Photochemical Nitration by Tetranitromethane. Part XVIII.[1] The Regiochemistry of Nitrito/trinitromethyl and Nitro/trinitromethyl Addition to 2,3-Dimethylnaphthalene: Thermal 1,3-Dipolar Additions of Nitro Groups to Alkenes

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The photolysis of the 2,3-dimethylnaphthalene–tetranitromethane charge-transfer complex gives 2,3-dimethyl-1-nitronaphthalene, 2,3-dimethyl-5-nitronaphthalene and adducts: epimeric pairs of 6,7-dimethyl-1-nitro-4-trinitromethyl-1,4-dihydronaphthalene **7** and **8**, 1-hydroxy-6,7-dimethyl-4-trinitromethyl-1,4-dihydronaphthalene **11** and **12**, 2,3-dimethyl-1-nitro-4-trinitromethyl-1,4-dihydronaphthalene **13** and **14**, and the structurally similar *trans*-6,7-dimethyl-2-nitro-1-trinitromethyl-1,2-dihydronaphthalene **9** and *trans*-2-hydroxy-6,7-dimethyl-1-trinitromethyl-1,2-dihydronaphthalene **10**. At +20 °C in either dichloromethane or acetonitrile the adducts **7–14** comprise some 70% of the product mixture, but at −20 °C in either solvent the total adduct yield is reduced to *ca.* 31%. In adduct formation trinitromethanide ion reacts preferentially at C-5 in the 2,3-dimethylnaphthalene radical cation. Adducts **9** and **10** undergo thermal cycloaddition in (^{2}H)chloroform at 22 °C to give the nitro cycloadduct **16** and hydroxy cycloadduct **15**, respectively. An X-ray crystal structure is reported for hydroxy cycloadduct **15**, as are preliminary results of a single crystal X-ray analysis of adduct **7**.

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

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

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)].[2] In determining

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

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

the structures of the adducts formed, the first bond formation involving reaction of trinitromethanide ion with $ArH^{\bullet +}$ is crucial. The subsequent coupling of the delocalized carbon radical, so formed, with nitrogen dioxide then yields either nitro/trinitromethyl adducts or labile nitrito/trinitromethyl adducts, the latter being hydrolysed during either the reaction or the work-up procedure to give hydroxy/trinitromethyl adducts.

In the photonitration of naphthalene[4] with TNM the initial bond formation between $ArH^{\bullet +}$ and trinitromethanide ion occurs at the 1-position of the naphthalene nucleus. The attack of trinitromethanide ion occurs at the favourable ring position in the corresponding aromatic radical cation, as judged by the calculated[5] (AM1)[6] atomic charges on the respective ring carbon atoms (Fig. 1). For the photonitration of naphthalene with TNM this and the subsequent reaction steps are illustrated in Scheme 1.[4] After the initial reaction of trinitromethanide ion with the naphthalene radical cation, the delocalized carbon radical **1** may then couple with nitrogen dioxide either at C-2 or at C-4. Reaction with nitrogen dioxide at C-4, with C–N bond formation, has been shown to yield the epimeric 1-nitro-4-trinitromethyl adducts **2** and **3**.[4] Alternatively, reaction of nitrogen dioxide at C-2 occurs with *both* C–N and C–O bond formation, the *trans* stereochemistry of the addition being determined by the shielding of one face of the naphthalene ring system by the bulky trinitromethyl group, and leading to the formation of the *trans*-2-nitro-1-trinitromethyl adduct **4** and the *trans*-1-trinitromethyl 2-nitrite **5**. Either during the reaction or during the isolation procedure, under the prevailing acidic conditions, the *trans*-1-trinitromethyl 2-nitrite **4** is hydrolysed to give the *trans*-2-hydroxy-1-trinitromethyl adduct **6**.[4] Of the adducts **2**, **3**, **4** and **6** formed in the photolysis of the naphthalene–TNM charge-transfer complex, only adduct **2** could be isolated sufficiently to permit structure determination by single-crystal X-ray analysis.[7] The identities of the remaining adducts **3**, **4** and **6** were inferred only from the ^{1}H NMR spectrum of the crude product, prior to the isolation of adduct **2**.[4] These spectroscopic/structural assignments are now confirmed *inter alia* in the present study of the photolysis of the 2,3-dimethylnaphthalene–TNM charge-transfer complex.

