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Photochemical Nitration by Tetranitromethane. Part XXIV.† Adduct Formation in the Photochemical Reaction of 1,4,6,7-Tetramethylnaphthalene; Some Rearrangement Studies of 1,4,6,7-Tetramethyl-*r*-1-nitro-*t*-4-trinitromethyl-1,4-dihydronaphthalene and Evidence for Inverted Spin Trapping of Trinitromethanide Ion

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The photolysis of the charge-transfer complex of 1,4,6,7-tetramethylnaphthalene and tetranitromethane in dichloromethane at −20 °C gave predominantly 1,4,6,7-tetramethyl-*r*-1-nitro-*t*-4-trinitromethyl-1,4-dihydronaphthalene (**7**), together with minor amounts of its epimer (**8**) and 2,3,5,8-tetramethyl-*r*-1-nitro-*c*-trinitromethyl-1,4-dihydronaphthalene (**9**), and nitroaromatic compounds **10**–**13**; the latter is a rearrangement product of nitro–trinitromethyl adducts **7** and **8**. Rearrangement of the nitro–trinitromethyl adduct **7** in acetonitrile gave mainly 2,3,5,8-tetramethyl-1-nitronaphthalene (**11**), 1,4,6,7-tetramethyl-2-nitronaphthalene (**12**) and 4,6,7-trimethyl-1-nitromethylnaphthalene (**13**). In contrast, in (^{2}H)chloroform the major product of rearrangement of the nitro–trinitromethyl adduct **7** was 4,6,7-trimethyl-1-(2′,2′,2′-trinitroethylnaphthalene (**10**), which appears to be formed via 1,4,6,7-tetramethyl-*t*-2-nitro-*r*-1-trinitromethyl-1,2-dihydronaphthalene **18**.

Evidence is presented for the incidence of inverted spin trapping by α-phenyl-*N*-*tert*-butylnitrone (PBN) in the rearrangement of the nitro–trinitromethyl adduct **7**. Rearrangement of the nitro–trinitromethyl adduct **7** on a silica gel Chromatotron plate gives the hydroxytrinitromethyl compound **15**, the hydroxynitro compound **16** and the diol **17**. X-Ray crystal structures are reported for the nitro–trinitromethyl adduct **7** and 1,4,6,7-tetramethyl-1,2-dihydronaphthalene-*r*-1-*c*-2-diol (**17**).

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[1,2] to occur by recombination of a triad consisting of $ArH^{\bullet+}$, trinitromethanide ion and nitrogen dioxide [eqn. (1)].[3]

$$\underset{\text{CT complex}}{ArH\cdots C(NO_2)_4} \xrightarrow[<3\text{ ps}]{h\nu_{CT}} \underset{\text{triad}}{ArH^{\bullet+}\ (O_2N)_3C^-\ NO_2} \qquad (1)$$

The first chemical step which occurs, leading to the formation of adducts, is reaction between $ArH^{\bullet+}$ and trinitromethanide ion [eqn. (2)] to give a carbon radical which then reacts with nitrogen dioxide to give adducts [eqn. (3)].[1,2]

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

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

The products of the photoreaction of 1,4-dimethylnaphthalene with tetranitromethane in dichloromethane at −50 °C[4] are the epimeric 1-nitro-4-trinitromethyl adducts **1** (81%) and **2** (9%), and the nitromethyl com-

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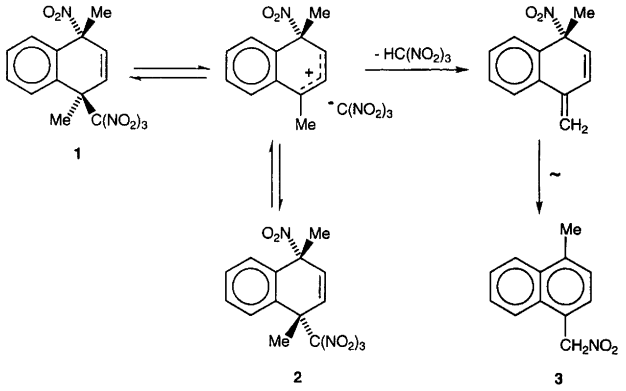
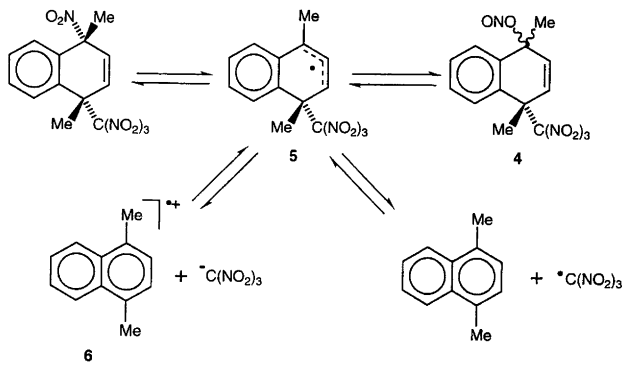


Scheme 1.

pound **3** (7%) (Scheme 1), the last of which is known to be a product of the rearrangement of adduct **1**.[4,5] Thus in this photolysis reaction the initial attack [eqn. (2)] by the trinitromethanide ion on the radical cation of 1,4-dimethylnaphthalene occurs almost exclusively *ipso* to one of the two methyl groups at C1(4). Subsequently radical coupling of nitrogen dioxide with the delocalized carbon radical [eqn. (3)] yields the epimeric nitro–trinitromethyl adducts **1** and **2**.

The rearrangement of the *trans*-1-nitro-4-trinitromethyl adduct **1** has been the subject of extensive study.[4] In either acetonitrile or dichloromethane the initial reactions involve epimerization to give the *cis*-1-nitro-4-trinitromethyl adduct **2** concurrently with the formation of the nitromethyl compound **3**. The rearrangement of adduct **1** to give adduct **2** was assumed to be polar on the basis of the rate ratio of 1.4×10^2 between acetonitrile and dichloromethane, and the proposed mode of formation of adduct **2** and nitromethyl compound **3** is given in Scheme 1.

In acetonitrile solution, after the build-up of the concentration of the *cis*-1-nitro-4-trinitromethyl adduct **2**, a pathway to the epimeric 1-nitrito-4-trinitromethyl adducts **4** opens up through a nitro–nitrito rearrangement[6] involving the delocalized carbon radical **5** as the intermediate (Scheme 2). This delocalized carbon radical **5** was envisaged also as being involved in two further equilibria, in



Scheme 2.

one case yielding the radical cation of 1,4-dimethylnaphthalene **6** and trinitromethanide ion, and in the other giving 1,4-dimethylnaphthalene and trinitromethyl radical. These two equilibria were seen as accounting for two observations, (i) the broadening due to $ArH^{\bullet+}/ArH$ electron exchange[7] of the methyl signal in the ^1H NMR spectrum of the 1,4-dimethylnaphthalene formed in the rearrangement, and (ii) the apparent trapping of the trinitromethyl radical with α-phenyl-*N*-*tert*-butylnitrone (PBN) giving a maximum spin adduct concentration at approximately the same time as $[\mathbf{2}]_{max}$ had been reached. However, as will be seen below, the mode of formation of this spin adduct seems most likely to be the result of reaction of the radical cation of the spin trap ($PBN^{\bullet+}$) with trinitromethanide ion.[8]

We now report the results of the photolysis of the charge-transfer complex of 1,4,6,7-tetramethylnaphthalene and tetranitromethane in dichloromethane and in acetonitrile. The major adduct **7** formed was analogous to the adduct **1** obtained from 1,4-dimethylnaphthalene, and the rearrangements of this adduct **7** although somewhat similar to those of adduct **1** exhibited some marked differences.

Results

General. The photochemical experiments were performed with filtered light (cut-off <435 nm, 5 cm water IR filter, from a 300 W lamp) as described before,[9] and small samples were withdrawn for analysis at suitable intervals. The work-up procedure, involving evaporation of solvent and tetranitromethane (also trifluoroacetic acid, if present), was conducted at a temperature ≤0°C. The crude product mixtures were stored at −20°C and were analysed (^1H NMR spectroscopy, see Experimental; Tables 1, 4 and 5) as soon as possible.

Photochemistry in dichloromethane at −20°C and identification of adducts. A solution of 1,4,6,7-tetramethylnaphthalene (0.34 mol dm^{-3}) and tetranitromethane (0.68 mol dm^{-3}) in dichloromethane was irradiated at −20°C. The composition of the reaction mixture was monitored by withdrawing samples for NMR spectral analysis (Table 1). The final solution (after 2 h, conversion ≈100%) after work-up contained the adduct **7** (58%), its epimer **8** (2%), an adduct tentatively identified as **9** (3%), 4,6,7-trimethyl-2′,2′,2′-trinitroethylnaphthalene **10** (2%), 2,3,5,8-tetramethyl-1-nitronaphthalene **11** (4%), 1,4,6,7-tetramethyl-2-nitronaphthalene **12** (3%) and 4,6,7-trimethyl-1-nitromethylnaphthalene **13** (27%).

The major adduct **7** was isolated by crystallization from dichloromethane–pentane and its structure determined by single-crystal X-ray analysis. A perspective drawing of 1,4,6,7-tetramethyl-*r*-1-nitro-*t*-4-trinitromethyl-1,4-dihydronaphthalene **7**, $C_{15}H_{16}N_4O_8$, m.p. 89°C (decomp.) is presented in Fig. 1, and corresponding atomic coordinates are given in Table 2. In the

Table 1. Overview of yields of products from the photolysis of 1,4,6,7-tetramethylnaphthalene (0.34 mol dm^{-3}) and tetranitromethane (0.68 mol dm^{-3}) in dichloromethane.

