}C NMR ($CDCl_3$) δ 15.8 (2-Me), 16.0 (3-Me), 21.2 (4-Me), 121.1 (C6), 127.6 (C5), 130.4 (C2), 137.6 (C3), 141.5 (C4), 149.4 (C1).

3,4,5-Trimethyl-1-nitrobenzene (27) isolated as an oil (90% pure) (Found: M^+ , 165.07886. $C_9H_{11}NO_2$ requires 165.07898). IR: ν_{\max} (liquid film) 1517 cm^{-1} . 1H NMR ($CDCl_3$) δ 2.26 (s, 4-Me), 2.37 (s, 3-Me, 5-Me), 7.87 (s, H2, H6).

Thermal cycloaddition of 5-nitro-6-trinitromethylcyclohexa-1,3-diene (8) in 2H -chloroform. A solution of a mixture (ca. 4:1:4:2) of the trinitromethyl diene **8**, nitrocycloadduct **9**, and the 1,2,3-trimethyl-3-nitro-6-trinitromethylcyclohexa-1,4-dienes **7** and **10**, respectively in 2H -chloroform was stored at 22°C in the dark and the 1H NMR spectrum monitored at appropriate time intervals. The adducts **7** and **10** were inert under these reaction conditions for the timescale of the reaction of compound **8**, but the trinitromethyl diene **8** was transformed (half-life 19.5 h) into the nitro cycloadduct **9**.

Rearrangement of 2,3,4-trimethyl-4-nitrocyclohexa-2,5-dien-1-one (20) in 2H -chloroform. A solution of a mixture (ca. 4:1) of the nitro dienone **20** and 1,2,3-trimethyl-*r*-3-nitro-*c*-6-trinitromethylcyclohexa-1,4-diene (**12**) in 2H -chloroform was stored at 22°C in the dark and the 1H NMR spectrum monitored at appropriate time intervals. The adduct **12** was inert under these reaction conditions but the nitro dienone **20** was transformed (half-life 6 h) into 4,5,6-trimethyl-2-nitrophenol (**28**).

Reaction of nitrotrinitromethyl adducts 7, 10–12 with 2,6-di-*tert*-butyl-4-methylpyridine in dichloromethane. A solution of each of the adducts **7** and **10–12** in dichloromethane was treated with 2,6-di-*tert*-butyl-4-methylpyridine (1.1 molar ratio) for 1 h at 20°C in the dark. Removal of the solvent under reduced pressure gave a residue, the 1H NMR spectrum of which was determined. Adducts **7** and **11** gave 3,4,5-trimethyl-1-trinitromethylbenzene (**22**), while adducts **10** and **12** gave 2,3,4-trimethyl-1-trinitromethylbenzene (**23**).

Photochemistry in dichloromethane at 20°C in the presence of trifluoroacetic acid. Reaction of 1,2,3-trimethylbenzene-tetranitromethane in dichloromethane at 20°C, as above, for 8 h except for the addition of trifluoroacetic acid (1.04 mol dm^{-3}) gave 3,4,5-trimethyl-1-trinitromethylbenzene (**22**) (62%), 2,3,4-trimethyl-1-trinitromethylbenzene (**23**) (10.5%), 3,4,5-trimethylbenzoic acid (**30**) (5%), 2,3,4-trimethylbenzoic acid (**31**) (2%), and unidentified material (20%). The carboxylic acids **30** and **31** were isolated by HPLC and were identified by comparison with literature data.^{14,15} Similar reaction to the above, but with trifluoroacetic acid (2.08 mol dm^{-3}) gave a mixture of 3,4,5-trimethyl-1-trinitromethylbenzene (**22**) (20%), 2,3,4-trimethyl-1-trinitromethylbenzene (**23**) (11.5%), 3,4,5-trimethylbenzoic acid (**30**) (10%), 2,3,4-trimethylbenzoic acid (**31**) (4.5%), 2,3,4-trimethyl-1-nitrobenzene (**26**) (11%), 3,4,5-trimethyl-1-nitrobenzene (**27**) (9%), and unidentified material (34%). Full time/yield data are given in Table 10.