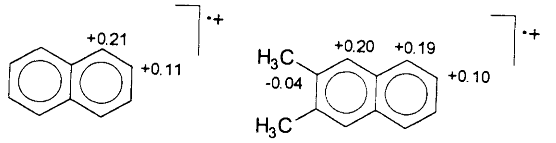
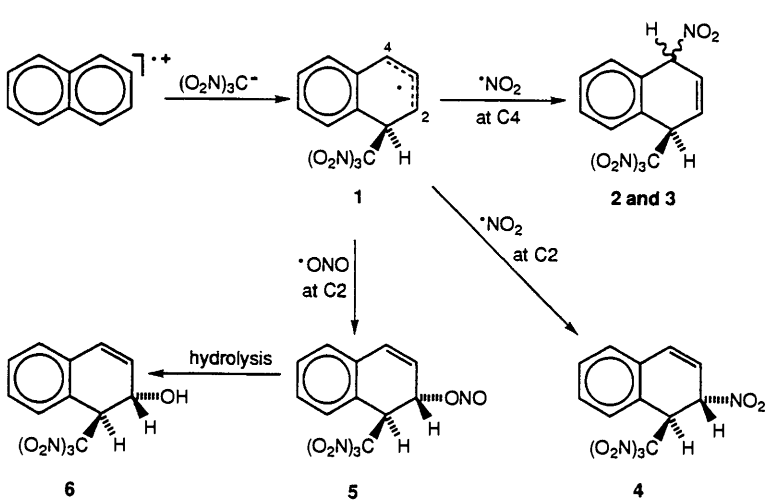
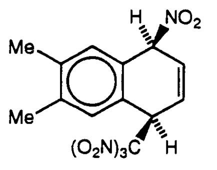


Fig. 1 Calculated (optimized AM1; UHF method) atomic charges on carbon atoms, including the overall charges for CH moieties, in the radical cations of naphthalene and 2,3-dimethylnaphthalene

The calculated[5] atomic charges on the ring carbon atoms of the radical cation of 2,3-dimethylnaphthalene are given in Fig. 1. On this basis it appeared that attack of trinitromethanide ion might occur at either C1(4) or C5(8) of the 2,3-dimethylnaphthalene radical cation, with consequent overall addition of



Scheme 1



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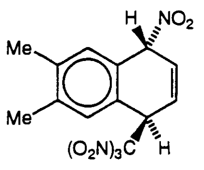

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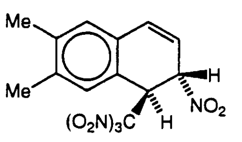

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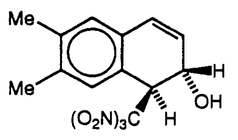

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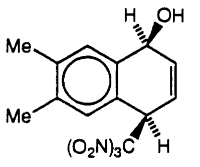

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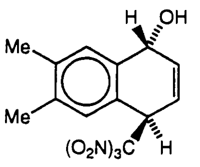

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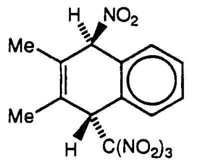

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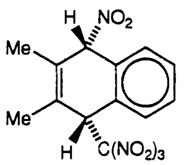

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TNM to the ring attacked initially. However, it was recognized that attack on the methylated ring by the bulky trinitromethanide ion might encounter steric hindrance from the methyl groups *ipso* and/or *vicinal* to the position being attacked. In the event, trinitromethanide ion attack occurred substantially, but not exclusively, in the unsubstituted ring. We now report the results of this study.

Results and Discussion

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,[8] and small samples withdrawn for analysis at suitable intervals. The work-up procedure, involving evaporation of the solvent and an excess of tetranitromethane, was conducted at a temperature ≤ 0 °C. The crude product mixtures were stored at -20 °C and were analysed (^1H NMR spectroscopy, see the Experimental section; Tables 1 and 2) as soon as possible.

Photochemistry in Dichloromethane and Identification of Products.—A solution of 2,3-dimethylnaphthalene (0.4 mol dm^{-3}) and TNM (0.8 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 4 h, conversion *ca.* 100%) after work-up contained the adducts **7** (14%), **8** (10%), **9** (7%), **10** (8%), **11** (9%), **12** (8%), **13** (9%), **14** (5%) and the nitroaromatics, 2,3-dimethyl-1-nitronaphthalene (24%) and 2,3-dimethyl-5-nitronaphthalene (5%). The adducts were separated partially by HPLC on a cyanopropyl column using hexane–dichloromethane mixtures as the eluting solvents. As noticed before,[4] the adducts were thermally unstable towards elimination, especially in solution, and therefore had to be handled with the utmost care. For the same reason, mass spectral determination of m/z of M^+ was not possible, even by CI–MS. Also, the cycloaddition of **9** and **10** described below presented some difficulties during separation. For the convenience of the ensuing discussion the identification of the adducts will be described for pairs of compounds, rather than in the order of elution given in the Experimental section.

