

Photochemical Nitration by Tetranitromethane. Part XXVII.[†] Adduct Formation in the Photochemical Reaction of 4-Methylanisole. Solvent and Temperature Effects on the Regiochemistry of Reaction of the Radical Cation of 4-Methylanisole

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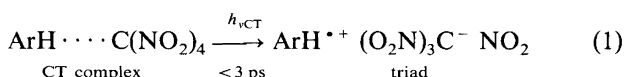
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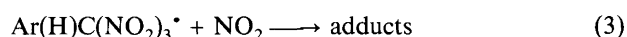
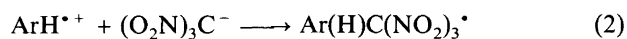
The photolysis of the charge-transfer complex of 4-methylanisole and tetranitromethane in dichloromethane gives four isomeric nitro–trinitromethyl adducts, including the epimeric 1-methoxy-4-methyl-3-nitro-6-trinitromethylcyclohexa-1,4-dienes **3** and **4** and the epimeric 1-methoxy-4-methyl-6-nitro-3-trinitromethylcyclohexa-1,4-dienes **5** and **6**, 4-methyl-2-trinitromethylanisole **1**, 4-methyl-2-nitroanisole **2**, nitrophenols **7** and **9**, and 4-methyl-4-nitrocyclohexa-2,5-dienone **8**. Similar reaction in acetonitrile also gives these products, with the exception of two of the adducts (**3** and **4**). The effect of reaction temperature on the yields of the various products indicates that they are formed either by attack of trinitromethanide ion on the radical cation of 4-methylanisole vicinal to the methoxy group at C2 (**1**, **3** and **4**), or by attack of trinitromethanide *ipso* to the methoxy group (**2**, **5**, **6** and **8**). By conducting the photolysis in dichloromethane with trifluoroacetic acid present, the trinitromethanide pathway is eliminated, and the products formed are derived from reaction between 4-methylanisole and/or its radical cation and NO₂.

The effects of added salts Bu₄N⁺ClO₄⁻ (TBAP) or Bu₄N⁺C(NO₂)₃⁻ (TBAT) to reactions in dichloromethane are seen as the consequences of changes in the polarity of the solvent and *not* to competition between ion-pair and radical-pair collapse during the reactions. By analogy with adducts **3** and **4**, two adducts **16** and **17** derived from similar photolysis reactions of 4-chloroanisole are shown to be the epimeric 4-chloro-1-methoxy-3-nitro-6-trinitromethylcyclohexa-1,4-dienes **16** and **17** rather than nitrito(or hydroxy)–trinitromethyl adducts. The X-ray crystal structure of 1-methoxy-4-methyl-*r*-3-nitro-*c*-6-trinitromethylcyclohexa-1,4-diene **3** is reported.

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



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



Earlier Kochi *et al.*⁵ reported the photochemical reactions of 4-methylanisole with tetranitromethane in dichloromethane and acetonitrile in the presence and absence of added salts at ambient or near-ambient

[†] Part XXVI, see Ref. 1.

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temperatures. In essence, reactions in dichloromethane solution without added salts gave high yields of 4-methyl-2-trinitromethylanisole (**1**), but the addition of salts (of either 'common-ion' or 'special salt' varieties) gave substantial yields of 4-methyl-2-nitroanisole (**2**). In acetonitrile solution the photochemical reaction with tetranitromethane was reported to give largely 4-methyl-2-nitroanisole (**2**).⁵ Similar photochemical reaction of 4-methylanisole with tetranitromethane in hexane solution at 0°C was reported to yield some materials exhibiting ¹H NMR olefinic proton resonances in the region between 5.0 and 6.5 ppm, but these presumed adducts decomposed at ambient temperatures to give 4-methyl-2-trinitromethylanisole (**1**).⁵

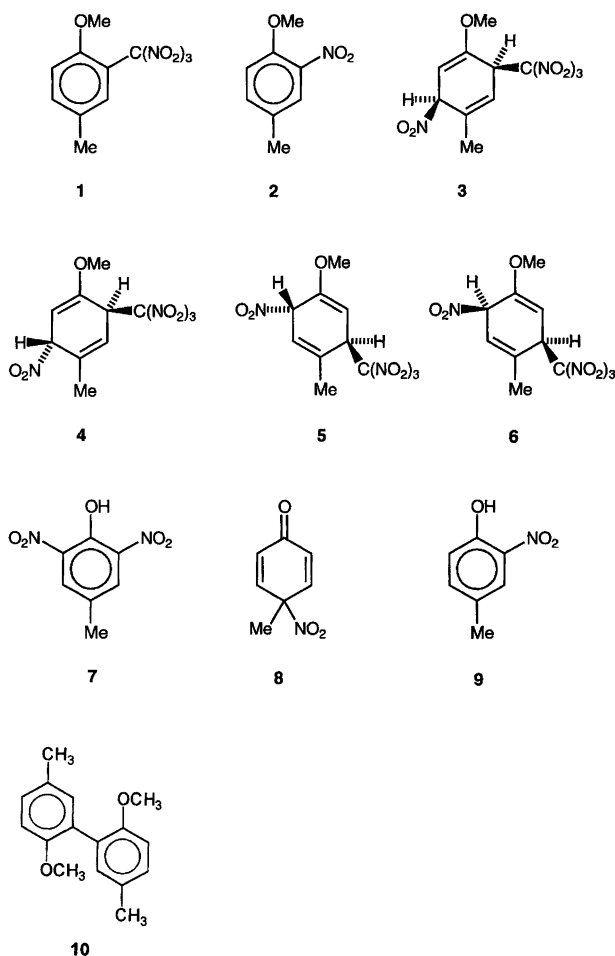
As part of our continuing study of the photolysis reactions of charge transfer complexes of aromatic compounds with tetranitromethane,¹ we have re-examined these reactions of 4-methylanisole in the light of our previous findings that addition pathways seem to be prevalent for this reaction.⁶ In the event, one nitro-trinitromethyl adduct **3** was isolated, the structure of which was confirmed by single crystal X-ray analysis, and a further three isomeric nitro-trinitromethyl adducts **4–6** were identified from their spectroscopic data. We now report the results of this study, which includes the examination

of photolysis reactions at 20, –20 and –50°C in both dichloromethane and acetonitrile.

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,⁷ and small samples were withdrawn for analysis at suitable intervals. The work-up procedure, involving evaporation of solvent and excess tetranitromethane, was conducted at a temperature ≤0°C. The crude product mixtures were stored at –78°C and were analysed (¹H NMR spectroscopy, see Experimental section; Tables 1 and 2) as soon as possible.

Photochemistry in dichloromethane at 20°C and identification of adducts. A solution of 4-methylanisole (0.51 mol dm⁻³) and tetranitromethane (1.02 mol dm⁻³) in dichloromethane was irradiated at 20°C. The composition of the mixture was monitored by withdrawing samples for NMR spectral analysis (Table 1). The solution after 1 h, on work-up, contained the adducts **3** (11%), **4** (3%), **5** (2%) and **6** (2%), 4-methyl-2-trinitromethylanisole (**1**) (47%), 4-methyl-2-nitroanisole (**2**) (10%), 4-methyl-2,6-dinitrophenol (**7**) (10%), 4-methyl-4-nitrocyclohexa-2,5-dienone (**8**) (3%), 4-methyl-2-nitrophenol (**9**) (1%), and other unidentified materials (total 11%). The products were separated partially by HPLC on a cyanopropyl column using hexane–dichloromethane mixtures as the eluting solvents. The order of elution of materials from the HPLC column is given in the Experimental section, but here for simplicity the evidence for structural assignments will be presented for groups of compounds.