		Yield (%)									
t/h	Conversion (%)	**7**	**8**	**9**	Total adducts	**10**	**11**	**12**	**13**	Unknown aromatics	Total aromatics
At −20 °C											
0.25	13	69.6	5.6	3.9	79.1	1.1	2.1	3.3	10.9	3.5	20.9
0.5	26	60.7	5.4	2.9	69.0	1.9	2.6	4.1	20.4	2.0	31.0
1	58	54.7	4.8	3.1	62.6	3.0	3.2	4.2	25.6	1.4	37.4
2	100	57.7	1.9	3.2	62.8	2.1	4.0	3.3	26.8	1.0	37.2
At 20 °C											
0.25	16	31.0	3.9	2.0	36.9	2.2	2.3	22.5	28.8	7.3	63.1
0.5	47	34.6	5.8	1.9	42.3	1.7	3.3	21.1	22.7	8.9	57.1
1	86	44.8	3.2	2.7	50.7	1.7	3.8	17.0	20.8	6.0	49.3
2	100	11.3	2.9	2.4	16.6	8.4	5.8	38.2	30.5	0.5	83.4

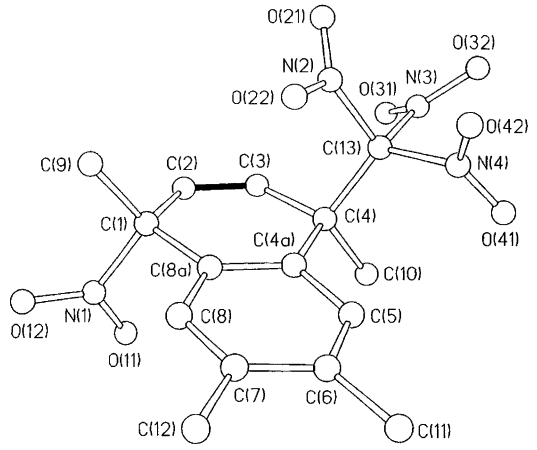


Fig. 1. Perspective drawing of compound **7**. Double bond shown in black.

solid state the alicyclic ring of adduct **7** is close to planar [torsional angles: C(2)–C(3)–C(4)–C(4a) 1.7(7)°; C(3)–C(2)–C(1)–C(8a) −6.3(7)°]. The orientations of the methyl and trinitromethyl substituents at C(4) relative to the plane of the aromatic ring reflect the difference in the size of the two substituents [torsional angles: C(5)–C(4a)–C(4)–C(10) 52.8(6)°; C(5)–C(4a)–C(4)–C(13) −70.7(6)°], the more similarly sized substituents at C(1) being more evenly displaced from that plane [torsional angles: C(8)–C(8a)–C(1)–C(9) 56.0(6)°; C(8)–C(8a)–C(1)–N(1) −62.7(6)°]. The plane of the nitro group at C(1) is close to eclipsed with the C(1)–C(9) bond [torsional angle: C(9)–C(1)–N(1)–O(12) −13.8(6)°]. The spectroscopic data for adduct **7** were in accord with the established structure.

The structure of the epimeric 1-nitro-4-trinitromethyl adduct **8**, which could not be isolated, was assigned on the basis of its ^{1}H NMR spectrum, which was closely similar to that reported earlier for the corresponding 1,4-dimethyl-*r*-1-nitro-*c*-4-trinitromethyl-1,4-dihydronaphthalene (**2**),[4] the minor upfield chemical shift of the signals

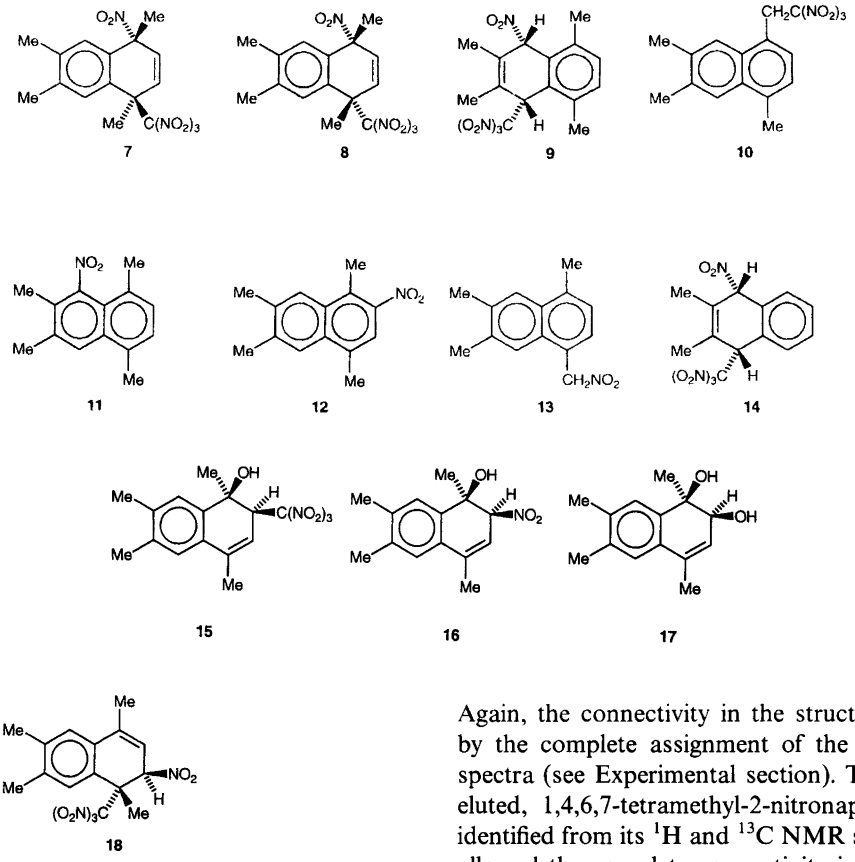
Table 2. Fractional coordinates for atoms in 1,4,6,7-tetramethyl-*r*-1-nitro-*t*-4-trinitromethyl-1,4-dihydronaphthalene (**7**).

Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	10^3U_{eq} [a]
O(11)	8284(2)	−2933(4)	7746(4)	39(1)
O(12)	8173(2)	−3931(4)	9339(4)	47(1)
O(21)	5031(2)	1311(4)	7376(4)	42(1)
O(22)	6213(2)	1368(4)	8861(4)	37(1)
O(31)	5481(2)	1473(4)	5087(3)	37(1)
O(32)	5266(2)	3598(4)	5790(3)	39(1)
O(41)	7058(2)	4215(4)	6828(4)	40(1)
O(42)	6485(3)	4178(4)	8259(4)	43(1)
N(1)	7981(3)	−2992(4)	8570(5)	32(1)
N(2)	5794(3)	1563(4)	7817(4)	32(1)
N(3)	5635(2)	2404(5)	5847(4)	30(1)
N(4)	6668(3)	3647(4)	7439(5)	33(1)
C(1)	7309(3)	−1766(5)	8635(5)	27(1)
C(2)	6692(3)	−1693(5)	7409(5)	29(1)
C(3)	6568(3)	−541(5)	6741(5)	29(1)
C(4)	7050(3)	915(5)	7040(5)	27(1)
C(4a)	7749(3)	843(5)	8265(4)	25(1)
C(5)	8330(3)	2012(5)	8644(5)	29(1)
C(6)	8982(3)	2005(5)	9714(5)	30(1)
C(7)	9054(3)	778(5)	10455(5)	30(1)
C(8)	8502(3)	−382(5)	10064(5)	29(1)
C(8a)	7859(3)	−377(5)	8975(5)	27(1)
C(9)	6856(3)	−2222(5)	9520(5)	35(1)
C(10)	7487(3)	1253(5)	6091(5)	33(1)
C(11)	9583(3)	3296(5)	10062(5)	36(1)
C(12)	9738(3)	723(6)	11648(5)	38(1)
C(13)	6334(3)	2084(5)	7045(5)	27(1)

[a] The equivalent isotropic temperature factor in Tables 2 and 3 is defined as one-third of the orthogonalized U_{ij} tensor (in Å^2).

due to the protons associated with the alicyclic ring presumably being due to the presence of the 6- and 7-methyl groups in adduct **8**.

The structure of the remaining nitro–trinitromethyl adduct **9**, which also could not be isolated, was assigned from a comparison of its ^{1}H NMR spectrum with that for 2,3-dimethyl-*r*-1-nitro-*c*-4-trinitromethyl-1,4-dihydronaphthalene **14**.[10] The ^{1}H NMR signals due to the C*H*NO_2



(δ 5.91) and C*H*C$(NO_2)_3$ (δ 5.89) appeared as broad singlets, consistent with their location flanking the 2,3-dimethyl structural feature.

Reaction in dichloromethane at 20°C and the identification of some of the nitroaromatic compounds. Reaction of 1,4,6,7-tetramethylnaphthalene–tetranitromethane in dichloromethane at 20°C, as above, for 2 h gave a product which was shown by ^{1}H NMR spectra to be a mixture (Table 1) of adducts (total 17%), 4,6,7-trimethyl-1-(2′,2′,2′-trinitroethyl)naphthalene (**10**) (8%), 2,3,5,8-tetramethyl-1-nitronaphthalene (**11**) (6%), 1,4,6,7-tetramethyl-2-nitronaphthalene (**12**) (38%), and 4,6,7-trimethyl-1-nitromethylnaphthalene (**13**) (31%). Chromatography of this mixture on a silica gel Chromatotron plate gave the following in elution order.

The first compound eluted, 4,6,7-trimethyl-1-(2′,2′,2′-trinitroethyl)naphthalene (**10**), was obtained only in low yield but gave a satisfactory parent molecular ion in the mass spectrum. The site of substitution of the trinitromethyl group was demonstrated by extensive NMR experiments which allowed the complete assignment of the ^{1}H and ^{13}C NMR spectra, except for the methyl groups at C6 and at C7 which had closely similar ^{13}C NMR resonances (see Experimental section). The second compound eluted, 2,3,5,8-tetramethyl-1-nitronaphthalene (**11**), was again isolated only in low yield but gave a satisfactory parent molecular ion in the mass spectrum. Again, the connectivity in the structure was established by the complete assignment of the ^{1}H and ^{13}C NMR spectra (see Experimental section). The third compound eluted, 1,4,6,7-tetramethyl-2-nitronaphthalene (**12**), was identified from its ^{1}H and ^{13}C NMR spectra, which again allowed the complete connectivity in the structure to be determined (see Experimental section).

The final compound eluted, 4,6,7-trimethyl-1-nitromethylnaphthalene (**13**), appeared to be unstable on the silica gel Chromatotron plate and could be isolated only in admixture with other materials. Notwithstanding this difficulty, there appears to be little doubt about the assignment of the structure to this compound.

*Rearrangement of 1,4,6,7-tetramethyl-*r*-1-nitro-*t*-4-trinitromethyl-1,4-dihydronaphthalene (7) on silica gel.* The nitro–trinitromethyl adduct **7** was adsorbed onto a silica gel Chromatotron plate, which was then eluted in the usual manner using first pentane and then pentane–ether mixtures. The first material eluted was unreacted nitro–trinitromethyl adduct **7**, identified from its spectroscopic characteristics.