Adducts **7** *and* **8**.—The epimeric 6,7-dimethyl-1-nitro-4-trinitromethyl adducts **7** and **8** were each isolated in a pure state but only adduct **7** gave crystalline material. The structure of adduct **7** was indicated by the preliminary results of a single

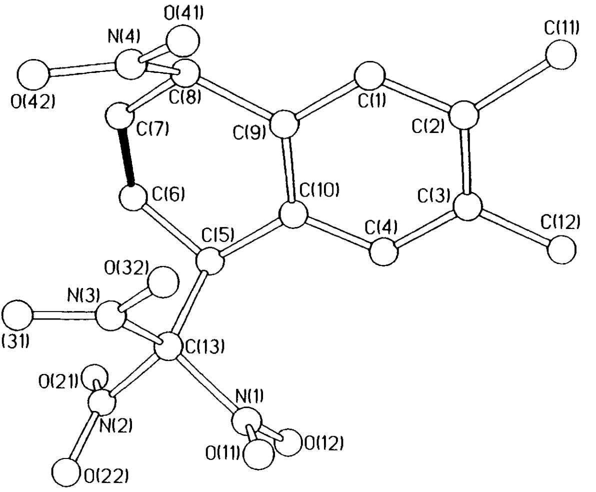


Fig. 2 Perspective drawing of compound **7**; the double bond is shown in black

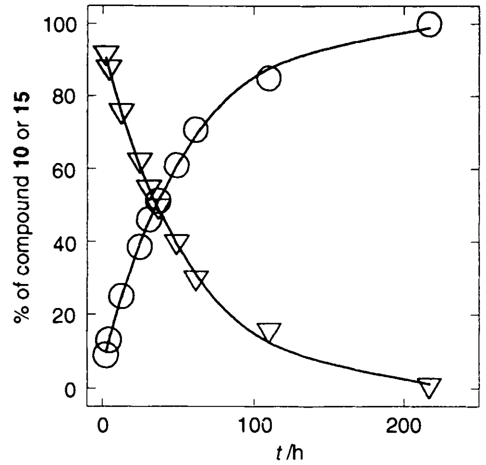


Fig. 3 Kinetics of cycloaddition **10** (▽)⟶**15** (○) in (^{2}H)chloroform at 22 °C. The solid lines were obtained by non-linear regression and correspond to a first-order rate constant of 0.018(1) h^{-1}.

crystal X-ray analysis.* Due to the mosaicity of the crystal, 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 *cis*-6,7-dimethyl-1-nitro-4-trinitromethyl-1,4-dihydronaphthalene **7** is presented in Fig. 2. The spectroscopic data for adducts **7** and **8** were consistent with their assignment as epimers. In particular, if the reasonable assumption is made that the conformation of the 1-NO$_2$ group in adduct **7** is the same in solution as in the solid state, H-1 should be somewhat shielded and H-8 deshielded by the nitro group.[9] For the epimeric adduct **8**, in the absence of steric interaction with the 4-trinitromethyl group present in adduct **7**, the conformation of the 1-NO$_2$ group would be expected to be such that its plane would be close to eclipsed with the C(1)–H bond. In that conformation, H-1 would be deshielded and H-8 shielded by the 1-NO$_2$ group. The observed ^{1}H NMR chemical shifts for adducts **7** [δ 5.87 (H-1), 7.53 (H-8)] and **8** [δ 6.17 (H-1), 7.22 (H-8)] were in accord with these predictions.

Adducts **9** *and* **10** *and Cycloadducts* **15** *and* **16**.—Neither the nitro/trinitromethyl adduct **9** nor the hydroxy/trinitromethyl adduct **10** could be isolated in a pure state by HPLC. On storage of a solution of the impure hydroxy/trinitromethyl adduct **10** in (^{2}H)chloroform in the dark at 22 °C it was converted into the hydroxy cycloadduct **15** with a half-life of 38 ± 3 h (Fig. 3). The structure of the hydroxy cycloadduct **15**, $C_{13}H_{13}N_3O_7$, m.p. 160 °C (decomp.), was determined by single-crystal X-ray analysis. A perspective drawing of the hydroxy cycloadduct **15** is presented in Fig. 4. The heterocyclic cage structure evident in Fig. 3 is formed from the hydroxy/trinitromethyl adduct **10** by thermal cycloaddition of a nitro group of the trinitromethyl function with the alkene system. In the hydroxy cycloadduct **15**, N(3) has a trigonal geometry and the C(13)–N(3) bond length [1.503(5) Å] is significantly shorter than the C(13)–N(1) [1.562(5) Å] or the C(13)–N(2) [1.532(5) Å] bond lengths. In the context of confirming the structure of the hydroxy/trinitromethyl adduct **10**, the C(5)–C(13) bond in hydroxy cycloadduct **15** is close to *anti* to the C(6)–O(6) bond, pointing to a *trans*-2-hydroxy-1-trinitromethyl stereochemistry for adduct **10** [torsion angle: O(6)–C(6)–C(5)–C(13) −165.2(3)°]. The spectroscopic data for the hydroxy/trinitromethyl adduct **10** and its derived hydroxy cycloadduct **15** were in accord with the assigned and determined structures, respectively.