Crystallography. Crystal data, established from precession photographs and measured accurately, by means of a Siemens R3m/V four-circle diffractometer 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

Nitro cycloadduct (9) $C_{10}H_{12}N_4O_4$, $M = 316.24$, monoclinic, space group $P2_1/c$, $a = 10.440(2)$, $b = 6.812(4)$, $c = 18.844(4)$ Å, $\beta = 101.17(1)^\circ$; $V = 1314.7(9)$ Å³, $D_c = 1.598$ g cm^{-3} , $Z = 4$, molybdenum X-radiation, $\mu(Mo\ K\alpha) = 0.71069$ Å, $\mu(Mo\ K\alpha) = 1.40$ cm^{-1} . The crystal was colourless and of approximate dimensions 0.90 × 0.25 × 0.17 mm. Data were collected at 130(2) K out to a maximum Bragg angle $\Theta = 25^\circ$. The number of independent reflections measured was 2316, 1598 with $I > 2\sigma(I)$. Absorption corrections were not applied; $g_1 = 0.0700$, $g_2 = 0.0000$; $R_{(obs)}$ -factor = 0.045, $wR_{(all\ data)} = 0.149$.

1,2,3-Trimethyl-*r*-3,*c*-4,*c*-6-trinitro-*t*-5-trinitromethylcyclohex-1-ene (13) $C_{10}H_{12}N_6O_{12}$, $M = 408.26$, monoclinic, space group $P2_1/n$, $a = 10.187(2)$, $b = 13.904(4)$, $c = 12.348(3)$ Å, $\beta = 110.84(3)^\circ$; $V = 1634.5(7)$ Å³, $D_c = 1.659$ g cm^{-3} , $Z = 4$, molybdenum X-radiation, $\mu(Mo\ K\alpha) = 0.71069$ Å, $\mu(Mo\ K\alpha) = 1.54$ cm^{-1} . The crystal was colourless and of approximate dimensions 1.02 × 0.21 × 0.16 mm. Data were collected at 173(2) K out to a maximum Bragg angle $\Theta = 24.66^\circ$. The number of independent reflections measured was 2122, 1222 with $I > 2\sigma(I)$. Absorption corrections were not applied;

$g_1 = 0.0396$, $g_2 = 0.0000$; $R_{(\text{obs})}$ -factor = 0.036, $wR_{(\text{all data})} = 0.077$.

2,3,4-Trimethyl-c-2,c-5-dinitro-t-6-trinitromethylcyclohex-3-en-r-1-ol (14) etherate, $C_{14}H_{23}N_5O_{12}$, $M = 453.37$, monoclinic, space group C_c , $a = 14.569(5)$, $b = 12.086(4)$, $c = 11.793(4)$ Å, $\beta = 105.63(3)^\circ$, $V = 2000(1)$ Å³, $D_c = 1.506$ g cm⁻³, $Z = 4$, copper X-radiation, $\mu(\text{Cu K}\alpha) = 1.54180$ Å, $\mu(\text{Cu K}\alpha) = 11.57$ cm⁻¹. The crystal was colourless and of approximate dimensions $0.37 \times 0.23 \times 0.16$ mm. Data were collected at 130(2) K out to a maximum Bragg angle $\Theta = 27.49^\circ$. The number of independent reflections measured was 1254, 1124 with $I > 2\sigma(I)$. Absorption corrections were not applied; $g_1 = 0.0618$, $g_2 = 0.0000$; $R_{(\text{obs})}$ -factor = 0.041, $wR_{(\text{all data})} = 0.096$.

Trinitro nitronic ester (18) $C_{10}H_{12}N_4O_8$, $M = 316.24$, orthorhombic, space group, $Pbca$, $a = 6.480(7)$, $b = 14.840(9)$, $c = 26.79(2)$ Å, $V = 2576(4)$ Å³, $D_c = 1.631$ g cm⁻³, $Z = 8$, molybdenum X-radiation, $\mu(\text{Mo K}\alpha) = 0.71069$ Å, $\mu(\text{Mo K}\alpha) = 1.43$ cm⁻¹. The crystal was colourless and of approximate dimensions of $0.40 \times 0.10 \times 0.06$ mm. Data were collected at 130(2) K out to a maximum Bragg angle $\Theta = 22.49^\circ$. The number of independent reflections measured was 1671, 837 with $I > 2\sigma(I)$. Absorption corrections were not applied; $g_1 = 0.0405$, $g_2 = 0.0000$; $R_{(\text{obs})}$ -factor = 0.047, $wR_{(\text{all data})} = 0.097$.

