

# Photochemical Nitration by Tetranitromethane. Part XLII.<sup>†</sup> Photolysis of Some 4-Methoxystyrene Derivatives with Tetranitromethane

Lennart Ebersson,<sup>a,\*</sup> Michael P. Hartshorn<sup>b,\*</sup> and Ola Persson<sup>a</sup>

<sup>a</sup>Department of Chemistry, Lund University, PO Box 124, S-221 00 Lund, Sweden and <sup>b</sup>Department of Chemistry, University of Canterbury, Christchurch, New Zealand

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The photochemical reaction of 4-methoxystyrene (**2a**) with tetranitromethane in dichloromethane gives the nitro-trinitromethyl adduct, 2-(4'-methoxyphenyl)-1-nitro-2-trinitromethylethane (**1**), which on chromatography on silica gel yields the (*E*)-nitroalkene, (*E*)-4'-methoxy-2-nitrostyrene (**3**); in acetonitrile solution adduct **1** is also the major product together with minor adducts. Similar reaction of *trans*-1-(4'-methoxyphenyl)-1-propene (**2b**) in dichloromethane gives exclusively the stereoisomeric nitro-trinitromethyl adducts, 1-(4'-methoxyphenyl)-2-nitro-1-trinitromethylpropanes **6** and **7**, but in acetonitrile adduct **7** is the major product together with a small amount of adduct **6** and a mixture of minor adducts. The base-catalysed reactions of adducts **1** and **6** gave nitroalkenes (*E*)-4'-methoxy-2-nitrostyrene (**3**) and (*E*)-1-(4'-methoxyphenyl)-2-nitro-1-propene (**8**), respectively, but reaction of adduct **7** gave a product of unknown structure. Kinetic studies of the base-catalysed reactions of nitro-trinitromethyl adducts **1**, **6** and **7**, and a nitro-trinitromethyl adduct derived from naphthalene, *cis*-1-nitro-4-trinitromethyl-1,4-dihydronaphthalene, are reported. A mixture of (*E*)- and (*Z*)-4-methoxycinnamitrile did not react on extended photolysis with tetranitromethane. The photochemical reactions of 4-methoxystyrenes **2a** and **2b** with tetranitromethane are assumed to proceed via a radical chain reaction mechanism.

In 1972 Ratsino *et al.*<sup>2</sup> reported the formation of the nitro-trinitromethyl adduct **1** on reaction of 4-methoxystyrene (**2a**) with tetranitromethane in diethyl ether solution for 24 h. The reaction conditions, in terms of incident light, were not specified, but a recent report by Mathew *et al.*<sup>3</sup> suggests that it was a thermal dark reaction. Under photochemical conditions, involving the specific irradiation of the **2a**-tetranitromethane charge transfer band, the latter authors reported<sup>3</sup> the formation in high yield of the *trans*-nitroalkene **3**, but notably after a workup procedure including chromatography on silica.

Thermal dark reactions of tetranitromethane in diethyl ether solution were reported to give other nitro-trinitromethyl adducts analogous to adduct **1** for a variety of other alkyl-substituted 4-methoxystyrene substrates **2b**,<sup>2,4</sup> **4**<sup>2</sup> and **5**.<sup>2</sup> Although the styrene derivatives **2b** and **5** could form potentially two stereoisomers of each of the corresponding nitro-trinitromethyl adducts, only one unspecified stereoisomer was isolated in each case.<sup>2,4</sup> It has been noted that for thermal dark reactions of

tetranitromethane in diethyl ether solution electron-withdrawing groups in the  $\beta$ -position of styrenes markedly reduce the reactivity of the double bond.<sup>5</sup> However, of the substrates to which reference was made, 4-methoxycinnamic acid **2c** might have been the most promising for adduct formation except for the potential for secondary and diversionary reactions at the carbonyl group.