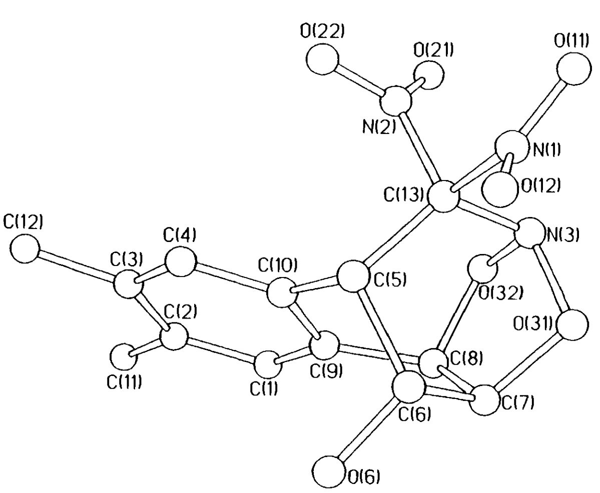
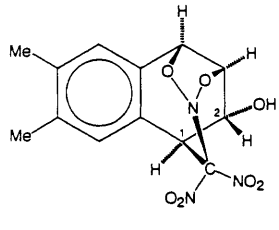


Fig. 4 Perspective drawing of compound **15**



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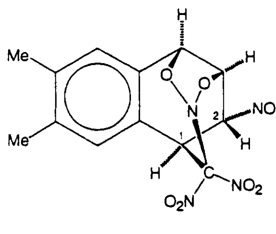

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The nitro/trinitromethyl adduct **9** also underwent thermal cycloaddition in the dark in (^{2}H)chloroform at 22 °C with a half-life of 141 ± 11 h (Fig. 5) to give the nitro cycloadduct **16**; the nitro/trinitromethyl isomers **8** and **13**, present in admixture with the nitro/trinitromethyl adduct **9**, were stable under these conditions. Unfortunately neither nitro/trinitromethyl adduct **9** nor the nitro cycloadduct **16** could be isolated in a pure state. The structures of these two compounds **9** and **16** are based on their ^{1}H NMR spectra and a comparison with those of their hydroxy analogues. The lower rate of cycloaddition of the nitro/trinitromethyl adduct **9**, compared with that of the hydroxy/trinitromethyl adduct **10**, is presumably the result of the greater electron-withdrawing effect of the 2-nitro group on the electron availability in the 3,4-alkene system in the nitro/trinitromethyl precursor **9**.

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* Crystal data for a poor-quality crystal of *cis*-6,7-dimethyl-1-nitro-4-trinitromethyl-1,4-dihydronaphthalene **7**, $C_{13}H_{12}N_4O_8$, m.p. 87–89 °C, *a* 15.517(4), *b* 15.680(2), *c* 12.648(3) Å, β 105.39(3)°, *V* 2967 Å^3.

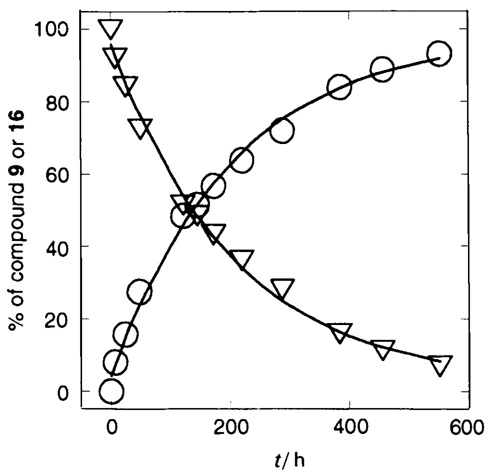

Fig. 5 Kinetics of cycloaddition **9** (▽) ⟶ **16** (○) in (^{2}H)chloroform at 22 °C. The solid lines were obtained by non-linear regression and correspond to a first-order rate constant of 0.0049(4) h^{-1}.

Adducts **11** *and* **12**.—Neither of these adducts could be isolated in a pure state. Their structural assignments are based on considerations of their NMR spectra. Their ^{13}C NMR spectra indicated that both compounds were hydroxy/trinitromethyl adducts, and their ^{1}H NMR spectra were consistent with their assignment as 1-hydroxy-6,7-dimethyl-4-trinitromethyl-1,4-dihydronaphthalenes. Such 4-trinitromethyl-1,4-dihydronaphthalene systems are known to exist with the alicyclic ring in a boat conformation with the trinitromethyl group in the flagpole orientation.[1,10] In the epimer **11**, assigned the *cis*-1-hydroxy-4-trinitromethyl stereochemistry, the 1-hydroxy group will also be in the flagpole orientation; epimer **12** will have the 1-hydroxy group in the bowsprit orientation. In these conformations the hydroxy function would be expected to have a greater deshielding effect on the *peri* H-8 in epimer **12** (12, δ 7.54; 11, δ 7.37). The order of elution of the two epimers on HPLC is consistent with the earlier elution of the *cis*-1-hydroxy-4-trinitromethyl epimer **11** with the more hindered hydroxy group in the *syn*-hydroxy-trinitromethyl environment.