(A) *1-Methoxy-4-methyl-3-nitro-6-trinitromethylcyclohexa-1,4-dienes (3 and 4).* The structure of the most polar of the four adducts **3–6**, nitro-trinitromethyl adduct **3**, was determined by single-crystal X-ray analysis. A perspective drawing for 1-methoxy-4-methyl-*r*-3-nitro-*c*-6-trinitromethylcyclohexa-1,4-diene, C₉H₁₀N₄O₉, m.p. 58–60°C (decomp.), is presented in Fig. 1, and corresponding atomic coordinates are given in Table 3. In the solid state the cyclohexa-1,4-diene ring system is close to planar [torsional angles: C(2)–C(1)–C(6)–C(5) 9.1(3)°; C(1)–C(2)–C(3)–C(4) –5.4(3)°], but with both the C(3)–NO₂ and C(6)–C(NO₂)₃ bonds tending towards the flagpole orientation in a boat conformation [torsional angles: O(1)–C(1)–C(6)–C(9) 65.5(2)°; N(1)–C(3)–C(4)–C(8) 64.9(2)°], presumably a compromise in terms of steric interactions between vicinal groups –OMe–C(NO₂)₃ and –NO₂–Me, and the two near-flagpole groups NO₂ and C(NO₂)₃. In the structure the methoxy group is close to coplanar with the C(1)–C(2) bond [torsional angle: C(2)–C(1)–O(1)–C(7) –4.4(3)°], and the plane of the 3-NO₂ group is eclipsed with the C(3)–H(3) bond [torsional angle: O(11)–N(1)–C(3)–H(3) 1.1(2)°]. The spectro-

Table 1. Overview of yields of products from the photolysis of 4-methylanisole (0.51 mol dm⁻³) and tetranitromethane (1.02 mol dm⁻³) in dichloromethane.

<i>t/h</i>	Yield (%)										
	3	4	5	6	Unknown adducts	1	2	7	8	9	Unknown aromatics
20 °C											
0.5	12.6	9.8	2.4	1.6	3.1	44.3	7.1	6.3	3.1	1.0	8.7
1	10.9	3.2	1.9	2.2	2.3	47.1	9.7	10.0	2.8	1.1	8.8
2	6.4	—	2.1	2.0	2.1	51.8	12.1	13.3	2.1	0.8	7.2
-20 °C											
0.5	2.5	2.5	2.5	3.4	1.1	19.6	29.6	—	29.1	2.5	5.0
1	2.5	1.9	2.0	^a	10.6	14.0	36.7	—	24.8	2.3	3.8
2	2.9	1.6	2.1	^a	15.7	13.3	32.5	—	26.0	2.4	3.3
-50 °C											
0.5	—	—	3.4	3.5	12.8	10.5	34.9	—	29.3	1.7	3.8
1	—	—	2.2	3.1	15.4	9.7	35.5	—	27.8	1.6	4.6
2	—	—	3.3	3.8	12.3	8.4	41.0	—	22.6	1.8	6.7

^aIntegral not reliable owing to overlapping signals.

Table 2. Overview of yields of products from the photolysis of 4-methylanisole (0.51 mol dm⁻³) and tetranitromethane (1.02 mol dm⁻³) in acetonitrile.

<i>t/h</i>	Yield (%)										
	3	4	5	6	Unknown adducts	1	2	7	8	9	Unknown aromatics
20 °C											
0.5	—	—	—	—	6.8	5.4	50.8	2.2	19.0	6.1	8.6
1	—	—	—	—	0.8	4.7	49.5	4.1	23.6	9.3	7.2
2	—	—	—	—	0.4	4.3	45.1	11.3	16.2	16.2	4.8
-20 °C											
0.5	—	—	0.8	1.1	8.7	8.7	34.8	—	34.3	4.3	6.7
1	—	—	0.8	0.8	7.6	9.0	42.5	—	29.7	3.6	3.7
2	—	—	1.7	^a	7.6	7.1	47.2	—	28.9	2.2	3.7
-50 °C											
0.5	—	—	1.4	1.5	2.1	14.5	29.5	—	38.7	1.9	10.4
1	—	—	1.5	1.3	4.6	13.0	35.5	—	39.1	2.0	2.8
2	—	—	1.4	1.7	4.0	10.0	36.6	—	37.7	2.2	6.4

scopic data for the nitro-trinitromethyl adduct **3** were in accord with the established structure. The ¹H NMR spectrum of **3** was assigned on the basis of the multiplicity of the various signals confirmed in many cases by double irradiation experiments, and vicinal protons on the structure were highlighted by the results of nuclear Overhauser experiments. Finally, the ¹³C NMR spectrum was assigned on the basis of the results of long-range reverse-detected heteronuclear correlation spectra (HMQC).

Although 1-methoxy-4-methyl-*r*-3-nitro-*t*-6-trinitromethylcyclohexa-1,4-diene (**4**) could not be obtained in a pure state, the structure of this adduct appears certain from its spectroscopic data and their comparison with those for the *r*-3-nitro-*c*-6-trinitromethyl adduct **3**, the structure of which is established above. The connectivity

in the *r*-3-nitro-*t*-6-trinitromethyl adduct **4** was established by a combination of nuclear Overhauser experiments and long-range reverse-detected heteronuclear correlation spectra (HMQC). To the extent that the ¹³C NMR spectrum of adduct **4** could be assigned from the spectrum of a mixture with adduct **5** below, the chemical shifts for adduct **4** mirror closely those for the *r*-3-nitro-*c*-6-trinitromethyl adduct **3**, viz. δ adduct **4**, 44.2 (adduct **3**, 44.6) C2; 119.2 (119.0) C3; 85.9 (84.8) C5; 95.1 (95.5) C6; 55.9 (56.2) O-CH₃. The multiplicities of signals in the ¹H NMR spectrum of the *r*-3-nitro-*t*-6-trinitromethyl adduct **4** were confirmed whenever possible by suitable double irradiation experiments. In the ¹H NMR spectra of adducts **3** and **4** the coupling constant, *J*_{H3,H6} = 4.9 Hz, was notable for both adducts. These homoallylic coupling

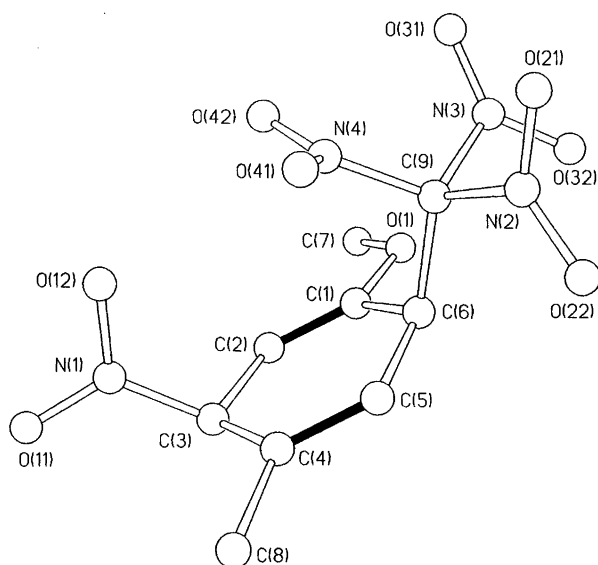


Fig. 1. Perspective drawing of compound **3**. Double bonds are shown in black.