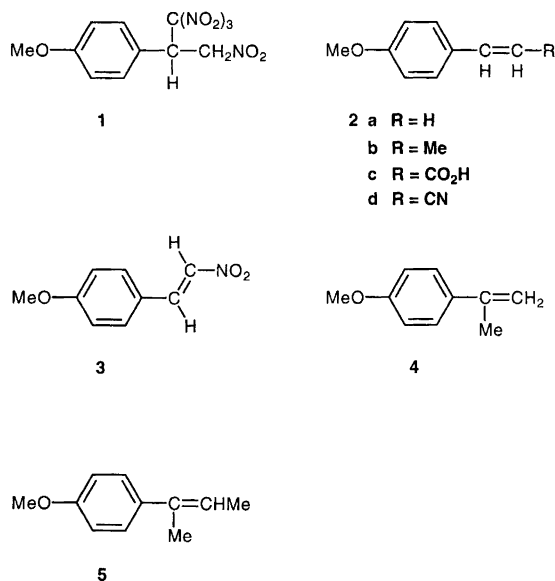
We now report the results of a study of the photochemical reactions of tetranitromethane with 4-methoxystyrene (**2a**) and its  $\beta$ -substituted derivatives, 1-(4'-methoxyphenyl)-1-propene (**2b**) and 4-methoxycinnamitrile (**2d**). In the event 4-methoxystyrene did yield the nitro-trinitromethyl adduct **1**, 1-(4'-methoxyphenyl)-1-propene (**2b**) gave two stereoisomeric nitro-trinitromethyl adducts, but reaction of 4-methoxycinnamitrile (**2d**) resulted only in partial *cis/trans* interconversion of the alkene function.

## Results

*General.* The photochemical experiments were performed with filtered light (cut-off at 435 nm, 5 cm water IR filter,

<sup>†</sup> Part XLI, see Ref. 1.

\* To whom correspondence should be addressed.



with a 300 W incandescent lamp) as described before.<sup>6</sup> The temperature of the photolysis solution was kept at 15 °C. The work-up procedure, involving evaporation of solvent and excess tetranitromethane, was conducted at a temperature of ≤0 °C. The crude product mixtures were stored at -78 °C and were analysed (<sup>1</sup>H NMR spectroscopy, see Experimental section) as soon as possible.

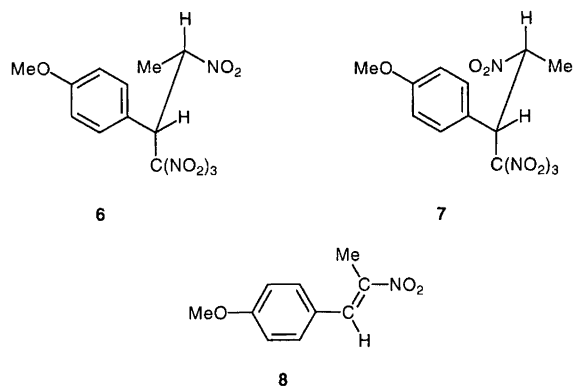
**Photolysis of 4-methoxystyrene (2a) with tetranitromethane in dichloromethane.** A solution of **2a** and tetranitromethane in dichloromethane was irradiated, and its composition monitored with time. After 30 min **2a** was converted completely into a single product identified as 2-(4'-methoxyphenyl)-1-nitro-2-trinitromethylethane (**1**) from its NMR spectra. The connectivity in **1** was determined from a consideration of its <sup>1</sup>H, <sup>13</sup>C NMR and heteronuclear correlation (HETCOR) spectra (Experimental section). In particular, the CH<sub>2</sub>-NO<sub>2</sub> structural feature exhibited a <sup>13</sup>C NMR resonance at δ 76.1, and in the <sup>1</sup>H NMR spectrum an AB-quartet with additional couplings to the adjacent CH-C(NO<sub>2</sub>)<sub>3</sub>. Correspondingly, the CH-C(NO<sub>2</sub>)<sub>3</sub> appeared in the <sup>1</sup>H NMR spectrum as a doublet of doublets, arising from couplings to the adjacent methylene group, and the <sup>13</sup>C NMR resonance at δ 47.9 was consistent with this point of attachment of the trinitromethyl group. Reaction of the nitro-trinitromethyl adduct **1** with the hindered base, 2,6-lutidine, in [<sup>2</sup>H]chloroform occurred rapidly (in <3 min at the concentrations employed) to yield only the (*E*)-nitroalkene **3**.<sup>7</sup>

The nitro-trinitromethyl adduct **1** in dichloromethane was adsorbed onto a silica gel chromatographic column. After 2 h elution with dichloromethane it gave a quantitative yield of the (*E*)-nitroalkene **3**. The instability of the nitro-trinitromethyl adduct **1** to silica in dichloromethane contrasts sharply with the apparent stability of that

compound to silica gel in the presence of the markedly less polar carbon tetrachloride.<sup>2</sup> As **1** is unaffected by washing its dichloromethane solution with saturated sodium bicarbonate, part of the work-up procedure employed by Mathew *et al.*,<sup>3</sup> it seems likely that those authors converted **1** into the (*E*)-nitroalkene **3** during silica gel chromatography.