The second compound eluted, 1,4,6,7-tetramethyl-2-trinitromethyl-1,2-dihydronaphthalen-1-ol (**15**), was isolated only in low yield and failed to give a molecular ion in the mass spectrum under a wide variety of operating conditions. However, the substituents present in the structure and its connectivity were established from extensive NMR spectroscopic experiments which allowed the complete assignment of the ^{1}H and ^{13}C NMR spectra (see Experimental section for full details). The locations of the hydroxy and trinitromethyl functions were defined by the chemical shifts for the 1-CH_3 (^{1}H NMR δ = 1.69) and *C*1 (^{13}C NMR δ = 72.8), and *H*2 (^{1}H NMR δ = 4.39) and *C*2 (^{13}C NMR δ = 49.3). The stereochemistry of this

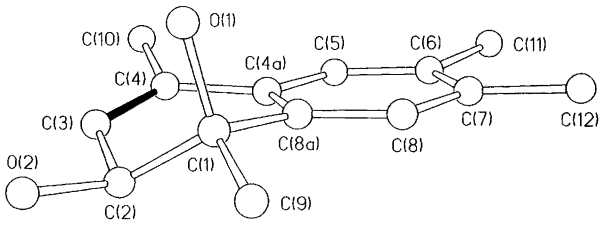


Fig. 2. Perspective drawing of compound **17**.

compound **15** remains uncertain, but arguments will be presented below which suggest that it has the *r*-1-hydroxy-*c*-2-trinitromethyl stereochemistry.

The third compound eluted, 1,4,6,7-tetramethyl-2-nitro-1,2-dihydronaphthalen-1-ol (**16**), was again isolated only in low yield and also failed to give a parent molecular ion in the mass spectrum under a wide variety of operating conditions. As for the 1-hydroxy-2-trinitromethyl compound **15** above, the substituents present and the connectivity in the 1-hydroxy-2-nitro compound **16** were established from NMR spectroscopic experiments which allowed the complete assignment of the ^{1}H NMR spectra (see Experimental section for full details). In particular, the location of the hydroxy function *ipso* to the 1-methyl group was indicated by the ^{1}H NMR chemical shift for the 1-CH_3 ($\delta = 1.52$) and the ^{13}C NMR chemical shift for *C*1 ($\delta = 72.3$), while the nitro function located at C2 was indicated by the ^{1}H NMR chemical shift for *H*2 ($\delta = 4.99$) and the ^{13}C NMR chemical shift for *C*2 ($\delta = 89.7$). The stereochemistry of this compound **16** is uncertain, but it seems likely that it has the *r*-1-hydroxy-*c*-2-nitro stereochemistry (see below).

The structure of the final compound eluted was determined by single crystal X-ray analysis. A perspective drawing of 1,4,6,7-tetramethyl-1,2-dihydronaphthalene-*r*-1,*c*-2-diol (**17**), $C_{14}H_{18}O_2$, m.p. 98–98.5 °C is presented in Fig. 2, and corresponding atomic coordinates are given in Table 3. In the solid state the alicyclic ring of diol **17** exists in a conformation in which the unsaturated systems are twisted from coplanarity [torsional angle: C(3)–C(4)–C(4a)–C(8a) = −16.3(2)°] and the conformation of the remainder of that ring is defined by torsional angles: C(4)–C(3)–C(2)–C(1) = 37.8(2)°; C(4a)–C(8a)–C(1)–C(2) = 35.9(2)°. In that conformation the C(2)–O(2) bond is staggered with respect to the vicinal C(1)–O(1) and C(1)–C(9) bonds [torsional angles: O(2)–C(2)–C(1)–O(1) = −58.9(1)°; O(2)–C(2)–C(1)–C(9) = 60.9(2)°], and the *peri* interactions involving the methyl groups on the alicyclic ring are somewhat relieved [torsional angles: C(10)–C(4)–C(4a)–C(5) = −15.1(2)°; C(9)–C(1)–C(8a)–C(8) = −27.3(2)°]. It is clear that diol **17** exists in a markedly different conformation in solution from that observed in the solid state. In the solid state the torsional angle H(3)–C(3)–C(2)–H(2a) = 99.2(1)° would be consistent with a vicinal H–H coupling constant close to zero. In solution the observed coupling constant $J_{H3,H2} = 5.9$ Hz would appear more consistent with an alternative twisting of the alicyclic ring in which the C(2)–O(2) and C(1)–C(9) bonds would have orientations close to perpendicular to the mean plane of the molecule, leading to a H(3)–C(3)–C(2)–H(2a) torsional angle close to 30°. In this conformation the *peri* interaction between the C1 methyl group and the adjacent aromatic ring would be minimized. The probable origin of this conformational difference in diol **17** in the solid state lies in the hydrogen bond between O(1) and H(2′) in a second molecule (Fig. 3). The O(1)/O(2′) distance is 2.713 Å, and the O(1)–H(2′)–O(2′) angle is 167.2°, consistent with a strong hydrogen bond.

In solution the vicinal coupling constants $J_{H3,H2}$ are closely similar for compounds **15** (5.9 Hz), **16** (6.5 Hz) and **17** (5.9 Hz). It is clear therefore that the H3–C3–C2–H2 torsional angles for these compounds are similar in solution with the C2–X bond [X = $C(NO_2)_3$, NO_2, and OH, respectively] perpendicular to the mean plane of the molecule in each case. Given the similar ratio of NOE enhancements to H8 and H2 on irradiation of the 1-methyl signal in the ^{1}H NMR spectra for compounds **15–17**, it appears that the three compounds have the same stereochemistry with the 1-methyl/H8 distance being greater than the 1-methyl/H2 distance. Given that diol **17** has been shown by single-crystal X-ray analysis to have the *r*-1-*c*-2-diol stereochemistry, the same stereochemistry, *r*-hydroxy-*c*-2-X, is assigned tentatively to compounds **15** and **16**.

Table 3. Fractional coordinates for atoms in 1,4,6,7-tetramethyl-1,2-dihydronaphthalene-*r*-1,*c*-2-diol (**17**).

Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	10^3U
O(1)	7039(2)	3863(1)	9217(1)	24(1)
O(2)	1790(2)	4518(1)	8787(1)	24(1)
C(1)	4928(3)	2554(2)	8740(1)	17(1)
C(2)	2717(3)	3209(2)	8141(1)	17(1)
C(3)	3575(3)	3764(2)	7288(1)	20(1)
C(4)	5143(3)	2968(2)	6745(1)	18(1)
C(4a)	6150(3)	1535(2)	7024(1)	17(1)
C(5)	7365(3)	445(2)	6386(1)	19(1)
C(6)	8487(3)	−839(2)	6665(1)	20(1)
C(7)	8347(3)	−1076(2)	7624(1)	21(1)
C(8)	7101(3)	−10(2)	8254(1)	20(1)
C(8a)	6014(3)	1292(2)	7986(1)	16(1)
C(9)	3669(3)	1894(2)	9559(1)	22(1)
C(10)	5998(3)	3510(2)	5881(1)	24(1)
C(11)	9956(3)	−1892(2)	5976(1)	27(1)
C(12)	9574(3)	−2426(2)	7979(1)	29(1)

Reaction in dichloromethane containing trifluoroacetic acid (0.68 mol dm^{-3}) at 20 °C. Reaction of 1,4,6,7-tetramethylnaphthalene (0.34 mol dm^{-3}), tetranitromethane (0.68 mol dm^{-3}), and trifluoroacetic acid (0.68 mol dm^{-3}), in dichloromethane at 20 °C, as above, for 2 h (conversion ≈ 69%) gave a product which was shown by ^{1}H NMR spectra to be a mixture (Table 4) of 2,3,5,8-tetramethyl-1-nitronaphthalene **11** (32%), 1,4,6,7-tetramethyl-2-nitronaphthalene **12** (48%), and 4,6,7-trimethyl-1-nitromethylnaphthalene **13** (6%) and some unidentified

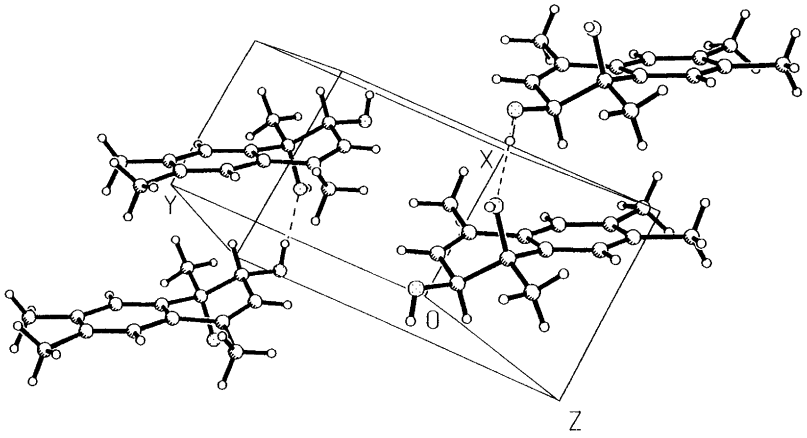


Fig. 3. Perspective drawing showing the hydrogen bond between O(1) and H(2′) in the solid state for compound **17**.

Table 4. Overview of yields of products from the photolysis of 1,4,6,7-tetramethylnaphthalene (0.34 mol dm^{-3}) and tetranitromethane (0.68 mol dm^{-3}) in dichloromethane containing trifluoroacetic acid (0.68 mol dm^{-3}).

		Yield (%)			
t/h	Conversion (%)	**11**	**12**	**13**	Unidentified material
0.5	16	28.8	44.4	10.0	16.8
1	33	29.5	48.0	8.5	14.0
2	69	32.1	48.2	5.9	13.8

material (14%). Notably neither nitro–trinitromethyl adducts nor 4,6,7-trimethyl-1-(2′,2′,2′-trinitroethyl)-naphthalene (**10**) were detected in this reaction mixture.

Reaction in acetonitrile at 20°C. Reaction of 1,4,6,7-tetramethylnaphthalene–tetranitromethane in acetonitrile at 20°C, as above, for 2 h gave a product which was shown by ^{1}H NMR spectra to be a mixture (Table 5) of adducts (total 1%), 4,6,7-trimethyl-1-(2′,2′,2′-trinitroethyl)naphthalene (**10**) (1%), 2,3,5,8-tetramethyl-1-nitronaphthalene (**11**) (33%), 1,4,6,7-tetramethyl-2-nitronaphthalene (**12**) (53%), and 4,6,7-trimethyl-1-nitromethylnaphthalene (**13**) (4%). After 0.5 h (conversion 33%) the yield of adducts was somewhat higher (total 15%), but compounds **11** (29%) and **12** (49%) were still predominant among the products detected by ^{1}H NMR spectroscopy.

Cyclic voltammetry of 1,4,6,7-tetramethylnaphthalene. Cyclic voltammetry of 1,4,6,7-tetramethylnaphthalene (2 mmol dm^{-3}) in dichloromethane–Bu_4NPF_6 at 0.2 V s^{-1} showed a reversible couple with E_{pa} = 1.52 V (vs. the Ag/AgCl electrode; all potentials in this paper will be referred to this electrode) and E_{pc} = 1.43 V, the reversible potential thus being 1.48 V. At 10 V s^{-1} the corresponding values were 1.53, 1.43 and 1.48 V. A literature value,[11] determined in dichloromethane–Bu_4NBF_4 at 200 K, was lower, ca. 1.16 V, presumably due to a difference in liquid junction potentials.