Table 3. Fractional coordinates for atoms in 1-methoxy-4-methyl-*r*-3-nitro-*t*-6-trinitromethylcyclohexa-1,4-diene (**3**).^a

Atom	10 ⁴ X/a	10 ⁴ Y/b	10 ⁴ Z/c	10 ³ U/Å ²
O(1)	1476(2)	9513(1)	9488(1)	23(1)
O(11)	147(3)	13476(1)	11427(1)	48(1)
O(12)	2879(3)	12569(1)	11262(1)	46(1)
O(21)	6933(3)	8312(1)	11478(1)	40(1)
O(31)	6227(3)	9090(1)	9654(1)	35(1)
O(32)	4161(3)	7730(1)	9924(1)	34(1)
O(41)	5723(2)	10531(1)	11711(1)	34(1)
O(42)	5270(2)	10972(1)	10415(1)	34(1)
N(1)	1095(3)	12616(1)	11295(1)	29(1)
N(2)	5139(3)	8378(1)	11501(1)	27(1)
N(3)	4938(3)	8644(1)	10055(1)	25(1)
N(4)	5209(3)	10330(1)	11003(1)	24(1)
C(1)	1173(3)	10042(2)	10225(1)	18(1)
C(2)	291(3)	11028(2)	10339(1)	20(1)
C(3)	-71(3)	11504(2)	11182(1)	22(1)
C(4)	468(3)	10738(2)	11888(1)	19(1)
C(5)	1357(3)	9754(2)	11760(1)	18(1)
C(6)	1970(3)	9315(2)	10919(1)	18(1)
C(7)	634(3)	10049(2)	8771(1)	27(1)
C(8)	-131(3)	11132(2)	12733(1)	24(1)
C(9)	4229(3)	9198(2)	10863(1)	20(1)

^aThe equivalent isotropic temperature factor is defined as one-third of orthogonalized U_{ij} tensor.

constants are comparable with those reported by Appel *et al.*⁸ (5 Hz), but significantly less than those reported by Durham *et al.*⁹ (7.4–11 Hz) for the coupling between the 1- and 4-protons of unsymmetrically substituted 1,4-dihydrobenzenes.

Finally, it should be noted that the *r*-3-nitro-*t*-6-trinitromethyl adduct **4** is eluted from the cyanopropyl HPLC column significantly earlier than the *r*-3-nitro-*c*-6-trinitromethyl adduct **3**. This pattern has been seen earlier for 1,4-nitro-trinitromethyl adducts derived from various

methylated naphthalenes,^{7,10,11} and this feature will be extended below to the assignment of the stereochemistry of the epimeric 3-trinitromethyl-6-nitro adducts **5** and **6**.

(B) *1-Methoxy-4-methyl-3-trinitromethyl-6-nitrocyclohexa-1,4-dienes (5 and 6)*. Neither of these 3-trinitromethyl-6-nitro adducts **5** and **6** could be obtained in a pure state, and the assignment of their structures is dependent on a consideration of their spectroscopic data, and of their stereochemistry to the established order of elution of such stereoisomers from a cyanopropyl HPLC column, the *r*-3-trinitromethyl-*t*-6-nitro adduct **5** being eluted significantly earlier than its *r*-3-trinitromethyl-*c*-6-nitro isomer **6**. The connectivity in adducts **5** and **6** was established, as for adduct **4** above, by a combination of nuclear Overhauser experiments and long-range reverse-detected heteronuclear correlation spectra (HMQC). The pattern of ¹³C NMR resonance assignments which emerged from the above techniques clearly placed the trinitromethyl group at C3, and the nitro group at C6 on a 1-methoxycyclohexa-1,4-diene system for both compounds: δ adduct **5**, 91.3 (adduct **6**, 93.0) C2; 47.1 (46.8) C3; 126.1 (124.7) C5; 81.9 (80.6) C6; 55.8 (55.9) O-CH₃. For adducts **5** and **6** the homoallylic coupling constant, $J_{H3,H6}$, was smaller than for the regioisomers **3** and **4**; for adduct **5** this coupling constant was $J_{H3,H6} = 3.9$ Hz, but for adduct **6** it was 2.9 Hz.

(C) *Aromatic products 1, 2, 7 and 9, and 4-methyl-4-nitrocyclohexa-2,5-dienone (8)*. The 4-methyl-2,6-dinitrophenol **7** and the nitro dienone **8** were isolated by HPLC separation of the reaction mixture which yielded the adducts **3–6** above, and they were identified by comparison of their ¹H NMR spectra with those of authentic samples. 4-Methyl-2-trinitromethylanisole (**1**) was obtained by crystallization of the crude reaction product of a photolysis reaction in dichloromethane at 20°C. The crystalline material gave essentially identical physical and spectroscopic data to that reported earlier.⁵ The remaining products, 4-methyl-2-nitroanisole (**2**) and 4-methyl-2-nitrophenol (**9**), were isolated by chromatography on a silica gel Chromatotron plate of the crude reaction mixture from a photolysis reaction in dichloromethane at -50°C, and were identical with authentic samples.

Photochemistry in dichloromethane at -20 and -50°C. The main effect of decreasing the reaction temperature was a decrease in the proportion of adducts, best seen at short reaction time (0.5 h) where the total adduct yield went from 26.4% at 20°C to 10.9% at -20°C and to 6.9% at -50°C. At the latter temperature, only adducts **5** and **6** were seen. Also, the yields of **1** and **7** decrease strongly with temperature, whereas the yields of **2** and **8** increase.

Photochemistry in acetonitrile at 20, -20 and -50°C. In acetonitrile none of the adducts **3–6** were detectable at 20°C, and only adducts **5** and **6** were detected at low

levels at -20 and -50°C (Table 2). There was an apparent increase in the yield of 4-methyl-2-trinitromethylanisole (**1**) with lower reaction temperatures, but this probably reflects a lower rate of decomposition of **1** to give 4-methyl-2-nitroanisole (**2**).¹² Otherwise the most notable feature of the data given in Table 2 is the steady increase of 4-methyl-4-nitrocyclohexa-2,5-dienone (**8**) as the temperature is lowered.

Photochemistry in dichloromethane at 20°C with trifluoroacetic acid present. It has been established^{3,6,13–15} that the addition of a sufficiently strong acid to the photolysis medium has the effect of eliminating all or almost all chemistry dependent on trinitromethanide ion, initiated via eqn. (2), since the latter is then converted into the very weakly nucleophilic nitroform. The photolysis of 4-methylanisole (0.51 mol dm^{-3}), tetranitromethane (1.02 mol dm^{-3}) and trifluoroacetic acid (0.7 mol dm^{-3}) in dichloromethane at 20°C after short reaction time (0.5 h) gave 4-methyl-4-nitrodienone (**8**) and the derived 4-methyl-2-nitrophenol **9** in a combined yield of 30%, 4-methyl-2-nitroanisole (**2**) in 52% yield and a 17% yield of an unidentified aromatic product, not seen under the conditions defined in Tables 1 and 2. No adducts were detected. Without TFA, the proportion of (**8** + **9**), **2** and total adducts was 4:7:26, the trinitromethyl derivative **1** being the predominant product (44%).