Adducts **13** *and* **14**.—These adducts were isolated only as minor components of mixtures with various other adducts. Adducts **13** and **14** were assigned epimeric 2,3-dimethyl-1-nitro-4-trinitromethyl structures on the basis of their ^{1}H NMR spectra. The stereochemical assignments to the adducts are based on a comparison of the ^{1}H NMR chemical shifts of the C*H*-NO$_2$ signals for the *cis*-1-nitro-4-trinitromethyl adducts **7** (δ 5.87) and **14** (δ 5.80), and the *cis*-1-nitro-4-trinitromethyl adducts **8** (δ 6.17) and **13** (δ 6.21), given the reasonable assumption that in each case the alicyclic ring system will adopt a boat conformation with the trinitromethyl group in the flagpole orientation.[1,10]

At −20 °C the photolysis of the 2,3-dimethylnaphthalene–TNM CT complex gave the same products, but the overall yields of adducts and nitroaromatic compounds were essentially inverted, *i.e.*, total adducts 31%, total nitroaromatic compounds 69% (Table 1).

Photochemistry in Acetonitrile.—In this solvent, irradiation at either +20 °C or −20 °C gave similar product yields (Table 2) to those found for the corresponding reactions in dichloromethane. The only exceptions to this generalization were the reduced yields of the 1-hydroxy-6,7-dimethyl-4-trinitromethyl adducts **11** and **12**.

The Regiochemistry of Trinitromethanide Ion Attack on the 2,3-*Dimethylnaphthalene Radical Cation*.—The yield data (Tables 1 and 2) for adducts formed on photolysis of the 2,3-dimethylnaphthalene–TNM CT complex indicate a clear preference for attack by trinitromethanide ion at C5(8) on the 2,3-dimethylnaphthalene radical cation, the only viable alternative appearing to be at C1(4). This preference for attack of trinitromethanide ion in the non-methylated ring is presumably the result of the steric interaction with a buttressed *vicinal* methyl group in the attack of the bulky trinitromethanide ion at C1(4).

Comparison of ^{1}H *NMR Data for Adducts* **7**–**10** *Derived from* 2,3-*Dimethylnaphthalene with Adducts from Naphthalene*.—Earlier we reported the isolation of adduct **2** from the photolysis of the naphthalene–TNM CT complex,[7] but could only identify further adduct products **3**–**5** from the ^{1}H NMR spectra of the crude product mixture.[4] The ^{1}H NMR spectra of the adducts **7**–**10**, albeit for adducts **9** and **10** of various degrees of impurity, closely parallel those for the corresponding naphthalene adducts **2**–**5**. This close correspondence of ^{1}H NMR spectra for the two sets of adducts, together with the structural assignments for the adducts from 2,3-dimethylnaphthalene above, provides confirmation of the earlier assignment of structures to the adducts from the photonitration of naphthalene.[4] For the naphthalene adducts **4** and **5** no evidence of cycloaddition reactions was detected.[4] However, this is perhaps not surprising because these reactions would be likely to be slower than those for the 2,3-dimethylnaphthalene adducts **9** and **10**, adducts **4** and **5** lacking the methyl groups which would be expected to raise the electron availability in the alkene function for cycloaddition precursors **9** and **10**.

Conclusions

From the above results it is clear that adduct formation is a major reaction pathway in the photochemical reaction between 2,3-dimethylnaphthalene with TNM in both dichloromethane and acetonitrile at +20 °C. Further, it appears that steric effects may play a significant role in determining the regiochemistry of the addition of the elements of tetranitromethane to form adducts. Finally it is evident that thermal intramolecular cycloaddition can occur of a nitro group, from a trinitromethyl function, with an alkene function which does not carry methyl substituents; the driving force for these cycloadditions is the presence of the two electron-withdrawing nitro groups *geminal* to the reacting nitro function.[1,10–13]

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. HPLC separations were carried out on a Varian 5000 liquid chromatograph equipped with an Alltech cyanopropyl column, and by using a Varian UV-50 ultraviolet spectrometric detector and hexane–dichloromethane as solvent mixtures. Tetranitromethane was purchased from Aldrich and 2,3-dimethylnaphthalene was available from earlier work. 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.[14]

Table 1 Overview of yields of products from the photolysis of 2,3-dimethylnaphthalene (0.4 mol dm^{-3}) and tetranitromethane (0.8 mol dm^{-3}) in dichloromethane

		Yield (%)									
t/h	Conversion (%)	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	Total adducts	Nitroaromatics
At +20 °C											
2	85	16.4	14.0	8.6	8.6	6.4	4.3	7.3	4.3	69.9	28.0
4	100	14.0	10.1	6.9	7.9	9.1	7.9	8.6	5.3	69.8	29.0
At −20 °C											
6	100	9.0	6.0	5.6	2.4	2.2	1.3	2.2	1.8	30.5	69.0