EPR detection of the radical cation of 1,4,6,7-tetramethylnaphthalene during photolysis with tetranitromethane and trifluoroacetic acid. Irradiation of a solution of 1,4,6,7-tetramethylnaphthalene, tetranitromethane and trifluoroacetic acid in dichloromethane at −60°C gave a strong signal of the monomeric radical cation, whereas in the absence of trifluoroacetic acid the solution was EPR-silent.[2]

*Rearrangement of 1,4,6,7-tetramethyl-*r*-1-nitro-*t*-4-trinitromethyl-1,4-dihydronaphthalene (**7**) in (^{2}H)chloroform at 20°C.* A solution of the nitro–trinitromethyl adduct **7** in (^{2}H)chloroform was stored at 20°C in the dark, and the ^{1}H NMR spectrum was monitored at appropriate time intervals (Table 6). The rate constant for the disappearance of **7** was 2.0(3) × 10^{-4} min^{-1}. The major products after 12 days were identified from their ^{1}H NMR spectra as 4,6,7-trimethyl-1-(2′,2′,2′-trinitroethyl)naphthalene

Table 5. Overview of yields of products from the photolysis of 1,4,6,7-tetramethylnaphthalene (0.34 mol dm^{-3}) and tetranitromethane (0.68 mol dm^{-3}) in acetonitrile (at 20 °C).

		Yield (%)											
t/h	Conversion (%)	**7**	**8**	**9**	**15**	**16**	Total adducts	**10**	**11**	**12**	**13**	Unknown aromatics	Total aromatics
0.5	33	6.7	2.2	4.8	0.6	0.5	14.8	0.6	28.9	48.8	2.8	4.1	85.2
1	68	3.3	1.0	3.4	0.6	0.2	8.5	0.9	33.6	51.7	2.7	2.6	91.5
2	100	–	–	1.3	–	–	1.3	1.3	33.0	52.9	4.2	7.3	98.7

Table 6. Rearrangement of 1,4,6,7-tetramethyl-*r*-1-nitro-*t*-4-trinitromethyl-1,4-dihydronaphthalene (**7**) in (^{2}H)chloroform at 20 °C.

	Composition (%)								
t/h	**7**	**8**	**9**	**18**	Total adducts	**10**	**13**	Unknown aromatics	Total aromatics
0	100	–	–	–	100	–	–	–	–
1	96.5	3.5	–	–	100	–	–	–	–
4	90.0	8.9	–	0.5	99.4	–	0.6	–	0.6
8	84.2	12.7	–	2.0	98.9	–	1.1	–	1.1
24	75.6	14.0	–	6.7	96.3	0.4	3.1	0.2	3.7
48	52.6	10.0	–	13.3	79.7	11.5	7.3	1.5	20.3
120	6.7	1.2	0.5	17.4	26.4	51.5	14.9	7.2	73.6
168	–	–	0.7	10.4	11.1	65.0	12.9	11.0	88.9
216	–	–	0.4	3.9	4.3	72.7	7.5	13.6	95.7

(**10**) [73%, rate constant of formation $1.3(3) \times 10^{-4}$ min^{-1}] and 4,6,7-trimethyl-1-nitromethylnaphthalene (**13**) (7%). In the early stages of the rearrangement epimerization of adduct **7** occurred to give 1,4,6,7-tetramethyl-*r*-1-nitro-*c*-4-trinitromethyl-1,4-dihydronaphthalene (**8**), its rate constant of formation being $2.0(3) \times 10^{-3}$ min^{-1} and of disappearance 3.8×10^{-4} min^{-1}, assuming that its kinetics are dependent on two consecutive first-order processes. Adduct **8** reached its maximum concentration at ca. 24 h. The equilibrium was apparently attained some time between 8 and 24 h (**7**:**8** ratio ca. 5:1). After some 4 h the concentration of a third adduct built up, reaching a maximum level (17%) after ca. 120 h [rate constants for build-up and decay $2(1) \times 10^{-4}$ and $2(1) \times 10^{-4}$ min^{-1}, respectively]; this adduct was tentatively identified as 1,4,6,7-tetramethyl-*r*-2-nitro-*t*-1-trinitromethyl-1,2-dihydronaphthalene (**18**) on the basis of its ^{1}H NMR spectrum. In this structure it would be expected that the bulky 1-trinitromethyl group would adopt a conformation such that the C1–C(NO$_2$)$_3$ bond was close to perpendicular to the plane of the aromatic ring. Given the magnitude of the coupling constant $J_{H2,H3} = 6.1$ Hz, it appears that the C2–NO$_2$ bond is close to anti-coplanar with the C1–C(NO$_2$)$_3$ bond, and that adduct **18** therefore has the *t*-2-nitro-*r*-1-trinitromethyl configuration.

*The rearrangement of 1,4,6,7-tetramethyl-*r*-1-nitro-*t*-4-trinitromethyl-1,4-dihydronaphthalene (**7**) in acetonitrile.* A quantitative study of the rearrangement of the nitro–trinitromethyl adduct **7** in acetonitrile was limited by the low solubility of adduct **7** in that solvent. However, it was clear that the reaction was much faster, the rate constant for disappearance of **7** now being $3(1) \times 10^{-2}$ min^{-1}. Thus the timescale of the acetonitrile rearrangement was > 100 times that in chloroform. Epimerization of adduct **7** to give the *r*-1-nitro-*c*-4-trinitromethyl adduct **8** was a rapid reaction [rate constant of formation of **8** 0.5(2) min^{-1}, of disappearance $3.1(6) \times 10^{-2}$ min^{-1}, the concentration of **8** reached its maximum after ca. 10 min] with the concurrent formation of the rearrangement product 4,6,7-trimethyl-1-nitromethylnaphthalene (**13**). These observations parallel closely the earlier report of the analogous rearrangement of 1,4-dimethyl-*r*-1-nitro-*t*-4-trinitromethylnaphthalene (**1**).[4] In the early stages of the rearrangement (1–5 min) two further adducts were present, 1,4,6,7-tetramethyl-*c*-2-trinitromethyl-1,2-dihydronaphthalen-*r*-1-ol (**15**) and 1,4,6,7-tetramethyl-*c*-2-nitro-1,2-dihydronaphthalen-*r*-1-ol (**16**); a further adduct, 2,3,5,8-tetramethyl-*r*-1-nitro-*c*-4-trinitromethyl-1,4-dihydronaphthalene (**9**), was present at low levels (maximum 3%) at reaction times between 3 min and 2 h. During the course of the rearrangement (over 4 h) the concentration of adducts **7**, **8**, **15** and **16** decreased steadily with the formation of increasing amounts of the nitroaromatic compounds, finally giving 2,3,5,8-tetramethyl-1-nitronaphthalene (**11**) [14%, rate constant of formation $2.0(2) \times 10^{-2}$ min^{-1}], 1,4,6,7-tetramethyl-2-nitronaphthalene (**12**) [52%, rate constant of formation $3.1(4) \times 10^{-2}$ min^{-1}] and 4,6,7-trimethyl-1-nitromethylnaphthalene (**13**) [27%, rate constant of formation $2.8(2) \times 10^{-2}$ min^{-1}].

*EPR studies of the rearrangement of 1,4,6,7-tetramethyl-r-1-nitro-t-4-trinitromethyl-1,4-dihydronaphthalene (**7**).* The nitro–trinitromethyl adduct **7** has a structure analogous to that of 1,4-dimethyl-*r*-1-nitro-*t*-4-trinitromethyl-1,4-dihydronaphthalene (**1**), and would be expected to behave in a similar manner to that reported earlier for adduct **1**.[4] As Fig. 4 (circles) demonstrates, a solution of adduct **7** (10 mmol dm^{-3}) and α-phenyl-*N*-*tert*-butylnitrone (PBN; IUPAC-recommended name: *N*-*tert*-butylbenzylideneamine *N*-oxide) (40 mmol dm^{-3}) in dichloromethane at 24 °C showed a steady build-up of (NO$_2$)$_3$C–PBN$^{\bullet}$ to a maximum concentration after about 4 h ($k \approx 0.010$ min^{-1}) followed by a slow decay (not shown, but separate measurements gave $k \approx 5 \times 10^{-4}$ min^{-1}). The addition of a *low* concentration of trifluoroacetic acid (TFA) (20 mmol dm^{-3}) did not influence this behaviour significantly (Fig. 4, triangles) whereas at [TFA] = 80 mmol dm^{-3} the trinitromethyl spin adduct concentration had decreased to a level of about 25% of the former values (Fig. 5, hollow squares). Additionally a second EPR signal due to the acylnitroxyl radical,

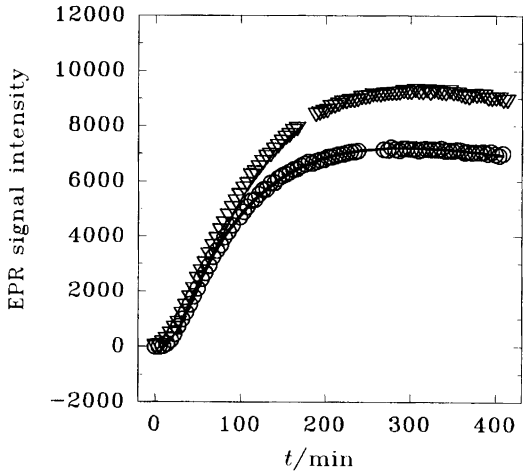


Fig. 4. The time development of the EPR signal intensity of $(NO_2)_3C$–PBN$^{\cdot}$ from (i) a solution of adduct **7** (10 mmol dm^{-3}) and PBN (40 mmol dm^{-3}) (circles) and (ii) a solution of adduct **7** (10 mmol dm^{-3}), PBN (40 mmol dm^{-3}) and TFA (20 mmol dm^{-3}) (triangles) in dichloromethane. The solid curve corresponds to a double exponential function with $k_{up}=0.0103(3)$ min^{-1} and $k_{down}\approx 5\times10^{-4}$ min^{-1} (measured separately).