EPR studies of the 4-methylanisole-tetranitromethane reaction. We have previously demonstrated^{3,6} the effect of added acid on the ArH–tetranitromethane reaction by an EPR spectroscopic method, aiming at detecting the radical cation when the trinitromethanide concentration has been suppressed to very low levels. In many cases of radical cations of intermediate reactivity, it was observed that no EPR signal appeared on irradiation of an ArH–tetranitromethane solution in dichloromethane at -60 or -70°C , whereas addition of trifluoroacetic acid (0.4 or 0.8 mol dm^{-3}) made it possible to detect the signal from the corresponding radical cation or a species resulting from further reactions of the latter. The ratio of radical cation EPR spectral intensities with or without trifluoroacetic acid present was denoted ζ .

Irradiation of PMT (0.10 mol dm^{-3}) in dichloromethane with tetranitromethane (0.80 mol dm^{-3}) at -70°C with light of $\lambda > 430\text{ nm}$ gave no EPR signal under the standardized conditions defined in Ref. 3. The presence of TFA (0.4 mol dm^{-3}) under otherwise identical conditions gave a weak, featureless signal ($\zeta = 2$), which had a spectral width of $0.7\text{--}0.8\text{ mT}$. With a higher [TFA] (0.80 mol dm^{-3}), the signal was stronger but had no fine structure (spectral width ca. 3.5 mT ; $\zeta \approx 8$). It was found separately that the photolysis of 4-methylanisole with trifluoroacetic acid alone gave no EPR signal. At -60°C with [TFA] = 0.8 mol dm^{-3} , a weak spectrum with some fine structure could be recorded (Fig. 2a).

Irradiation of a solution of PMT (0.10 mol dm^{-3}) in dichloromethane with DDQ present¹⁶ at -60°C with

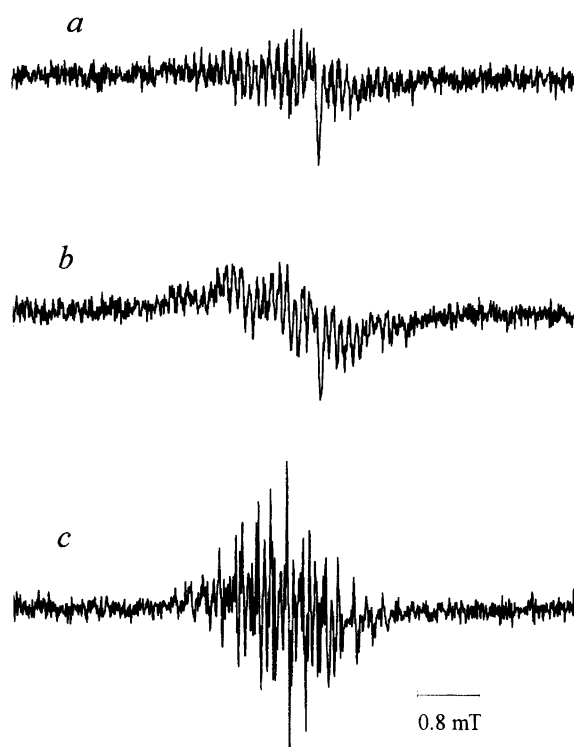


Fig. 2. EPR signal obtained by irradiation ($\lambda > 430\text{ nm}$) at -60°C of (a) a solution of 4-methylanisole (0.1 mol dm^{-3}), tetranitromethane (0.8 mol dm^{-3}) and trifluoroacetic acid (0.8 mol dm^{-3}), (b) a solution of 4-methylanisole (0.1 mol dm^{-3}), DDQ (0.03 mol dm^{-3}) and trifluoroacetic acid (0.8 mol dm^{-3}) and (c) a solution of 2,2'-dimethoxy-5,5'-dimethylbiphenyl (**10**, 0.005 mol dm^{-3}), tetranitromethane (0.8 mol dm^{-3}) and trifluoroacetic acid (0.8 mol dm^{-3}). All spectra were recorded with the same modulation amplitude.

light of $\lambda > 430\text{ nm}$ gave a weak spectrum with a fine structure (Fig. 2b) resembling that of Fig. 2a, and with a width $3.7\text{--}3.8\text{ mT}$. Since experiments performed under different conditions,¹⁷ as well as simulations based on literature data,¹⁸ showed that the monomeric radical cation of 4-methylanisole has a much wider EPR spectrum (about 8.0 mT), the spectrum of Fig. 2b must be due either to the dimeric radical cation, or more likely, the dehydromer radical cation.^{13,19,20} The spectrum is similar to that of the authentic dehydromer, 2,2'-dimethoxy-5,5'-dimethylbiphenyl (**10**), as recorded by photolysis of **10**, tetranitromethane and trifluoroacetic acid in dichloromethane at -60°C (Fig. 2c).

Discussion

Overview of photolysis reaction products in dichloromethane at 20 , -20 and -50°C . In dichloromethane at 20°C all four adducts **3–6** are formed, but with adducts **3** and **4** predominant at short reaction times (0.5 h); at longer reaction times (2 h) adducts **5** and **6** remain at their earlier levels, but adducts **3** and **4** clearly undergo further reac-

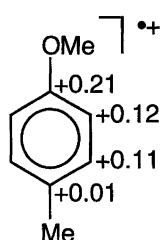


Fig. 3. Calculated (optimized AM1; UHF method) atomic charges on carbon atoms, including overall charges for CH groups, in the radical cation of 4-methylanisole.

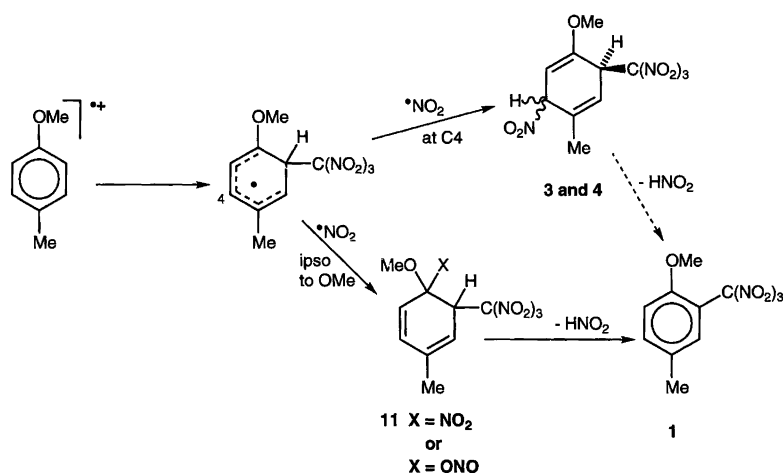
tion to give apparently 4-methyl-2-trinitromethylanisole **1** and some 4-methyl-2-nitroanisole **2** (Table 1). For photolysis reactions in dichloromethane at lower temperatures there is a progressive reduction in the yields of adducts **3** and **4**, and correspondingly also in 4-methyl-2-trinitromethylanisole **1**, the relative yield of which drops (for 0.5 h reaction times) progressively from 44% at 20°C, through 20% at -20°C to 10.5% at -50°C. At lower reaction temperatures the yield of the 4-methyl-2-nitroanisole **2** increases steadily, and this increase is accompanied by increased yields of 4-methyl-4-nitrocyclohexa-2,5-dienone **8**, and some marginal increase in the yields of adducts **5** and **6**. These changes in product yields with reaction temperature are interpreted below in terms of changes in the balance of the regiochemistry of reaction of trinitromethanide ion with the radical cation of 4-methylanisole with reaction temperature.