**Photolysis of 4-methoxystyrene (2a) with tetranitromethane in acetonitrile.** A solution of **2a** and tetranitromethane in acetonitrile was irradiated, and its composition monitored with time. After 15 min **2a** was converted completely into a mixture of the nitro-trinitromethyl adduct **1** (66%) and a complex mixture of other products (total 34%) which were evident from <sup>1</sup>H NMR resonances in the regions δ 4.62–4.65 and δ 3.75–3.85. Given the instability of **1** even to a silica gel Chromatotron plate and solvent mixtures containing dichloromethane, it was not possible to examine this reaction product further.

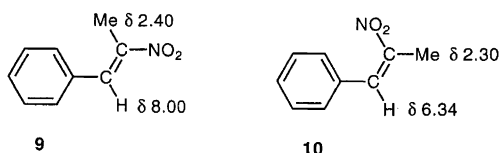
**Photolysis of trans-1-(4'-methoxyphenyl)-1-propene (2b) with tetranitromethane in dichloromethane and the identification of the stereoisomeric 1-(4'-methoxyphenyl)-2-nitro-1-trinitromethylpropanes 6 and 7.** A solution of **2b** and tetranitromethane in dichloromethane was irradiated, and its composition monitored with time. After 10 min **2b** was converted completely into a mixture of the stereoisomeric 1-(4'-methoxyphenyl)-2-nitro-1-trinitromethylpropanes **6** (29%) and **7** (71%). These nitro-trinitromethyl adducts were separated by chromatography on a silica gel Chromatotron plate. The connectivity in each of **6** and **7** was established from a consideration of their <sup>1</sup>H, <sup>13</sup>C NMR and heteronuclear correlation (HETCOR) spectra (Experimental section). In the <sup>1</sup>H NMR spectrum of each adduct, H2 appeared as a doublet of quartets arising from coupling to the adjacent methyl group and H1; correspondingly for each adduct H1 appeared as a doublet with coupling to H2. The location of the trinitromethyl and nitro groups in the adducts was revealed by the <sup>13</sup>C NMR chemical shifts for **6** [δ 52.3 (C1), δ 86.5 (C2)] and **7** [δ 52.9 (C1), δ 82.9 (C2)]. From the melting points of **6** (81–82 °C) and **7** (61–62 °C), it appears that the earlier workers<sup>2,4</sup> isolated



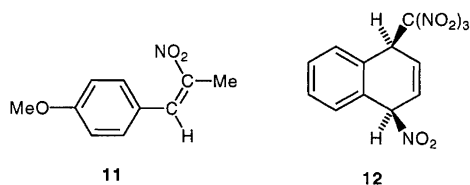
the more readily crystallized stereoisomer **6** with the higher melting point.

*Photolysis of trans-1-(4'-methoxyphenyl)-1-propene (2b) with tetranitromethane in acetonitrile.* A solution of **2b** and tetranitromethane in acetonitrile was irradiated at 15 °C, and its composition monitored with time. After 15 min **2b** was converted completely into a mixture of the stereoisomeric 1-(4'-methoxyphenyl)-2-nitro-1-trinitromethylpropanes **6** (6%) and **7** (64%) and a complex mixture of other products (total 30%) which were evident from <sup>1</sup>H NMR resonances in the regions δ 4.02–5.10 and δ 3.75–3.85.

*Treatment of (1RS,2SR)-1-(4'-methoxyphenyl)-2-nitro-1-trinitromethylpropane (6) with bases in (2H)chloroform.* Attempted reaction of **6** with the hindered base, 2,6-lutidine, in (2H)chloroform solution resulted in no conversion of **6** into products. In contrast, reaction with (2H<sub>5</sub>)pyridine in (2H)chloroform was complete in 4.25 h to give exclusively (*E*)-1-(4'-methoxyphenyl)-2-nitro-1-propene (**8**). The structure of **8** was assigned on the basis of its <sup>1</sup>H, <sup>13</sup>C NMR and heteronuclear correlation (HETCOR) spectra (Experimental section). The stereochemistry of **8** was assigned by comparison of the <sup>1</sup>H NMR chemical shifts of H1 (δ 8.03) and 3-CH<sub>3</sub> (δ 2.43) with corresponding data for the stereoisomeric 2-nitro-1-phenyl-1-propenes **9** and **10**.<sup>8</sup> On the reasonable assumption that the elimination of nitroform from **6** occurs by the *E*<sub>2</sub> mechanism (see Discussion), adduct **6** is assigned the (1RS,2SR)-configuration, and by exclusion 2-nitro-1-trinitromethyl adduct **7** has the (1RS,2RS)-configuration.