Table 2 Overview of yields of products from the photolysis of 2,3-dimethylnaphthalene (0.4 mol dm^{-3}) and tetranitromethane (0.8 mol dm^{-3}) in acetonitrile

		Yield (%)									
t/h	Conversion (%)	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	Total adducts	Nitroaromatics
At +20 °C											
0.5	36	17.9	14.6	11.6	9.6	trace	2.3	8.1	6.4	74.6	23.0
1	76	20.3	12.7	10.8	8.0	1.2	2.9	8.0	6.8	74.7	24.0
At −20 °C											
2.8	100	7.4	5.4	1.2	1.4	0	0	6.2	3.9	30.6	67.0

General Procedure for the Photonitration of 2,3-*Dimethylnaphthalene with Tetranitromethane*.—A solution of 2,3-dimethylnaphthalene (500 mg, equal to a 0.4 mol dm^{-3} solution) and tetranitromethane (0.8 mol dm^{-3}) in dichloromethane or acetonitrile (8 cm^3) was irradiated at +20 °C with filtered light (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). For reactions in dichloromethane or acetonitrile at −20 °C the product composition was determined by NMR spectral analysis only after the bleaching of the CT band had occurred.

Reaction in Dichloromethane at +20 °C *and the Identification of Products*.—Reaction of 2,3-dimethylnaphthalene–tetranitromethane in dichloromethane at +20 °C, as above, gave, after bleaching of the CT band, a product which was shown by ^{1}H NMR spectroscopy to be a mixture (Table 1) of 2,3-dimethyl-1-nitronaphthalene (24%), 2,3-dimethyl-5-nitronaphthalene (5%) and adducts (total 70%). The nitroaromatic compounds were identified by comparison of their ^{1}H NMR spectra with those of authentic samples. The adducts were partially separated by HPLC and gave in elution order:

trans-*Dimethyl*-1-*nitro*-4-*trinitromethyl*-1,4-*dihydronaphthalene* **13**, isolated only as a minor component of a mixture containing mainly adduct **9** and some adduct **8**, δ_H(CDCl$_3$) 6.21 (br s, H-1), 5.46 (br s, H-4), 2.04 and 1.88 (Me-2, Me-3), aromatic protons obscured by signals of the other components.

trans-6,7-*Dimethyl*-2-*nitro*-1-*trinitromethyl*-1,2-*dihydronaphthalene* **9**, isolated as the major component of a mixture of adducts **8** and **13**, δ_H(CDCl$_3$) 7.01 (s, H-5 or H-8), 6.92 (s, H-8 or H-5), 6.78 (d, $J_{4,3}$ 9.3 Hz, H-4), 5.95 (dd, $J_{3,4}$ 9.3 Hz, $J_{3,2}$ 6.6 Hz, H-3), 5.73 (d, $J_{1,2}$ 1.0 Hz, H-1), 5.65 (dd, $J_{2,3}$ 6.6 Hz, $J_{2,1}$ 1.0 Hz, H-2) and 2.24 (s, 6 H, 6-Me, 7-Me), confirmed by double irradiation experiments.

trans-6,7-*Dimethyl*-1-*nitro*-4-*trinitromethyl*-1,4-*dihydronaphthalene* **8**, isolated as a pure waxy solid (insufficient for elemental analysis; no parent ion visible in the mass spectrum). ν_{max}(film)/cm^{-1} 1615 and 1596; δ_H(CDCl$_3$) 7.22 (s, H-8), 7.08 (s, H-5), 6.62 (ddd, $J_{3,2}$ 10.2 Hz, $J_{3,4}$ 4.9 Hz, $J_{3,1}$ 2.4 Hz, H-3), 6.56 (ddd, $J_{2,3}$ 10.2 Hz, $J_{2,1}$ 2.0 Hz, $J_{2,4}$ 0.9 Hz, H-2), 6.17 (br s, H-1), 5.32 (br s, H-4) and 2.28, 2.26 (s, 6-Me, 7-Me); δ_C(CDCl$_3$) 19.6, 19.7 (6-Me, 7-Me), 44.5 (C-4), 82.3 (C-1), 121.5 (C-8a), 123.6 (C-8), 127.8 (C-2), 128.1 (C-4a), 129.2 (C-5), 131.4 (C-3), 139.8 (C-7) and 139.9 (C-6); a resonance for C(NO$_2$)$_3$ was not observed. Asssignments were confirmed by long-range reverse-detected ^{1}H–^{13}C heteronuclear correlation spectra (HMBC).

cis-2,3-*Dimethyl*-1-*nitro*-4-*trinitromethyl*-1,4-*dihydronaphthalene* **14**, isolated only as a minor component in a mixture with adduct **7**, δ_H(CDCl$_3$) 5.80 (br s, H-1), 5.60 (br s, H 4), 2.07, 2.00 (Me-2, Me-3), aromatic protons obscured by signals of the other component.