The calculated atomic charges on the ring carbon atoms of the radical cation of 4-methylanisole are given in Fig. 3. On this basis it seems likely that trinitromethanide ion would attack the radical cation of 4-methylanisole either *ipso* to the methoxy group or at the *vicinal* 2-position, the third possibility at the 3-position being disfavoured by the known reluctance of trinitromethanide ion to attack a radical cation *vicinal* to a methyl group.¹⁰

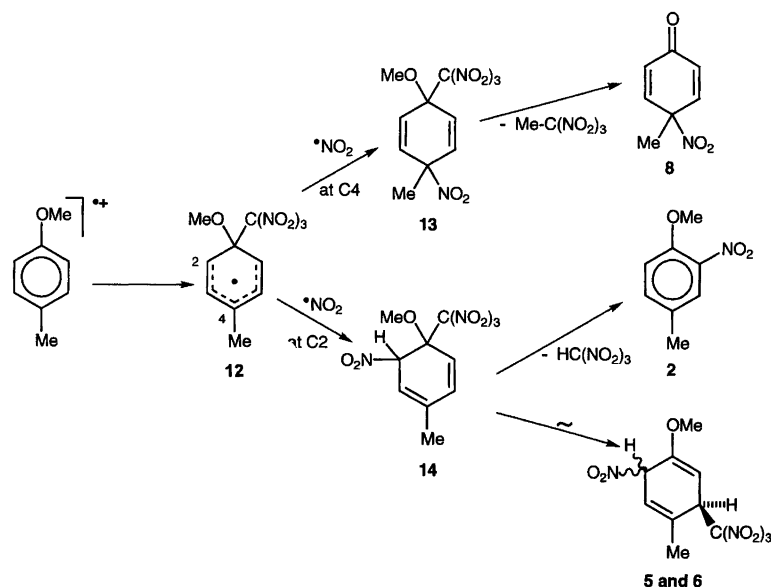
Attack of trinitromethanide ion at the 2-position of 4-methylanisole radical cation would give a delocalized carbon radical, the stability of which would be enhanced by the position of the methoxy group (Scheme 1). Attack of nitrogen dioxide at C4 in this delocalized carbon radical would yield adducts **3** and **4**. Alternatively, nitrogen dioxide could attack *ipso* to the methoxy group to give the diene **11** (where X = NO₂ or ONO); loss of nitrous acid from this sterically compressed diene **11** would provide a mechanistic pathway to 4-methyl-2-trinitromethylanisole (**1**) which does not require the intermediacy of adducts **3** and **4**; it appears likely, therefore, that 4-methyl-2-trinitromethylanisole (**1**) is formed via decomposition of adducts **3** and **4** (evident in the photolysis reaction at 20°C) and by decomposition of diene **11** (Scheme 1).

Alternatively, attack of trinitromethanide ion *ipso* to the methoxy group would give the delocalized carbon radical **12**, the stability of which would be enhanced by the position of the methyl group (Scheme 2). Attack of nitrogen dioxide *ipso* to the methyl group at C4 in the delocalized carbon radical **12** would give the diene **13**, which could lose the elements of Me-C(NO₂)₃ to give 4-methyl-4-nitrocyclohexa-2,5-dienone (**8**). The alternative coupling of nitrogen dioxide at C2(C6) in the carbon radical **12** would give the diene **14**, for which an easy decomposition pathway would involve the elimination of nitroform and yield 4-methyl-2-nitroanisole (**2**). A possible alternative reaction pathway for diene **14** would involve allylic rearrangement, with migration of the trinitromethyl group, to form the 3-trinitromethyl-6-nitro adducts **5** and **6**. This type of allylic migration of trinitromethanide ion has been observed in rearrangements of 1,4,6,7-tetramethyl-*r*-1-nitro-*t*-trinitromethyl-1,4-dihydronaphthalene¹⁵ and an adduct of 1,5-dimethylnaphthalene.²¹

Returning to the observed effects of reaction temperature on product yields, these effects can be rationalized if the assumption is made that at lower temperatures reaction of trinitromethanide ion *ipso* to the methoxy group



Scheme 1.



Scheme 2.

in the radical cation of 4-methylanisole becomes more favoured, relative to attack vicinal to the methoxy group. Thus the products from Scheme 2, i.e. 4-methyl-2-nitroanisole (**2**), 4-methyl-4-nitrocyclohexa-2,5-dienone (**8**) and the 3-trinitromethyl-6-nitro adducts **5** and **6**, would become more dominant at lower temperatures, at the expense of the products formed via Scheme 1, i.e. 4-methyl-2-trinitromethylanisole (**1**) and the 3-nitro-6-trinitromethyl adducts **3** and **4**. What is the cause of the observed 'temperature effect' in dichloromethane? It appears likely that at lower temperatures the inherent reactivity of trinitromethanide ion is lower, and the magnitude of the charge at the reacting carbon of the radical cation becomes more important, therefore leading to reaction *ipso* to the methoxy group.

Overview of photolysis reaction products in acetonitrile at 20, -20 and -50°C. The pattern of product yields relative to photolysis reaction temperature in acetonitrile (Table 2) is interpreted in terms of the lower reactivity of trinitromethanide ion in the more polar acetonitrile even at 20°C. Essentially this leads to the substantial operation of the reaction pathways illustrated in Scheme 2. The 'solvent effect' in the photolysis of the charge transfer complex between 4-methylanisole and tetranitromethane⁵ is thus now seen as being the consequence of the lower reactivity in acetonitrile of trinitromethanide ion towards the radical cation of 4-methylanisole, which affects the regiochemistry of attack of trinitromethanide ion on that radical cation.

Effect of trifluoroacetic acid. Photolysis of 4-methylanisole and tetranitromethane in the presence of trifluoroacetic acid leads to a situation where the 4-methylanisole radical cation is generated in the presence of only NO₂, trinitromethanide ion being effectively removed by protonation.

The radical cation can undergo at least two types of reaction, namely coupling with NO₂ to give 4-methyl-2-nitroanisole (**2**) after proton loss from the Wheland intermediate, and dehydrodimerization eventually to give **10**, a reaction pattern shown earlier¹³ to apply to 1-methoxynaphthalene radical cation. The formation of **10** is indicated by the EPR experiment (Fig. 2), the monomeric radical cation being too reactive to be observed under these conditions. Another way of forming **2** would be nitration of 4-methylanisole by NO₂,^{22,23} formed in the photolysis reaction and known to build up in a sizeable concentration during photolysis.²⁴ The formation of the nitroketone **8** is also best explained by attack of NO₂ at the position *ipso* to the methyl group, leading to 4-methoxy-1-methyl-1-nitrocyclohexadienyl cation which is converted to **8** by reaction with a nucleophilic species.