*Treatment of (1RS,2RS)-1-(4'-methoxyphenyl)-2-nitro-1-trinitromethylpropane (7) with bases in (2H)chloroform.* Attempted reaction of **7** with the hindered base, 2,6-lutidine, in (2H)chloroform solution, as for the analogous reaction of **6**, also resulted in no conversion of **7** into products. Reaction of **7** with (2H<sub>5</sub>)pyridine in (2H)chloroform was complete in 2.5 h, but no trace of the nitroalkene **11** was detected among the products of reaction. The structure of the anisyl



product of reaction of **7** is not known. However, from the kinetic study (below) it is clear that trinitromethanide ion is liberated in the reaction. Further, in the <sup>1</sup>H NMR spectrum of the anisyl product the C2–CH<sub>3</sub> signal appeared as a sharp singlet at δ 2.39 indicating the absence of a hydrogen atom at C2 and probably also at C1.

*Photolysis of 4-methoxycinnamionitrile (2d) (cis/trans ratio 1.6:1) with tetranitromethane in dichloromethane.* A solution of **2d** and tetranitromethane in dichloromethane was irradiated at 15 °C. After 6 h, the residue after removal of the solvent and tetranitromethane under reduced pressure at ≤0 °C was shown (<sup>1</sup>H NMR spectra) to be exclusively a mixture (1:1.7) of *cis*- and *trans*-4-methoxycinnamionitrile (**2d**).

*Kinetics of elimination of nitroform from nitro-trinitromethyl adducts 1, 6, 7 and 12.* The adducts **1**, **6** and **7** were treated with excess 3,5-lutidine in dichloromethane, and the appearance of the 350 nm maximum of trinitromethanide ion was monitored vs. time by UV spectroscopy. The reactions obeyed first-order kinetics, and runs at different concentrations of 3,5-lutidine gave satisfactory second-order rate constants (Table 1). As expected, the less hindered adduct **1** from 4-methoxystyrene **2a** reacted significantly faster than either of the two adducts **6** and **7** from *trans*-1-(4'-methoxyphenyl)-1-propene (**2b**).

It was of interest to compare rate constants of elimination of the acyclic adducts above with that of an adduct derived from the addition of the elements of tetranitromethane to naphthalene. The reaction of the *cis*-1,4-nitro-trinitromethyl adduct **12**<sup>9</sup> with 3,5-lutidine was therefore included in this study. This reaction was very fast, ca. 10<sup>3</sup> times faster than that of nitro-trinitromethyl adduct **1**, showing the effect of fully restoring the aromatic system in the reaction of adduct **12**.

## Discussion

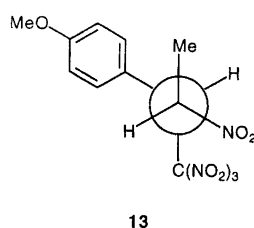
*The formation of nitro-trinitromethyl adducts from 4-methoxystyrene derivatives.* Contrary to findings in a recent report,<sup>3</sup> the formation of nitro-trinitromethyl adduct **1** occurs readily on irradiation of the charge transfer band of the CT complex of 4-methoxystyrene (**1a**) and tetranitromethane, quantitatively in dichloromethane and still in high yield in acetonitrile. It is not clear what factors control the ratio of nitro-trinitromethyl adducts **6** and **7** formed in the analogous reaction of *trans*-1-(4'-methoxyphenyl)-1-propene (**2b**), but it is perhaps notable that the staggered conformation (**13**) of the major nitro-trinitromethyl adduct **7** is thermodynamically the most stable structure among the possible products of the addition of the elements of tetranitromethane to **2b** in the regiochemical direction observed.

The lack of reaction on irradiation of the charge transfer band of the CT complex between 4-methoxycinnamionitrile (**2d**) and tetranitromethane is a clear

Table 1. Rates of 3,5-lutidine induced elimination from nitro-trinitromethyl adducts **1**, **6** and **7** in dichloromethane at 23 °C and comparison with the naphthalene adduct **12**.