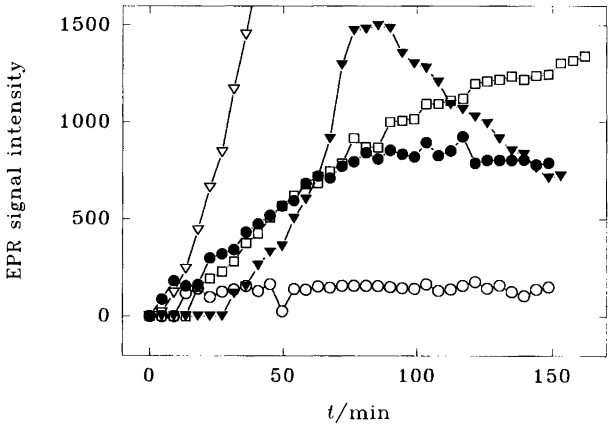


Fig. 5. The time development of the EPR signal intensity of $(NO_2)_3C$–PBN$^{\cdot}$ from a solution of adduct **7** (10 mmol dm^{-3}), PBN (40 mmol dm^{-3}) and (i) TFA (20 mmol dm^{-3}; hollow triangles), (ii) TFA (80 mmol dm^{-3}; hollow squares), (iii) TFA (0.12 mol dm^{-3}; hollow circles) in dichloromethane. The time development of PBNOx is shown for [TFA]=0.12 mol dm^{-3} (filled circles) and 0.19 mol dm^{-3} (filled triangles). The lines are drawn only to assist visibility.

PhCON(O$^{\cdot}$)-Bu^{t} (PBNOx), was just detectable. A further increase of [TFA] to 120 mmol dm^{-3} decreased the trinitromethyl spin adduct to almost zero concentration (Fig. 5, hollow circles), whereas [PBNOx] increased (Fig. 5, filled circles). At [TFA] = 190 mmol dm^{-3}, only PBNOx was seen (Fig. 5, filled triangles).

In acetonitrile, analogous behaviour was observed, except that the maximum level of spin adduct concentration was about 3% of the one recorded in dichloromethane under the same conditions of concentrations and temperature. Also, the processes were somewhat faster, the trinitromethyl spin adduct appearing with a rate constant of $3.0(4)\times10^{-2}$ min^{-1} and decaying with $k=2.8(3)\times10^{-3}$ min^{-1}.

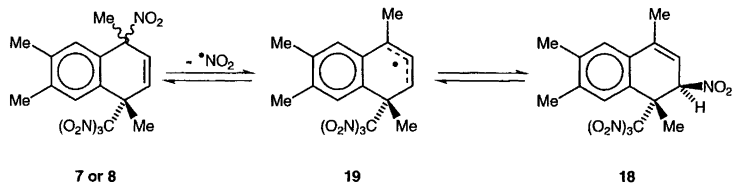
In chloroform, the appearance and disappearance of the trinitromethyl spin adduct was slower than in dichloromethane, rate constants being $1.2(1)\times10^{-3}$ and $1.5(1)\times10^{-4}$ min^{-1} (see below). The maximum intensity of the EPR spectrum was of about the same magnitude and it appeared after ca. 24 h. The hfs constants of the EPR spectrum were $a^{N}=0.146$ and $a^{H}=0.042$ mT, about the same as in dichloromethane.[8] In chloroform, it was also possible to resolve the spectrum enough for the coupling constant to the three NO_2 nitrogens to be measurable, ca. 0.03 mT.

Experiments performed in the same way, but using 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) as the spin trap in dichloromethane, failed to show the formation of the $(NO_2)_3C$–DMPO$^{\cdot}$ spin adduct.

Discussion

Photochemistry in dichloromethane. As in the photochemical reactions of 1,4-dimethylnaphthalene in dichloromethane,[4] it appears that the major primary products of the photochemical reaction of the 1,4,6,7-tetramethylnaphthalene–tetranitromethane charge-transfer complex are nitro–trinitromethyl adducts (Table 1), in this case adducts **7–9**. Although the identification of adduct **9** is somewhat uncertain, it is interesting that this adduct will have been formed by trinitromethanide ion attack at the ring position hindered by *vicinal* and *peri* methyl substituents. In the presence of trifluoroacetic acid the formation of adducts **7–9** and 4,6,7-trimethyl-1-(2′,2′,2′-trinitroethyl)naphthalene (**10**) is totally suppressed (Table 4), as the result of protonation of the trinitromethanide ion, and the formation of the nitro compounds **11–13** are seen as the products of reaction of nitrogen dioxide with the radical cation of 1,4,6,7-tetramethylnaphthalene.

Photochemistry in acetonitrile. The substrate was insufficiently soluble in acetonitrile at −20 °C for a meaningful reaction to be carried out. At 20 °C the reaction was characterized by low adduct yields (Table 6) and clear indications of the instability of adducts in acetonitrile under the reaction conditions. Subsequently, it was demonstrated (see below) that 1,4,6,7-tetramethyl-*r*-1-nitro-*t*-4-trinitromethyl-1,4-dihydronaphthalene (**7**) was markedly unstable in acetonitrile at 20 °C, giving rise predominantly to 2,3,5,8-tetramethyl-1-nitronaphthalene (**11**) (14%), 1,4,6,7-tetramethyl-2-nitronaphthalene (**12**) (52%) and 4,6,7-trimethyl-1-nitromethylnaphthalene (**13**) (27%). On the basis of a comparison of the relative yields of aromatic products from the photochemical reaction in acetonitrile and from the rearrangement of the nitro–trinitromethyl adduct **7** in acetonitrile, it appears however that much of the nitroaromatics **11** and **12** may arise by



7 or 8 19 18

Scheme 3.

direct coupling of nitrogen dioxide with the radical cation of 1,4,6,7-tetramethylnaphthalene.

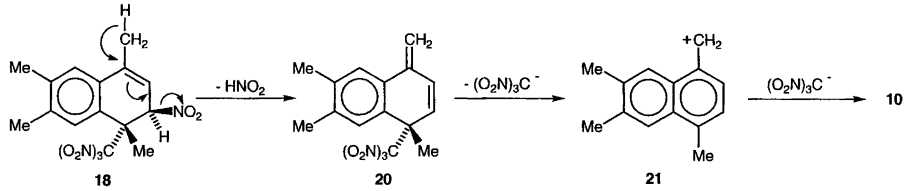
*Rearrangement of 1,4,6,7-tetramethyl-*r*-1-nitro-*t*-4-trinitromethyl-1,4-dihydronaphthalene (7) in (^{2}H)chloroform at 20°C.* In the early stages of the rearrangement it was clear that epimerization was occurring to give adduct **8** accompanied by the formation of 4,6,7-trimethyl-1-nitromethylnaphthalene (**13**); this behaviour mirrors closely the rearrangement of 1,4-dimethyl-*r*-1-nitro-*t*-4-trinitromethyl-1,4-dihydronaphthalene (**1**) (Scheme 1).[4] Early in the rearrangement a further adduct, 1,4,6,7-tetramethyl-*t*-2-nitro-*r*-1-trinitromethyl-1,2-dihydronaphthalene (**18**), was detected. This adduct **18** is seen as arising by homolytic cleavage of the C1–NO_2 bond in either adduct **7** or adduct **8**, with recombination of the radical species occurring on the less hindered face of the delocalized carbon radical **19** *anti* to the bulky trinitromethyl group (Scheme 3). The detection, at low levels, of 2,3,5,8-tetramethyl-*r*-1-nitro-*c*-4-trinitromethyl-1,4-dihydronaphthalene (**9**) is a clear indication that one or more of the adducts present in the rearrangement mixture was capable of reverting to some equivalent of the triad [$ArH^{\bullet+}$ $NO_2(O_2N)_3C^-$] in the original photochemical reaction. In the later stages of the rearrangement the amount of adduct **9** remained at a low level, but adduct **18** clearly reacted further under the prevailing reaction conditions. Indeed, adduct **18** is seen as the precursor of the major final product 4,6,7-trimethyl-1-(2′,2′,2′-trinitroethyl)naphthalene (**10**). A possible mechanism for this transformation is given in Scheme 4. Loss of nitrous acid from adduct **18** would yield the trinitromethyl diene **20**, which might be expected to rearrange via the ion pair **21** to give the trinitromethylaromatic compound **10**.

The formation of the trinitromethyl spin adduct of α*-phenyl-*N*-tert-butylnitrone (PBN) in the rearrangement of 1,4,6,7-tetramethyl-*r*-1-nitro-*t*-4-trinitromethyl-1,4-dihydronaphthalene – evidence for the intervention of the trinitromethyl radical or a case of inverted spin trapping?* The rearrangement of **7** is accompanied by the formation of radical intermediates, as evidenced by the appearance of spin adducts when the reaction is allowed to take place in the presence of PBN. The timing of the development of a few critical reaction components (**7**, **8**, **10** and **18**) with the development of the spin adduct EPR signal is shown in Fig. 6 for chloroform solutions; the maximum of the spin adduct concentration approximately coincides with that of adduct **8**, indicating that the further rearrangement of **8** is homolytic, most likely via loss of NO_2 to form a neutral radical of trinitromethylcyclohexadienyl type (Scheme 5). This is the same reaction scheme as was invoked to explain the behaviour of the 1,4-dimethyl-*r*-1-nitro-*t*-4-trinitromethyl-1,4-dihydronaphthalene (**1**) system.[4] In this, the trinitromethyl radical was assumed to be formed by cleavage of the trinitromethylcyclohexadienyl radical (Scheme 2).

The formation of the trinitromethyl spin adduct of PBN would seem to constitute unambiguous evidence for the intervention of the trinitromethyl radical in the rearrangement of 1,4-dimethyl-*r*-1-nitro-*t*-4-trinitromethyl-1,4-dihydronaphthalene (**1**) and 1,4,6,7-tetramethyl-*r*-1-nitro-*t*-4-trinitromethyl-1,4-dihydronaphthalene (**7**). The trinitromethyl radical is a species which has been detected by EPR spectroscopy at 77 K,[12] and from its chemistry appears to be an unstable species.[13] Theoretical calculations[14] on the nitromethyl and dinitromethyl radicals also extrapolate to high instability of the trinitromethyl radical. Nevertheless, spin trapping by PBN is usually a fast process,[15] and it was therefore assumed that it would compete favourably with decomposition pathways of the trinitromethyl radical.[4]

However, the demonstration[8] that spin adducts may also be formed by reaction of the radical cation of the spin trap with a nucleophile (as an example, from $PBN^{\bullet+}$ and Nu^-, instead of PBN and $Nu^\bullet$) introduces an analogous interpretational problem into Scheme 5: can $ArH^{\bullet+}$ oxidise PBN to $PBN^{\bullet+}$, the latter then trapping trinitromethanide ion to give the spin adduct?

Evidence in this direction is provided by the effect of



18 20 21

Scheme 4.