The effects of added salts Bu₄N⁺ ClO₄⁻ (TBAP) or Bu₄N⁺ C(NO₂)₃⁻ (TBAT) on the photolysis products in dichloromethane. Earlier Kochi *et al.*⁴ reported the effect of the added salt, Bu₄N⁺ ClO₄⁻ (0.2 M), on the photolysis reaction in dichloromethane, which resulted in the formation of 4-methyl-2-nitroanisole (**2**) (65%) and the rearrangement product of 4-methyl-4-nitroanisole (**8**), 4-methyl-2-nitrophenol (**9**) (35%). In the context of this present study, the above result can be reinterpreted. It is clear that the effect is not a matter of competition between ion-pair and radical-pair collapse, but is more probably a consequence of the increased polarity of the solvent system due to the added salt, leading to an 'acetonitrile-like' solvent environment for the attack of trinitromethanide ion on the radical cation of 4-methylanisole.

The addition of Bu₄N⁺ C(NO₂)₃⁻ at a considerably lower concentration (0.01 M) had a notably less marked effect on the products formed, relative to the products

formed in dichloromethane without added salts: 4-methyl-2-trinitromethylanisole (**1**) (76%) and 4-methyl-2-nitroanisole (**2**) (24%).⁵ Given that low levels of added salts would affect the polarity of the solvent only marginally, the reported outcome of this photolysis reaction is unremarkable.

The reassignment of structures to two adducts from the photolysis of the charge-transfer complex between 4-chloroanisole and tetranitromethane. Recently²⁵ we reported the structures of two adducts from the photolysis of the charge transfer complex of 4-chloroanisole with tetranitromethane as the epimeric 1-chloro-4-methoxy-3-trinitromethyl-6-nitrocyclohexa-1,4-dienes **15a** and **15b** (**3a** and **3b** in Ref. 25). With the establishment of the structures of the 3-nitro-6-trinitromethyl adducts **3** and **4** from similar reaction of 4-methylanisole, and the complete assignment of their ¹H and ¹³C NMR spectra, it is now possible to identify with certainty the structures of adducts **3a** and **3b**. These compounds are now assigned as 1-chloro-4-methoxy-*r*-3-trinitromethyl-*c*-6-nitrocyclohexa-1,4-diene (**16**, formerly **3a**) ¹H NMR δ 4.97 (H3), 5.40 (H5), 5.60 (H6), 6.60 (H2); ¹³C NMR δ 45.7 (C3), 85.2 (C6), 95.4 (C5), 121.7 (C2), and 1-chloro-4-methoxy-*r*-3-trinitromethyl-*t*-6-nitrocyclohexa-1,4-diene (**17**, formerly **3b**) ¹H NMR δ 5.12 (H3), 5.30 (H5), 5.70 (H6), 6.45 (H2); ¹³C NMR δ 45.3 (C3), 86.2 (C6), 94.8 (C5), 122.0 (C2); the above spectroscopic data involve the interchange of ¹H NMR data for C(5)-H and C(6)-H systems which were previously uncertain.²⁵

Experimental

Melting points are uncorrected. Infrared spectra were recorded on a Perkin Elmer 1600 series FTIR spectrometer; ¹H NMR spectra were recorded on a Varian Unity 300 spectrometer with SiMe₄ as an internal standard. Tetranitromethane and 4-methylanisole were purchased from Aldrich. 2,2'-Dimethoxy-5,5'-dimethylbiphenyl (**10**) was available from another study.¹⁷ Dichloromethane (AR) and acetonitrile (HiPerSolv) were from BDH.

EPR spectra were recorded by the Upgrade version ESP 3220-200SH of a Bruker ER-200D spectrometer. Photolyses were performed in the photolysis cavity (ER 4104 OR), using a 50 W high-pressure Hg lamp from Bruker (ER 202) and a filter with cut-off at <430 nm from Schott, Germany.

Warning! While we did not experience any incidents in working with tetranitromethane, it should be noted that

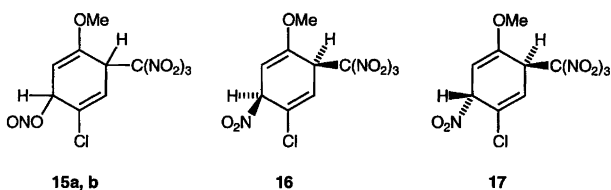
its mixtures with hydrocarbons are detonative within certain concentration limits and that due care should be taken in handling mixtures of tetranitromethane and organic compounds.²⁶

General procedure for the photonitration of 4-methylanisole with tetranitromethane. A solution of 4-methylanisole (500 mg, 0.51 mol dm⁻³) and tetranitromethane (1.02 mol dm⁻³) in dichloromethane (at 20, -20 or -50 °C) or acetonitrile (20, -20 or -50 °C) was irradiated with filtered light (λ_{cut-off} <435 nm). Aliquots were withdrawn from the reaction mixture at appropriate time intervals, the volatile material removed rapidly under reduced pressure at ≤0 °C, and the product composition determined by NMR special analysis (Tables 1 and 2).

Reaction in dichloromethane at 20 °C and the identification of adducts 3–6 aromatic products 1, 2, 7 and 9, and 4-methyl-4-nitrocyclohexa-2,5-dienone (8). Reaction of 4-methylanisole–tetranitromethane in dichloromethane at 20 °C, as above, for 1 h gave a product which was shown by ¹H NMR spectra to be a mixture (Table 1) of adducts **3** (11%), **4** (3%), **5** (2%), and **6** (2%), 4-methyl-2-trinitromethylanisole (**1**) (47%), 4-methyl-2-nitroanisole (**2**) (10%), 4-methyl-2,6-dinitrophenol (**7**) (10%), 4-methyl-4-nitrocyclohexa-2,5-dienone (**8**) (3%), 4-methyl-2-nitrophenol (**9**) (1%) and other unidentified materials (total 11%). These products were partially separated by HPLC and gave the following in elution order:

*1-Methoxy-4-methyl-*r*-3-nitro-*t*-6-trinitromethylcyclohexa-1,4-diene (4)* isolated only in admixture with 1-methoxy-4-methyl-*t*-6-nitro-*r*-3-trinitromethylcyclohexa-1,4-diene (**5**), ¹H NMR (CDCl₃) δ 1.90 (br s, 4-Me), 3.64 (s, OMe), 4.96 (dddq, *J*_{H6,H2} 1.0 Hz, *J*_{H6,H3} 4.9 Hz, *J*_{H6,4-Me} 1.5 Hz, *J*_{H6,H5} 2.9 Hz, H6), 5.26 (dd, *J*_{H2,H3} 3.9 Hz, *J*_{H2,H6} 1.0 Hz, H2), 5.57 (dd, *J*_{H3,H2} 3.9 Hz, *J*_{H3,H6} 4.9 Hz, H3), 5.99 (dq, *J*_{H5,4-Me} 1.5 Hz, *J*_{H5,H6} 2.9 Hz, H5). Nuclear Overhauser experiments gave the following results: irradiation at δ 1.90 gave enhancements at δ 5.57 (3.3%) and at δ 5.99 (4.0%); irradiation at δ 3.64 gave an enhancement at δ 5.26 (10.5%); irradiation at δ 4.96 gave an enhancement at δ 5.99 (3.1%); irradiation at δ 5.26 gave enhancements at δ 3.64 (0.6%) and at δ 5.57 (4.3%); irradiation at δ 5.57 gave an enhancement at δ 5.26 (2.0%); irradiation at δ 5.99 gave enhancements at δ 1.90 (0.3%) and at δ 4.96 (3.8%). ¹³C NMR (CDCl₃) δ 44.1 (C6), 55.9 (OMe), 85.9 (C3), 95.1 (C2), 119.2 (C5), resonances for 4-CH₃, C1 and C4 were not assigned in the spectrum of the mixture of adducts **4** and **5**. The above assignments were confirmed by long-range reverse detected heteronuclear correlation spectra (HMQC).