cis-6,7-*Dimethyl*-1-*nitro*-4-*trinitromethyl*-1,4-*dihydronaphthalene* **7**, m.p. 87–89 °C, X-ray structure analysis attempted for a poor-quality crystal (see the Discussion) (insufficient for elemental analysis; parent ion not visible in mass spectrum). ν_{max}(film)/cm^{-1} 1601 and 1559; δ_H 7.53 (s, H-8), 6.97 (s, H-5), 6.72 (m, H-2, H-3), 5.87 (d, $J_{1,2}$ 3.9 Hz, H-1), 5.27 (d, $J_{4,3}$ 3.0 Hz, H-4) and 2.34, 2.28 (s, 6-Me, 7-Me), confirmed by double irradiation experiments; δ_C insufficient pure material available for a spectrum.

cis-1-*Hydroxy*-6,7-*dimethyl*-4-*trinitromethyl*-1,4-*dihydronaphthalene* **11**, isolated only in an impure state, δ_H(CDCl$_3$) 7.37 (s, H-8), 6.89 (s, H-5), 6.54 (ddd, $J_{3,2}$ 10.2 Hz, $J^{3,4}$ 4.9 Hz, $J_{3,1}$ 1.0 Hz, H-3), 6.34 (dd, $J_{2,3}$ 10.2 Hz, $J_{2,1}$ 4.4 Hz, H-2), 5.18 (m, H-4) and 5.00 (m, H-1); δ_C(CDCl$_3$) 138.0, 132.0, 128.3, 122.3 (ArC-H or =C–H), 64.3 (C-1), 44.2 (C-4), 19.7, 19.5 (6-Me, 7-Me), the remaining resonances were uncertain in this poor quality spectrum.

trans-2-*Hydroxy*-6,7-*dimethyl*-1-*trinitromethyl*-1,2-*dihydronaphthalene* **10**, isolated as the major component (*ca.* 90%) of a mixture, ν_{max}(film)/cm^{-1} 3381 and 1598; δ_H($CDCl_3$) 6.98 (s, H-5), 6.90 (s, H-8), 6.54 (d, $J_{4,3}$ 9.3 Hz, H-4), 5.90 (dd, $J_{3,4}$ 9.3 Hz, $J_{3,2}$ 5.9 Hz, H-3), 4.85 (dd, $J_{2,3}$ 5.9 Hz, $J_{2,1}$ 1.0 Hz, H-2), 4.75 (d, $J_{1,2}$ 1.0 Hz, H-1) and 2.26, 2.23 (s, 6-Me, 7-Me), confirmed by double-irradiation experiments; δ_C($CDCl_3$) 19.5 (6-Me), 19.6 (7-Me), 47.7 (C-1), 62.5 (C-2), 123.1 (C-6 or C-7), 129.2 (C-3), 129.4 (C-7 or C-6), 130.6 (C-4a), 131.1 (C-4), 131.9 (C-8), 133.0 (C-8a); a resonance for $C(NO_2)_3$ was not observed. Assignments were confirmed by long-range reverse-detected $^1H-^{13}C$ heteronuclear correlation spectra (HMBC).

trans-1-*Hydroxy*-6,7-*dimethyl*-4-*trinitromethyl*-1,4-*dihydronaphthalene* **12**, isolated only in an impure state, δ_H($CDCl_3$) 7.54 (s, H-8), 6.98 (s, H-5), 6.55 (ddd, $J_{3,2}$ 10.2 Hz, $J_{3,4}$ 2.0 Hz, $J_{3,1}$ 1.0 Hz, H-3), 6.31 (ddd, $J_{2,3}$ 10.2 Hz, $J_{2,1}$ 5.0 Hz, $J_{2,4}$ 2.5 Hz, H-2), 5.19 (m, H-4), 5.07 (m, H-1) and 2.31, 2.25 (s, 6-Me, 7-Me); δ_C($CDCl_3$) 142.2, 138.9, 137.6, 128.6, 128.5, 123.1, 121.0, 118.4, 63.8 (C-1), 45.5 (C-4) and 19.6, 19.5 (6-Me, 7-Me).