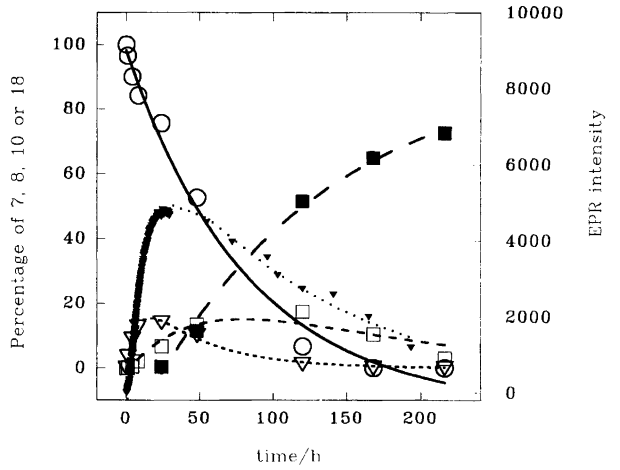
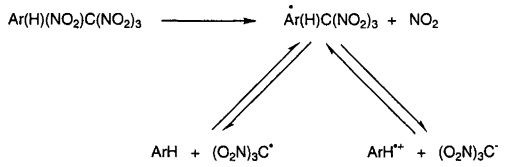


Fig. 6. The time development of **7** (hollow circles; the solid line corresponds to an exponential with $k = 2.0 \times 10^{-4}$ min^{-1}), **8** (hollow triangles; the small dash line corresponds to a double exponential with $k_{up} = 2.0 \times 10^{-3}$ min^{-1} and $k_{down} = 3.8 \times 10^{-4}$ min^{-1}), **10** (filled squares; the large dash line corresponds to an exponential with $k = 1.3 \times 10^{-4}$ min^{-1}) and **18** (hollow squares; the medium dash line corresponds to a double exponential with $k_{up} = 2 \times 10^{-4}$ min^{-1} and $k_{down} = 2 \times 10^{-4}$ min^{-1}), compared to that of the EPR signal of $(NO_2)_3C$–PBN$^{\bullet}$. (small filled triangles; the dotted line corresponds to a double exponential with $k_{up} = 1.2 \times 10^{-3}$ min^{-1} and $k_{down} = 1.5 \times 10^{-4}$ min^{-1}) in [^{2}H]-chloroform at ambient temperature.



Scheme 5.

added acid in the rearrangement of the nitro–trinitromethyl adduct **7**; at a [TFA] of about 0.2 mol dm^{-3} the trinitromethyl spin adduct has become completely suppressed, a phenomenon best explicable in terms of the removal of trinitromethanide ion from reaction by protonation. Instead PBNOx, the product of reaction between PBN and NO_2, is formed.[16] This effect of added acid is analogous to that shown by EPR spectroscopy and preparative experiments for the photolysis of many ArH–tetranitromethane CT complexes: all or almost all chemistry due to trinitromethanide ion can be suppressed by adding TFA in concentrations of 0.2 mol dm^{-3} and upwards.[2,17] Another indication is the failure of DMPO to give any trinitromethyl spin adduct. Since DMPO is about 0.2 V more difficult to oxidise than PBN (E_p = 1.72 and 1.54 V, respectively, in acetonitrile–Bu_4NPF_6),[15] the redox potential of the present ArH$^{\bullet+}$/ArH system,

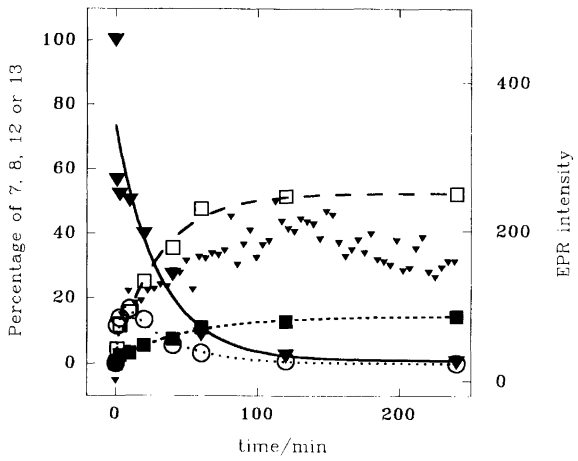


Fig. 7. The time development of **7** (filled triangles; the solid line corresponds to an exponential with $k = 3 \times 10^{-2}$ min^{-1}), **8** (hollow circles; the dotted line corresponds to a double exponential with $k_{up} = 0.5$ min^{-1} and $k_{down} = 3.1 \times 10^{-2}$ min^{-1}), **12** (hollow squares; the large dashed line corresponds to an exponential with $k = 3.1 \times 10^{-2}$ min^{-1}) and **13** (filled squares; the small dashed line corresponds to an exponential with $k = 2.8 \times 10^{-2}$ min^{-1}), compared to that of the EPR signal of $(NO_2)_3C$–PBN$^{\bullet}$ (small filled triangles) in acetonitrile at ambient temperature.

1.48 V, is not sufficient to oxidise DMPO to DMPO$^{\bullet+}$ at a sufficiently high rate.

*Rearrangement of 1,4,6,7-tetramethyl-*r*-1-nitro-*t*-4-trinitromethyl-1,4-dihydronaphthalene (7) in acetonitrile at 20°C.* In acetonitrile the title rearrangement is >100 times faster than in chloroform, indicating that polar mechanisms are predominant in acetonitrile. The EPR activity in acetonitrile is weak and its time dependence is not correlated with that of the main reaction components **7**, **8**, **12** and **13** (Fig. 7).

*The rearrangement of 1,4,6,7-tetramethyl-*r*-1-nitro-*t*-4-trinitromethyl-1,4-dihydronaphthalene (7) on silica gel.* The mode of formation of the three 1,4,6,7-tetramethyl-*c*-2-X-1,2-dihydronapthalen-*r*-1-ols **15–17** [X = $C(NO_2)_3$, NO_2 and OH respectively] on adsorption of the nitro–trinitromethyl adduct **7** onto a silica gel Chromatotron plate remains uncertain. However, at a superficial level it appears that 1,3-migration of a trinitromethyl group (to form **15**) and of a nitro group (to form **16**) occurs under these conditions. In conclusion, these results imply that chromatography of such adducts on silica gel may not give a simple chromatographic outcome.

Concluding remarks. It is clear that the photoreaction of 1,4,6,7-tetramethylnaphthalene with tetranitromethane and the rearrangements of the adducts formed, while broadly similar to those for 1,4-dimethylnaphthalene, have still provided some interesting deviations.

Experimental

Melting points are uncorrected. Infrared spectra were recorded on a Perkin Elmer 1600 series FTIR spectrometer; ^{1}H NMR spectra were recorded on a Varian Unity 300 spectrometer with $SiMe_4$ as an internal standard. EPR measurements were performed as described earlier.[2,4] Tetranitromethane was purchased from Aldrich and 1,4,6,7-tetramethylnaphthalene from Wiley Organics. 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.[18]

General procedure for the photonitration of 1,4,6,7-tetramethylnaphthalene with tetranitromethane. A solution of 1,4,6,7-tetramethylnaphthalene (500 mg, 0.34 mol dm^{-3}) and tetranitromethane (0.68 mol dm^{-3}) in dichloromethane (at 20 or −20°C) or acetonitrile (at 20°C) was irradiated with filtered light ($\lambda_{cut\text{-}off}$ <435 nm). Aliquots were withdrawn from the reaction mixture at appropriate time intervals, the volatile material removed under reduced pressure at ≤0°C, and the product composition determined by NMR spectral analysis (Tables 1, 4 and 5).

*Reaction in dichloromethane at −20°C and the identification of 1,4,6,7-tetramethyl-*r*-1-nitro-*t*-4-trinitromethyl-1,4-dihydronaphthalene (**7**) and adducts **8** and **9**.* Reaction of 1,4,6,7-tetramethylnaphthalene–tetranitromethane in dichloromethane at −20°C, as above, for 2 h gave a product which was shown by ^{1}H NMR spectra to be a mixture (Table 1) of 1,4,6,7-tetramethyl-*r*-1-nitro-*t*-4-trinitromethyl-1,4-dihydronaphthalene (**7**) (58%), its epimer (**8**) (2%), an adduct tentatively identified as 2,3,5,8-tetramethyl-*r*-1-nitro-*c*-4-trinitromethyl-1,4-dihydronaphthalene (**9**) (3%), 4,6,7-trimethyl-2′,2′,2′-trinitroethylnaphthalene (**10**) (2%), 2,3,5,8-tetramethyl-1-nitronaphthalene (**11**) (4%), 1,4,6,7-tetramethyl-2-nitronaphthalene (**12**) (3%), 4,6,7-trimethyl-1-nitromethylnaphthalene (**13**) (27%) and unidentified aromatic products (total 1%). Crystallization of the product mixture from dichloromethane–pentane gave the major product:

*1,4,6,7-Tetramethyl-*r*-1-nitro-*t*-4-trinitromethyl-1,4-dihydronaphthalene (**7**).* M.p. 89°C (decomp.) (X-ray crystal structure determined, see below). IR: ν_{max} (KBr) = 1613, 1588, 1544 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.07 (s, 1-Me), 2.19 (s, 4-Me), 2.26 (s, 6-Me), 2.27 (s, 7-Me), 6.22 (d, $J_{H2,H3}$ 10.5 Hz, H2), 6.64 (d, $J_{H3,H2}$ 10.5 Hz, H3), 7.12 (br s, H5), 7.28 (br s, H8). Nuclear Overhauser experiments gave the following results: irradiation at δ 2.07 gave enhancements at δ 6.22 (4.7%) and at δ 7.28 (8.6%); irradiation at δ 2.19 gave enhancements at δ 6.64 (5.7%) and at δ 7.12 (9.3%); irradiation at δ 6.22 gave enhancements at δ 2.07 (0.4%) and at δ 6.64 (7.2%); irradiation at δ 6.64 gave enhancements at δ 2.19 (0.4%) and at δ 6.22 (7.5%); irradiation at δ 7.12 gave enhancements at δ 2.19 (0.7%) and at δ 2.26 (0.7%); irradiation at δ 7.28 gave enhancements at δ 2.07 (0.6%) and at δ 2.27 (0.6%). ^{13}C NMR ($CDCl_3$) δ 19.6 (6-Me or 7-Me), 19.9 (7-Me or 6-Me), 26.2 (1-Me or 4-Me), 26.8 (4-Me or 1-Me), 48.9 (C4), 86.7 (C1), 127.05 (C8), 127.7 (C3), 128.2 (C4a), 128.3 (C5), 131.3 (C8a), 131.6 (C2), 139.25 (C6 or C7), 139.65 (C7 or C6), resonance for $C(NO_2)_3$ not observed. The above assignments were confirmed by long-range reverse detected heteronuclear correlation spectra (HMBC).