*1-Methoxy-4-methyl-*t*-6-nitro-*r*-3-trinitromethylcyclohexa-1,4-diene (5)* isolated only in admixture with 1-methoxy-4-methyl-*r*-3-nitro-*t*-6-trinitromethylcyclohexa-1,4-diene (**4**), ¹H NMR (CDCl₃) δ 1.90 (br s, 4-Me), 3.64 (s, OMe), 4.93 (ddd, *J*_{H3,H2} 4.4 Hz, *J*_{H3,H5} 1.0 Hz, *J*_{H3,H6} 4.9 Hz,



H3), 5.10 (dd, J_{H_2,H_3} 4.4 Hz, J_{H_2,H_6} 1.0 Hz, H2), 5.49 (ddd, J_{H_6,H_2} 1.0 Hz, J_{H_6,H_3} 4.9 Hz, J_{H_6,H_5} 2.9 Hz, H6), 6.04 (ddq, J_{H_5,H_3} 1.0 Hz, J_{H_5,H_6} 2.9 Hz, $J_{H_5,4-Me}$ 1.5 Hz, H5). Nuclear Overhauser experiments gave the following results: irradiation at δ 1.90 gave enhancements at δ 4.93 (4.0%) and at δ 6.04 (6.3%); irradiation at δ 3.64 gave an enhancement at δ 5.10 (11.5%); irradiation at δ 4.93 gave an enhancement at δ 5.10 (3.2%); irradiation at δ 5.10 gave an enhancement at δ 4.93 (3.5%); irradiation at δ 5.49 gave an enhancement at δ 6.04 (1.0%). ^{13}C NMR (CDCl_3) δ 47.1 (C3), 55.8 (OMe), 81.9 (C6), 91.3 (C2), 126.1 (C5), resonances for 4-CH₃, C1 and C4 were not assigned in the spectrum of the mixture of adducts 4 and 5. The above assignments were confirmed by long-range reverse-detected heteronuclear correlation spectra (HMQC).

4-Methyl-2,6-dinitrophenol (7) isolated only in admixture with adducts 3, 5 and 6, and identified by comparison of its ^1H NMR spectrum with that of authentic material.

*1-Methoxy-4-methyl-*c*-6-nitro-*r*-3-trinitromethylcyclohexa-1,4-diene* (6) isolated only in admixture with 1-methoxy-4-methyl-*r*-3-nitro-*c*-6-trinitromethylcyclohexa-1,4-diene (3), ^1H NMR (CDCl_3) δ 1.81 (s, 4-Me), 3.60 (s, OMe), 4.88 (dd, J_{H_3,H_6} 2.9 Hz, J_{H_3,H_2} 4.4 Hz, H3), 5.27 (d, J_{H_2,H_3} 4.4 Hz, H2), 5.38 (dd, J_{H_6,H_5} 5.4 Hz, J_{H_6,H_3} 2.9 Hz, H6), 6.18 (dq, J_{H_5,H_6} 5.4 Hz, $J_{H_5,4-Me}$ 1.5 Hz, H5). Nuclear Overhauser experiments gave the following results: irradiation at δ 1.81 gave enhancements at δ 4.88 (6.5%) and at δ 6.18 (8.5%); irradiation at δ 3.60 gave an enhancement at δ 5.27 (18.6%); irradiation at δ 4.88 gave enhancements at δ 5.27 (4.8%) and at δ 1.81 (1.2%); irradiation at δ 5.27 gave enhancements at δ 3.60 (1.5%) and at δ 4.88 (4.7%); irradiation at δ 5.38 gave an enhancement at δ 6.18 (2.6%). ^{13}C NMR (CDCl_3) δ 21.6 (4-Me), 46.8 (C3), 55.9 (OMe), 80.9 (C6), 93.0 (C2), 124.7 (C5), resonances for C1 and C4 were not assigned in the spectrum of the mixture of adducts 3 and 6. The above assignments were confirmed by long-range reverse-detected heteronuclear correlation spectra (HMQC).

*1-Methoxy-4-methyl-*r*-3-nitro-*c*-6-trinitromethylcyclohexa-1,4-diene* (3) m.p. 58–60°C (decomp.) (X-ray crystal structure determined, see below). IR: ν_{max} (KBr) 1664, 1622, 1600, 1561 cm^{-1} . ^1H NMR (CDCl_3) δ 1.80 (d, J_{4-Me,H_5} 1.5 Hz, 4-Me), 3.57 (s, OMe), 4.80 (dddq, J_{H_6,H_2} 1.9 Hz, J_{H_6,H_3} 4.9 Hz, J_{H_6,H_5} 3.9 Hz, $J_{H_6,4-Me}$ 1.7 Hz, H6), 5.36 (dd, J_{H_2,H_3} 4.8 Hz, J_{H_2,H_6} 1.9 Hz, H2), 5.44 (dd, J_{H_3,H_2} 4.8 Hz, J_{H_3,H_6} 4.9 Hz, H3), 6.11 (dq, J_{H_5,H_6} 3.9 Hz, $J_{H_5,4-Me}$ 1.5 Hz, H5). Nuclear Overhauser experiments gave the following results: irradiation at δ 1.90 gave enhancements at δ 5.44 (4.4%) and at δ 6.11 (5.7%); irradiation at δ 3.57 gave an enhancement at δ 5.36 (10.0%); irradiation at δ 4.80 gave an enhancement at δ 6.11 (2.1%); irradiation at δ 5.36 gave enhancements at δ 3.57 (1.4%) and at δ 5.44 (2.4%); irradiation at δ 5.44 gave enhancements at δ 5.36 (1.2%) and at δ 1.90

(0.5%); irradiation at δ 6.11 gave enhancements at δ 1.90 (0.7%) and at δ 4.80 (3.9%). ^{13}C NMR (CDCl_3) δ 21.0 (4-Me), 44.6 (C6), 56.2 (OMe), 84.8 (C3), 95.5 (C2), 119.0 (C5), 135.6 (C4), 152.0 (C1), resonance for C(NO₂)₃ not observed. The above assignments were confirmed by long-range reverse-detected heteronuclear correlation spectra (HMQC).

4-Methyl-4-nitrocyclohexa-2,5-dienone (8) obtained only in admixture with adduct 3, and identified by comparison of its ^1H NMR spectrum with that of authentic material.

From a separate photolysis reaction at 20°C in dichloromethane the crude reaction product was crystallized from dichloromethane–hexane to give 4-methyl-2-trinitromethylanisole (1), m.p. 105–107°C; ^1H NMR (CDCl_3) δ 2.35 (s, 4-Me), 3.80 (s, OMe), 7.00 (d, J_{H_6,H_5} 8.8 Hz, H6), 7.05 (s, H3), 7.49 (d, J_{H_5,H_6} 8.8 Hz, H5).⁵

From a separate photolysis reaction at –50°C in dichloromethane the crude reaction mixture was adsorbed onto a silica gel Chromatotron plate. Elution with pentane and pentane–ether mixtures gave:

4-Methyl-2-nitrophenol (9). ^1H NMR (CDCl_3) δ 2.35 (s, Me), 7.06 (d, J_{H_6,H_5} 8.8 Hz, H6), 7.40 (dd, J_{H_5,H_3} 1.9 Hz, J_{H_5,H_6} 8.8 Hz, H5), 7.90 (d, J_{H_3,H_5} 1.9 Hz, H3), 10.45 (s, OH), identical with authentic material.