Thermal Cycloaddition of trans-2-*Hydroxy*-6,7-*dimethyl*-1-*trinitromethyl*-1,2-*dihydronaphthalene* **10**.—A solution of the hydroxy-trinitromethyl adduct **10** in (^{2}H)chloroform was stored at 22 °C in the dark and the ^{1}H NMR spectrum monitored at appropriate time intervals. The impurities in the sample of the hydroxy trinitromethyl adduct **10** remained unchanged, but the adduct **10** was slowly transformed (half-life 38 ± 3 h) into the hydroxy cycloadduct **15** (see Fig. 3). After 10 days the solvent was removed under reduced pressure and the residue crystallized from chloroform–hexane to give the pure *hydroxy cycloadduct* **15**, m.p. 160 °C (decomp.) (X-ray crystal structure determined, below). ν_{max}(film)/cm^{-1} 3443 and 1592; δ_H($CDCl_3$) 7.20 (s, H-5), 7.10 (s, H-8), 5.42 (d, $J_{4,3}$ 5.9 Hz, H-4), 5.12 (ddd, $J_{3,4}$ 5.9 Hz, $J_{3,2}$ 2.5 Hz, $J_{3,1}$ 1.9 Hz, H-3), 4.97 (m, H-2), 4.69 (dd, $J_{1,3}$ 2.5 Hz, $J_{1,2}$ 3.9 Hz, H-1) and 2.27 (s, 6-Me, 7-Me). NOE experiments gave the following results: irradiation at δ 4.69 gave an enhancement at δ 7.10 (2.9%); irradiation at δ 5.42 gave enhancements at δ 7.20 (4.7%) and at δ 5.12 (2.4%), δ_C($CDCl_3$), 19.6 (6-Me), 19.8 (7-Me), 48.3 (C-1), 66.9 (C-2), 79.3 (C-3), 79.9 (C-4), 125.8 (C-6), 129.4 (C-5), 131.4 (C-7) and 133.0 (C-5); C-4a, C-8a, and $C(NO_2)_2$ were not observed in this weak spectrum. Assignments were confirmed by long-range reverse-detected $^1H-^{13}C$ heteronuclear correlation spectra (HMBC).

Thermal Cycloaddition of trans-6,7-*Dimethyl*-2-*nitro*-1-*trinitromethyl*-1,2-*dihydronaphthalene* **9**.—A solution of a mixture of the 2-nitro-1-trinitromethyl adduct **9** (50%), and the isomeric nitro-trinitromethyl adducts **8** (27%) and **13** (23%) in (^{2}H)chloroform was stored at 22 °C in the dark and the ^{1}H NMR spectrum monitored at appropriate time intervals. The isomeric nitro trinitromethyl adducts **8** and **13** were stable under these conditions, but the nitro-trinitromethyl adduct **9** was slowly converted (half-life 141 ± 11 h) into the nitro cycloadduct **16** (Fig. 5). The nitro cycloadduct **16** could not be isolated in a pure state, but by subtraction its ^{1}H NMR spectrum is δ_H($CDCl_3$) 7.09 (s, H-5), 7.04 (s, H-8), 5.92 (ddd, $J_{3,4}$ 5.9 Hz, $J_{3,2}$ 2.0 Hz, $J_{3,1}$ 2.4 Hz, H-3), 5.72 (dd, $J_{2,1}$ 3.9 Hz, $J_{2,3}$ 2.0 Hz, H-2), 5.62 (d, $J_{4,3}$ 5.9 Hz, H-4), 5.17 (dd, $J_{1,2}$ 3.9 Hz, $J_{1,3}$ 2.4 Hz, H-1) and 2.23 (s, 6-Me, 7-Me).

Crystallography.—Crystal data, established from precession photographs and measured accurately, by means of a Siemens R3 m/V four-circle diffractometer [molybdenum X-radiation, λ(Mo Kα) 0.71069 Å, from a crystal monochromator] are given below. The space group was determined unambiguously as a result of the structure analysis reported below, but was initially indicated by conditions limiting possible reflections. ω-Scans were used to collect reflection intensities out to a maximum Bragg angle θ. The cell parameters were determined by least-squares refinements for which the setting angles of 25 accurately centred high-angle reflections were used.

Hydroxy Cycloadduct **15**.—$C_{13}H_{13}N_3O_7$, *M* 323.26, monoclinic, $P2_1/c$, $a = 9.955(2)$, $b = 7.196(1)$, $c = 19.315(9)$ Å, $\beta = 101.65(2)°$, $V = 1355.1(7)$ Å^3, D_c 1.584 mg m^{-3}, $Z = 4$, μ(Mo-Kα) = 0.131 mm^{-1}. The crystal was colourless and of approximate dimensions 0.72 × 0.36 × 0.34 mm. Data were collected at 130 K. The number of independent reflections measured was 2118, 1269 with $I > 2\sigma(I)$; absorption corrections were not applied; $g_1 = 0.0423$, g_2 0.0000, $R_{obs} = 0.053$, $wR_{(all\ data)} = 0.111$.

Structure Determination.—The structure was solved by direct methods and difference-Fourier syntheses. Full-matrix least-squares refinements (SHELXL-93)[15] were employed. This program is based on intensities and uses all data. The observed threshold $I > 2\sigma(I)$ was used only for calculating R_{obs}, shown here as a comparison for the refinements 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 showed no abnormal discrepancies between observed and calculated structure factors. Atomic coordinates, bond lengths, and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.*

Acknowledgements

Financial support (to L. E.) from the Swedish Natural Science Research Council is gratefully acknowledged.

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Paper 4/01123F
Received 23rd *February* 1994
Accepted 6th *April* 1994

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* For details of the CCDC deposition scheme see, 'Instructions for Authors (1994),' *J. Chem. Soc., Perkin Trans. 2*, 1994, issue 1.