The minor adducts **8** and **9** were not isolated but were characterized by their ^{1}H NMR ($CDCl_3$) spectra: 1,4,6,7-tetramethyl-*r*-1-nitro-*c*-4-trinitromethyl-1,4-dihydronaphthalene (**8**) – δ 1.99 (s, 1-Me), 2.08 (s, 4-Me), 2.18 (s, C6 or C7), 2.35 (s, C7 or C6), 6.45 (d, $J_{H2,H3}$ 10.4 Hz, H2), 6.62 (d, $J_{H3,H2}$ 10.4 Hz, H3), 7.06 (s, H5), 7.72 (s, H8). 2,3,5,8-Tetramethyl-*r*-1-nitro-*c*-4-trinitromethyl-1,4-dihydronaphthalene (**9**) – δ 1.97 (br s, 2-Me or 3-Me), 2.15 (br s, 3-Me or 2-Me), 2.28 (s, 5-Me or 8-Me), 2.32 (s, 8-Me or 5-Me), 5.89 (br s, H4), 5.91 (br s, H1), 7.20 (s, H6 or H7), 7.49 (s, H7 or H6).

The aromatic compounds **10–13** were isolated by chromatography on a silica gel Chromatotron plate of the product mixture formed in the photolysis of 1,4,6,7-tetramethylnaphthalene–tetranitromethane in dichloromethane at 20°C (see below).

Reaction in dichloromethane at 20°C and the identification of some of the nitroaromatic products. Reaction of 1,4,6,7-tetramethylnaphthalene–tetranitromethane in dichloromethane at 20°C, as above, for 2 h gave a product which was shown by ^{1}H NMR spectra to be a mixture (Table 1) of adducts (total 17%), 4,6,7-trimethyl-1-(2′,2′,2′-trinitroethyl)naphthalene (**10**) (8%), 2,3,5,8-tetramethyl-1-nitronaphthalene (**11**) (6%), 1,4,6,7-tetramethyl-2-nitronaphthalene (**12**) (38%) and 4,6,7-trimethyl-1-nitromethylnaphthalene (**13**) (31%). Chromatography of this mixture on a silica gel Chromatotron plate gave in elution order:

*4,6,7-Trimethyl-1-(2′,2′,2′-trinitroethyl)naphthalene (**10**).* M.p. 131–133°C (insufficient for elemental analysis. Found: $M^{\bullet+}$, 333.0961. $C_{15}H_{15}N_3O_6$ requires 333.0962). IR: ν_{max} (KBr) 1605, 1590 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.43 (s, 7-Me), 2.45 (s, 6-Me), 2.65 (s, 4-Me), 4.84 (s, CH_2), 7.16 (m, H2, H3), 7.44 (s, H8), 7.78 (s, H5). Nuclear Overhauser experiments gave the following results: irradiation at δ 2.65 gave enhancements at δ 7.16 (5.9%) and at δ 7.78 (8.2%); irradiation at δ 4.84 gave enhancements at δ 7.16 (6.5%) and at δ 7.44 (14.1%); irradiation at δ 7.16 gave enhancements at δ 2.65 (0.8%) and at δ 4.84 (1.0%); irradiation at δ 7.44 gave enhancements at δ 2.43 (1.1%) and at δ 4.84 (3.4%); irradiation

at δ 7.78 gave enhancements at δ 2.45 (0.8%) and at δ 2.65 (1.4%). ^{13}C NMR ($CDCl_3$) δ 19.0 (4-Me), 20.3 (6-Me or 7-Me), 20.5 (7-Me or 6-Me), 35.7 (CH_2), 119.85 (C1), 121.45 (C8), 125.2 (C3), 125.4 (C5), 127.5 (C2), 130.9 (C4a), 131.9 (C8a), 136.0 (C6), 136.2 (C4), 136.9 (C7), resonance for $C(NO_2)_3$ not observed. The above assignments were confirmed by long range reverse detected heteronuclear correlation spectra (HMBC).

*2,3,5,8-Tetramethyl-1-nitronaphthalene (***11***).* M.p. 155.5–156.5 °C (insufficient for elemental analysis. Found: $M^{\cdot+}$, 229.1103. $C_{14}H_{15}NO_2$ requires 229.1103). IR: ν_{max} (KBr) 1531 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.31 (s, 2-Me), 2.50 (s, 3-Me), 2.53 (s, 8-Me), 2.64 (s, 5-Me), 7.20 (m, H6, H7), 7.88 (s, H4). Nuclear Overhauser experiments gave the following results: irradiation at δ 2.31 gave an enhancement at δ 2.50 (0.2%); irradiation at δ 2.64 gave enhancements at δ 7.19 (1.7%) and at δ 7.88 (6.1%); irradiation at δ 7.20 gave enhancements at δ 2.53 (0.7%) and at δ 2.64 (0.5%); irradiation at δ 7.88 gave enhancements at δ 2.50 (0.7%) and at δ 2.64 (1.0%). ^{13}C NMR ($CDCl_3$) δ 14.7 (2-Me), 18.9 (5-Me), 19.9 (8-Me), 20.9 (3-Me), 121.95 (C8a), 126.6 (C4), 127.15 (C6), 127.2 (C2), 128.9 (C8), 130.2 (C7), 132.20 (C5), 132.23 (C4a), 134.3 (C3), 148.35 (C1). The above assignments were confirmed by long-range reverse detected heteronuclear correlation spectra (HMBC).

*1,4,6,7-Tetramethyl-2-nitronaphthalene (***12***).* M.p. 100–101 °C (Anal.: $C_{14}H_{15}NO_2$ C, H, N). IR: ν_{max} (KBr) 1586 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.49 (s, 6-Me and 7-Me), 2.66 (s, 4-Me), 2.77 (s, 1-Me), 7.57 (s, H3), 7.76 (s, H5), 7.93 (s, H8). Nuclear Overhauser experiments gave the following results: irradiation at δ 2.49 gave enhancements at δ 7.76 (4.1%) and at δ 7.93 (4.0%); irradiation at δ 2.66 gave enhancements at δ 7.57 (5.0%) and at δ 7.76 (6.4%); irradiation at δ 2.77 gave an enhancement at δ 7.93 (6.5%); irradiation at δ 7.57 gave an enhancement at δ 2.66 (0.5%); irradiation at δ 7.93 gave enhancements at δ 2.49 (1.1%) and at δ 2.77 (2.0%). ^{13}C NMR ($CDCl_3$) δ 14.2 (1-Me), 19.1 (4-Me), 20.3 (6-Me and 7-Me), 119.6 (C3), 124.4 (C8), 125.9 (C5), 127.0 (C1), 131.0 (C8a), 132.5 (C4a), 133.1 (C4), 136.95 (C6), 138.2 (C7), 146.6 (C2). The above assignments were confirmed by long-range reverse detected heteronuclear correlation spectra (HMBC).

4,6,7-Trimethyl-1-nitromethylnaphthalene (**13**) was unstable on silica gel and was obtained only in admixture with other materials. ^{1}H NMR ($CDCl_3$) δ 2.47 (s, 6-Me or 7-Me), 2.49 (s, 7-Me or 6-Me), 2.69 (s, 4-Me), 5.85 (s, CH_2), 7.25 (d, $J_{H,H}$ 7.2 Hz, H2 or H3), 7.38 (d, $J_{H,H}$ 7.2 Hz, H3 or H2), 7.72 (s, H5 or H8), 7.80 (s, H8 or H5).

Reaction in dichloromethane at 20 °C containing trifluoroacetic acid (0.68 mol dm^{-3}). Reaction of 1,4,6,7-tetramethylnaphthalene (0.34 mol dm^{-3}) and tetranitromethane (0.68 mol dm^{-3}) in dichloromethane containing trifluoroacetic acid (0.68 mol dm^{-3}) at 20 °C, as above, for 2 h gave a product which was shown by ^{1}H NMR spectra to be a mixture (Table 4) of 2,3,5,8-tetramethyl-1-nitronaphthalene (**11**) (32%), 1,4,6,7-tetramethyl-2-nitronaphthalene (**12**) (48%) and 4,6,7-trimethyl-1-nitromethylnaphthalene (**13**) (6%).

*Rearrangement of 1,4,6,7-tetramethyl-*r*-1-nitro-*t*-4-trinitromethyl-1,4-dihydronaphthalene (***7***) on silica gel.* The adduct **7** (30 mg) was adsorbed onto a silica gel Chromatotron plate and then eluted with first pentane and then pentane–ether mixtures. The identified materials eluted were in elution order:

Recovered adduct **7** (7 mg), identical with authentic material, above.

1,4,6,7-Tetramethyl-2-trinitromethyl-1,2-dihydronaphthalen-1-ol (**15**) (3.3 mg), m.p. 102 °C (decomp.) (insufficient for elemental analysis; found: $M^{+\cdot}$, 351.10611. $C_{15}H_{17}N_3O_7$ requires 351.10665). IR: ν_{max} (KBr) 3590, 1620, 1593 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.69 (s, 1-Me), 2.11 (d, $J_{4\text{-Me,H3}}$ 1.5 Hz, 4-Me), 2.26 (s, 6-Me), 2.29 (s, 7-Me), 2.45 (br s, OH), 4.39 (d, $J_{H2,H3}$ 5.9 Hz, H2), 5.63 (dq, $J_{H3,H2}$ 5.9 Hz, $J_{H3,4\text{-Me}}$ 1.5 Hz, H3), 7.03 (s, H5), 7.25 (s, H8). Nuclear Overhauser experiments gave the following results: irradiation at δ 1.69 gave enhancements at δ 4.38 (12.8%) and at δ 7.25 (4.7%); irradiation at δ 2.11 gave enhancements at δ 5.63 (6.4%) and at δ 7.03 (9.5%); irradiation at δ 4.38 gave enhancements at δ 1.69 (1.2%) and at δ 5.63 (4.6%); irradiation at δ 5.63 gave enhancements at δ 2.11 (1.1%) and at δ 4.38 (4.3%); irradiation at δ 7.03 gave enhancements at δ 2.11 (1.7%) and at δ 2.26 (1.2%); irradiation at δ 7.25 gave enhancements at δ 1.69 (0.4%) and at δ 2.29 (1.2%). ^{13}C NMR ($CDCl_3$) δ 19.6 (6-Me), 19.9 (7-Me), 20.0 (4-Me), 34.45 (1-Me), 49.3 (C2), 72.8 (C1), 112.65 (C3), 124.7 (C8), 125.6 (C5), 128.0 (C4a), 136.1 (C7), 136.3 (C8a), 138.6 (C6), 140.6 (C4), resonance for $C(NO_2)_3$ not observed. The above assignments were confirmed by long-range reverse detected heteronuclear correlation spectra (HMBC).