4-Methyl-2-nitroanisole (2). ^1H NMR (CDCl_3) δ 2.34 (s, Me), 3.93 (s, OMe), 6.98 (d, J_{H_6,H_5} 9.3 Hz, H6), 7.35 (dd, J_{H_5,H_3} 1.9 Hz, J_{H_5,H_6} 9.3 Hz, H5), 7.65 (d, J_{H_3,H_5} 1.9 Hz, H3), identical with authentic material.

Reaction in dichloromethane in the presence of trifluoroacetic acid at 20°C. Reaction conditions as above, except for the addition of trifluoroacetic acid (0.70 mol dm⁻³) gave after 0.5 h a product which was shown by ^1H NMR spectroscopy to be a mixture of 4-methyl-4-nitrodienone (8) and 4-methyl-2-nitrophenol (9) in a combined yield of 30%, 4-methyl-2-nitroanisole (2) (52%) and an unidentified aromatic product (17%).

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 determined unambiguously as a result of the structure analysis reported below, but indicated initially by conditions limiting possible reflections. ω -Scans were used to collect reflection intensities out to a maximum Bragg angle $\theta = 25^\circ$. The cell parameters were determined by least-squares refinements for which the setting angles of 17 accurately centred high-angle reflections were used.

Crystal data. 1-Methoxy-4-methyl-*r*-3-nitro-*c*-6-trinitromethylcyclohexa-1,4-diene (3), C₉H₁₀N₄O₉, $M = 318.21$, orthorhombic, space group $P 2_1 2_1 2_1$, $a = 6.786(1)$, $b = 11.817(5)$, $c = 16.180(2)$ Å; $V = 1297.5(6)$ Å³, $D_c = 1.629$ g cm⁻³, $Z = 4$, molybdenum X-radiation,

$\mu(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$, $\mu(\text{Mo K}\alpha) = 1.48 \text{ cm}^{-1}$. The crystal was colourless and of approximate dimensions $0.70 \times 0.68 \times 0.28 \text{ mm}$. Data were collected at $130(2) \text{ K}$. The number of independent reflections measured was 1945, 1823 with $I > 2\sigma(I)$. Absorption corrections were not applied; $g_1 = 0.0304$, $g_2 = 0.4404$; $R_{(\text{obs})}$ -factor = 0.028, $wR_{(\text{all data})} = 0.066$.

Structure determination. Full-matrix least-squares refinements (SHELXL-93)²⁷ 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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References

- Butts, C. P., Ebersson, L., Hartshorn, M. P., Robinson, W. T., Timmerman-Vaughan, D. J. and Young, D. A. W. *Acta Chem. Scand.* 50 (1996) 29.
- Ebersson, L., Hartshorn, M. P. and Svensson, J. O. *J. Chem. Soc., Chem. Commun.* (1993) 1614.
- Ebersson, L., Hartshorn, M. P., Radner, F. and Svensson, J. O. *J. Chem. Soc., Perkin Trans. 2* (1994) 1719.
- Kochi, J. K. *Acc. Chem. Res.* 25 (1992) 39.
- Sankararaman, S., Haney, W. A. and Kochi, J. K. *J. Am. Chem. Soc.* 109 (1987) 7824.
- Ebersson, L., Hartshorn, M. P. and Radner, F. *Acta Chem. Scand.* 48 (1994) 937.
- Butts, C. P., Calvert, J. L., Ebersson, L., Hartshorn, M. P., Maclagan, R. G. A. R. and Robinson, W. T. *Aust. J. Chem.* 47 (1994) 1087.
- Appel, H. H., Bond, R. P. M. and Overton, K. H. *Tetrahedron* 19 (1963) 635.
- Durham, L. J., Studebaker, J. and Perkins, M. J. *Chem. Commun.* (1965) 456.
- Calvert, J. L., Ebersson, L., Hartshorn, M. P., Maclagan, R. G. A. R. and Robinson, W. T. *Aust. J. Chem.* 47 (1994) 1591.
- Calvert, J. L., Ebersson, L., Hartshorn, M. P., Maclagan, R. G. A. R. and Robinson, W. T. *Aust. J. Chem.* 47 (1994) 1211; Butts, C. P., Calvert, J. L., Ebersson, L., Hartshorn, M. P., Radner, F. and Robinson, W. T. *J. Chem. Soc., Perkin Trans. 2* (1994) 1485; Calvert, J. L., Ebersson, L., Hartshorn, M. P., Robinson, W. T. and Timmerman-Vaughan, D. J. *Acta Chem. Scand.* 48 (1994) 917.
- Butts, C. P., Ebersson, L., Hartshorn, M. P. and Svensson, J. O. *To be published.*
- Butts, C. P., Ebersson, L., Hartshorn, M. P., Persson, O. and Robinson, W. T. *Acta Chem. Scand.* 49 (1995) 253.
- Ebersson, L., Hartshorn, M. P., Persson, O., Robinson, W. T. and Timmerman-Vaughan, D. J. *Acta Chem. Scand.* 49 (1995) 482.
- Ebersson, L., Hartshorn, M. P., Robinson, W. T. and Timmerman-Vaughan, D. J. *Acta Chem. Scand.* 49 (1995) 571.
- Davies, A. G. and Ng, K.-M. *Aust. J. Chem.* 48 (1995) 167; Handoo, K. L. and Gadru, K. *Curr. Sci.* 55 (1986) 920.
- Ebersson, L., Hartshorn, M. P. and Persson, O. *J. Chem. Soc., Chem. Commun.* (1995) 1131. Ebersson, L., Hartshorn, M. P. and Persson, O. *J. Chem. Soc., Perkin Trans. 2.* (1995) 1735.
- Dixon, W. T. and Murphy, D. *J. Chem. Soc., Perkin Trans. 2.* (1976) 1823; Fleischhauer, J., Ma, S., Schleker, W., Gersonde, K., Twilfer, H. and Dallacker, F. *Z. Naturforsch., Teil A* 87 (1982) 680.
- Ebersson, L., Hartshorn, M. P. and Persson, O. *J. Chem. Soc., Perkin Trans. 2* (1995) 409.
- Ebersson, L., Hartshorn, M. P. and Persson, O. *Acta Chem. Scand.* 49 (1995) 640.
- Butts, C. P., Ebersson, L., Hartshorn, M. P. and Robinson, W. T. *To be published.*
- Ebersson, L. and Radner, F. *Acc. Chem. Res.* 20 (1987) 53.
- Bosch, E. and Kochi, J. K. *J. Org. Chem.* 59 (1994) 3314.
- Ebersson, L. and Radner, F. *J. Am. Chem. Soc.* 113 (1991) 5825.
- Ebersson, L., Hartshorn, M. P. and Svensson, J. O. *Acta Chem. Scand.* 47 (1993) 925.
- Tschinkel, J. G. *Ind. Eng. Chem.* 48 (1965) 732.
- Sheldrick, G. M. *J. Appl. Crystallogr.* (1994) *In preparation.*

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