Hydroxydinitro nitronic ester (19) $C_{10}H_{13}N_3O_7$, $M = 287.23$, monoclinic, space group $P2_1/c$, $a = 10.004(2)$, $b = 8.287(3)$, $c = 14.671(3)$ Å, $\beta = 96.93(1)^\circ$, $V = 1207.4(6)$ Å³, $D_c = 1.580$ g cm⁻³, $Z = 4$, molybdenum X-radiation, $\mu(\text{Mo K}\alpha) = 0.71069$ Å, $\mu(\text{Mo K}\alpha) = 1.36$ cm⁻¹. The crystal was colourless and of approximate dimensions $0.97 \times 0.91 \times 0.15$ mm. Data were collected at 130(2) K out to a maximum Bragg angle $\Theta = 27.5^\circ$. The number of independent reflects measured was 2769, 2064 with $I > 2\sigma(I)$. Absorption corrections were not applied; $g_1 = 0.0735$; $g_2 = 0.0000$; $R_{(\text{obs})}$ -factor = 0.037, $wR_{(\text{all data})} = 0.124$.

3,4,5-Trimethyl-1-trinitromethylbenzene (22) $C_{10}H_{11}N_3O_6$, $M = 269.22$, monoclinic, space group P , $a = 9.602(2)$, $b = 7.528(2)$, $c = 16.923(3)$ Å, $\beta = 99.88(3)^\circ$, $V = 1205.1(5)$ Å³, $D_c = 1.484$ g cm⁻³, $Z = 4$, molybdenum X-radiation $\mu(\text{Mo K}\alpha) = 0.71069$ Å, $\mu(\text{Mo K}\alpha) = 1.25$ cm⁻¹. The crystal was colourless and of approximate dimensions $0.90 \times 0.84 \times 0.20$ mm. Data were collected at 130(2) K out to a maximum Bragg angle $\Theta = 28.26^\circ$. The number of independent reflections measured was 1569, 1231 with $I > 2\sigma(I)$. Absorption corrections were not applied; $g_1 = 0.0500$, $g_2 = 0.7111$; $R_{(\text{obs})}$ -factor = 0.040; $wR_{(\text{all data})} = 0.108$.

t-6-Hydroxy-4,5,6-trimethyl-2,r-4,t-5-trinitrocyclohex-2-ene (29) $C_9H_{11}N_3O_8$, $M = 289.21$, monoclinic, space group $P2_1/n$, $a = 6.943(4)$, $b = 20.410(3)$, $c = 8.281(1)$ Å, $\beta = 101.23(3)^\circ$, $V = 1151.0(7)$ Å³, $D_c = 1.669$ g cm⁻³, $Z = 4$, molybdenum X-radiation, $\mu(\text{Mo K}\alpha) = 0.71069$ Å, $\mu(\text{Mo K}\alpha) = 1.49$ cm⁻¹. The crystal was colourless and of approximate dimensions $0.62 \times 0.30 \times 0.19$ mm. Data were collected at 173(2) K out to a maximum Bragg angle $\Theta = 25.0^\circ$. The number of independent reflections measured was 2031, 1307 with $I > 2\sigma(I)$. Absorption corrections were not applied; $g_1 = 0.0285$, $g_2 = 0.0000$; $R_{(\text{obs})}$ -factor = 0.030, $wR_{(\text{all data})} = 0.059$.

Structure determination. Full-matrix least-squares refinements (SHELXL-93)²⁰ were employed. This program is based on intensities and uses all data. The observed threshold $I > 2\sigma(I)$ was used only for calculating $R_{(\text{obs})}$, shown here as a comparison for the refinement based on F . Reflection weights $1/[\sigma^2(F_0^2) + (g_1P)^2 + g_2P]$, where $P = [F_0^2 + 2F_c^2]/3$, were used. All non-hydrogen atoms were assigned anisotropic thermal parameters. Methyl hydrogens were included as rigid groups pivoting about their carbon atoms. Final Fourier syntheses show no significant residual electron density, and there were no abnormal discrepancies between observed and calculated structure factors.

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