1,4,6,7-Tetramethyl-2-nitro-1,2-dihydronaphthalen-1-ol (**16**) (2.3 mg), m.p. 54 °C (decomp.) (insufficient for elemental analysis; Found: parent ion not visible, $M^{\cdot+} - H_2O$, 229.11054. $C_{14}H_{15}NO_2$ requires 229.11028). IR: ν_{max} (KBr) 3378, 1548 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.52 (s, 1-Me), 2.14 (br s, 4-Me), 2.28 (s, 6-Me), 2.30 (s, 7-Me), 2.94 (s, OH), 4.99 (d, $J_{H2,H3}$ 6.5 Hz, H2), 5.88 (dq, $J_{H3,H2}$ 6.3 Hz, $J_{H3,4\text{-Me}}$ 1.4 Hz, H3), 7.09 (s, H5), 7.41 (s, H8). Nuclear Overhauser experiments gave the following results: irradiation at δ 1.52 gave enhancements at δ 4.99 (9.0%) and at δ 7.91 (4.0%); irradiation at δ 2.14 gave enhancements at δ 5.88 (5.4%) and at δ 7.09 (8.0%); irradiation at δ 4.99 gave enhancements at δ 1.52 (0.9%) and at δ 5.88 (3.7%); irradiation at δ 5.88 gave enhancements at δ 2.14 (0.7%) and at δ 4.99 (3.6%); irradiation at δ 7.09 gave enhancements at δ 2.14 (1.2%) and at δ 2.28 (0.9%); irradiation at δ 7.41 gave enhancements at δ 1.52 (0.5%) and at δ 2.30 (0.9%). ^{13}C NMR

($CDCl_3$) δ 19.5 (4-Me), 19.55 (6-Me), 19.8 (7-Me), 28.7 (1-Me), 72.3 (C1), 89.7 (C2), 115.5 (C3), 124.7 (C8), 126.1 (C5), 128.8 (C4a), 135.9 (C7), 138.1 (C8a), 138.3 (C6), 140.3 (C4). The above assignments were confirmed by long-range reverse detected heteronuclear correlation spectra (HMBC).

1,4,6,7-Tetramethyl-1,2-dihydronaphthalene-r-*1*,c-*2-diol* (**17**) *(6.7 mg).* M.p. 98–98.5°C (X-ray crystal structure determined, see below). IR: ν_{max} (KBr) 3291 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.38 (s, 1-Me), 2.08 (d, $J_{4\text{-Me,H3}}$ 1.5 Hz, 4-Me), 2.26 (s, 6-Me), 2.29 (s, 7-Me), 3.84 (d, $J_{H2,H3}$ 5.9 Hz, H2), 5.93 (dq, $J_{H3,H2}$ 5.9 Hz, $J_{H3,4\text{-Me}}$ 1.5 Hz, H3), 7.04 (s, H5), 7.49 (s, H8). Nuclear Overhauser experiments gave the following results: irradiation at δ 1.38 gave enhancements at δ 3.84 (6.3%) and at δ 7.49 (3.8%); irradiation at δ 2.08 gave enhancements at δ 5.93 (5.2%) and at δ 7.04 (8.9%); irradiation at δ 3.84 gave enhancements at δ 1.38 (0.9%) and at δ 5.93 (4.0%); irradiation at δ 5.93 gave enhancements at δ 2.08 (0.9%) and at δ 3.84 (2.6%); irradiation at δ 7.04 gave enhancements at δ 2.08 (1.2%) and at δ 2.26 (0.9%); irradiation at δ 7.49 gave enhancements at δ 1.38 (0.5%) and at δ 2.29 (0.9%). ^{13}C NMR ($CDCl_3$) δ 19.3 (4-Me), 19.55 (6-Me), 19.7 (7-Me), 26.4 (1-Me), 71.7 (C2), 73.05 (C1), 123.5 (C3), 125.3 (C5), 126.8 (C8), 129.7 (C4), 135.3 (C7), 135.4 (C4a), 137.2 (C6), 139.0 (C8a). The above assignments were confirmed by long-range reverse detected heteronuclear correlation spectra (HMBC).

Rearrangement of 1,4,6,7-tetramethyl-r-*1-nitro*-t-*4-trinitromethyl-1,4-dihydronaphthalene (7) in (^2H)chloroform at 20°C.* A solution of the adduct **1** (20 mg) in (^2H)chloroform (0.6 ml) was stored at 20°C in the dark and the ^1H NMR spectrum monitored at appropriate time intervals (Table 6). The major products of the rearrangement after 12 days were identified from comparison of their ^1H NMR spectra as 4,6,7-trimethyl-1-(2′,2′,2′-trinitroethyl)-naphthalene (**10**) (73%) and 4,6,7-trimethyl-1-nitromethylnaphthalene (**13**) (7%). In the early stages of the rearrangement it was clear that epimerization of adduct **7** was occurring to give 1,4,6,7-tetramethyl-*r*-1-nitro-*c*-4-trinitromethyl-1,4-dihydronaphthalene (**8**), equilibrium being approached after 8 h [**7**:**8** ratio ca. 6.6: 1]. Subsequently two further adducts were formed tentatively identified from their ^1H NMR spectra as 2,3,5,8-tetramethyl-*r*-1-nitro-*c*-4-trinitromethyl-1,4-dihydronaphthalene (**9**) (after 5 days), above, and 1,4,6,7-tetramethyl-*t*-2-nitro-*r*-1-trinitromethyl-1,2-dihydronaphthalene (**18**) (after 4 h): ^1H NMR ($CDCl_3$) δ 2.08 (s, 1-Me), 2.09 (d, $J_{4\text{-Me,H3}}$ 1.3 Hz, 4-Me), 2.33 (s, 6-Me or 7-Me), 2.35 (s, 7-Me or 6-Me), 5.61 (d, $J_{H2,H3}$ 6.1 Hz, H2), 5.72 (dq, $J_{H3,H2}$ 6.1 Hz, $J_{H3,4\text{-Me}}$ 1.3 Hz, H3), 7.13 (s, H5 or H8), 7.21 (s, H8 or H5).

Rearrangement of 1,4,6,7-tetramethyl-r-*1-nitro*-t-*4-trinitromethyl-1,4-dihydronaphthalene (7) in acetonitrile at 20°C.* A quantitative study of the progress of this reaction was not possible because of the limited solubility of the adduct **7** in acetonitrile. Initially a slurry of the adduct **7** (110 mg) in acetonitrile (11 ml) was stirred at 20°C in the dark and aliquots of the solution were removed at appropriate time intervals. The solvent was removed rapidly (< 30 s) from each sample under reduced pressure at ≤0°C, and the composition of the residue determined from ^1H NMR spectra. The reaction of adduct **7** in acetonitrile was rapid, being essentially complete in 4 h [cf. 9 days in (^2H)chloroform] and gave predominantly different products. In acetonitrile after 4 h the rearrangement of **7** yielded mainly the nitroaromatic compounds 2,3,5,8-tetramethyl-1-nitronaphthalene (**11**) (14%), 1,4,6,7-tetramethyl-2-nitronaphthalene (**12**) (52%) and 4,6,7-trimethyl-1-nitromethylnaphthalene (**13**) (27%), these compounds being identified by comparison with the ^1H NMR spectra of authentic samples; 4,6,7-trimethyl-1-(2′,2′,2′-trinitroethyl)naphthalene (**10**) (1%) was only a minor product in this rearrangement. Apart from rapid (after 1 min) epimerization of adduct **7** to give **8**, adducts **15**, **16**, and two unidentified adducts could be detected in the ^1H NMR spectrum at that time, and 2,3,5,8-tetramethyl-*r*-1-nitro-*c*-4-trinitromethyl-1,4-dihydronaphthalene (**9**) was detectable at reaction times between 3 min and 2 h, reaching a maximum level (3%) after 40 min.

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

1,4,6,7-Tetramethyl-r-*1-nitro*-t-*4-trinitromethyl-1,4-dihydronaphthalene (7).* $C_{15}H_{16}N_4O_8$, M 380.32, monoclinic, space group $P2_1/c$, $a = 16.054(3)$, $b = 9.085(1)$, $c = 11.909(2)$ Å, $\beta = 107.69(2)°$; $V = 1654.8(5)$ Å^3, $D_c = 1.527$ g cm^{-3}, $Z = 4$, copper radiation, $\lambda(CuK\alpha) = 1.54180$ Å, $\mu(CuK\alpha) = 10.84$ cm^{-1}. The crystal was colourless and of approximate dimensions $0.56 \times 0.30 \times 0.21$ mm. Data were collected at 130(2) K out to a maximum Bragg angle $\theta = 26.75°$. Number of independent reflections measured 1938, 1424 with $I > 2\sigma(I)$. Absorption corrections were not applied; $g_1 = 0.1531$, $g_2 = 0.0000$; $R_{(obs)} = 0.080$, $wR_{all\ data} = 0.215$.

1,4,6,7-Tetramethyl-1,2-dihydronaphthalene-r-*1*,c-*2-diol* (**17**). $C_{14}H_{18}O_2$, $M = 218.28$, triclinic, space group $P\bar{1}$, $a = 5.264(1)$, $b = 8.505(2)$, $c = 13.864(3)$ Å, $\alpha = 104.08(3)$, $\beta = 100.04(3)$, $\gamma = 94.96(3)°$; $V = 587.4(2)$ Å^3,

$D_c = 1.234$ g cm^{-3}, $Z = 2$, molybdenum radiation, $\lambda(\text{MoK}\alpha) = 0.710\ 69$ Å, $\mu(\text{MoK}\alpha) = 0.81$ cm^{-1}. The crystal was colourless and of approximate dimensions $0.70 \times 0.27 \times 0.25$ mm. Data were collected at 130(2) K out to a maximum Bragg angle $\theta = 27.5°$. Number of independent reflections measured 2667,1798 with $I > 2\sigma(I)$. Absorption corrections were not applied; $g_1 = 0.0757$, $g_2 = 0.0000$; $R_{(\text{obs})} = 0.043$, $wR_{(\text{all data})} = 0.114$.

Structure determination. Full-matrix least-squares refinements (SHELXL-93)[19] 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 $1/[\sigma^2(F_o^2) + (g_1P)^2 + g_2P]$, where $P = [F_o^2 + 2F_c^2]/3$, were used. All non-hydrogen atoms were assigned anisotropic thermal parameters. Methyl hydrogens were included as rigid groups pivoting about their carbon atoms. Final Fourier syntheses show no significant residual electron density, and there were no abnormal discrepancies between observed and calculated structure factors.

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