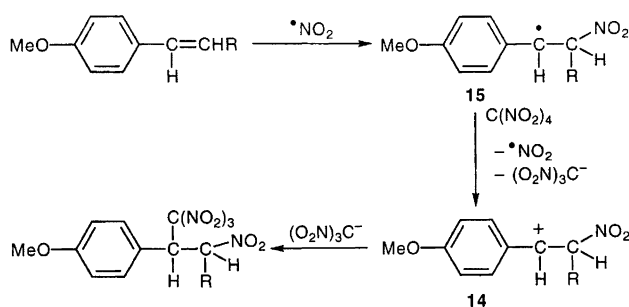
Compound	[3,5-lutidine]/ mol dm <sup>-3</sup>	k/s <sup>-1</sup>	k <sub>2</sub> /dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	Rel. rate
<b>6</b>	0.044	1.55 × 10 <sup>-4</sup>	0.00352	1.0
	0.117	4.64 × 10 <sup>-4</sup>	0.00397	
	0.293	1.08 × 10 <sup>-3</sup>	0.00369	
			Ave: 0.0037	
<b>7</b>	0.117	1.01 × 10 <sup>-3</sup>	0.0086	2.3
	0.234	1.98 × 10 <sup>-3</sup>	0.0085	
	0.293	2.41 × 10 <sup>-3</sup>	0.0082	
			Ave: 0.0084	
<b>1</b>	0.117	1.39 × 10 <sup>-2</sup>	0.119	31
	0.117	1.48 × 10 <sup>-2</sup>	0.126	
	0.234	2.49 × 10 <sup>-2</sup>	0.106	
	0.293	3.15 × 10 <sup>-2</sup>	0.108	
	0.176	1.97 × 10 <sup>-2</sup>	0.112	
		Ave: 0.114		
<b>12</b>	0.00058	6.9 × 10 <sup>-2</sup>	119	3.2 × 10 <sup>4</sup>
	<sup>a</sup>		0.18(5)	

<sup>a</sup> Base = 2,6-Di(*tert*-butyl)pyridine.<sup>9</sup>



confirmation that, even in the presence of an activating 4-methoxy group, a strong electron-withdrawing group on the β-carbon of a styrene system markedly reduces the reactivity of the alkene system.

The rates of formation of the nitro-trinitromethyl adducts **1**, and **6** and **7**, from 4-methoxystyrene (**2a**) and *trans*-1-(4'-methoxyphenyl)-1-propene (**2b**), respectively, on photolysis with tetranitromethane are too great to be accounted for in terms of the photochemical formation and recombination of the triad [ArH<sup>•+</sup> ·NO<sub>2</sub> (O<sub>2</sub>N)<sub>3</sub>C<sup>-</sup>]. Also the regiochemistry of the addition would be expected to be the reverse of what is observed if such a recombination mechanism were operative, radical cations ArH<sup>•+</sup> characteristically reacting more rapidly with trinitromethanide ion than with nitrogen dioxide.<sup>10</sup> These observations are in accord with the proposal<sup>2,4,5</sup> that the reaction proceeds via a benzylic cation **14** (Scheme 1). This radical chain reaction, which has been well characterized for other olefinic substrates,<sup>11</sup> is initiated by attack of nitrogen dioxide to give the benzylic radical **15**, which on oxidation with tetranitromethane would yield the benzylic cation **14**, trinitromethanide ion and nitrogen dioxide. Ionic bond formation between the benzylic cation **14** and trinitromethanide ion would then yield the nitro-trinitromethyl adducts **1**. Analogous reactions of **2b** would give **6** and



Scheme 1.

**7**. The mechanism is further discussed in an accompanying paper.<sup>12</sup>

*Base-induced eliminations of the nitro-trinitromethyl adducts 1, 6, 7 and 12.* The marked difference in the reactivity of the nitro-trinitromethyl adduct **1** and adducts **6** and **7** on reaction with 3,5-lutidine is a clear indication that the elimination reaction proceeds via the *E2* mechanism, access to the hydrogen atom involved in the elimination process being more hindered in the cases of **6** and **7**. With a less hindered base, (<sup>2</sup>H<sub>5</sub>)pyridine, the elimination of nitroform from **6** proceeds efficiently to give the (*E*)-nitroalkene **3**. Unfortunately the structure of the product of reaction of **7** with pyridine remains unknown, but it is clear from the kinetic study that trinitromethanide ion is liberated in the reaction. Although the (*Z*)-nitroalkene **11** was not detected in the course of the base-catalysed elimination reaction of **7**, it seems possible that compound **11** underwent subsequent rapid reaction with the excess pyridine present.

## Experimental

Infrared spectra were recorded on a Perkin Elmer 298 spectrophotometer, and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra on a Bruker 400 spectrometer. Mass spectrometry was performed on a JEOL JMS SX-102 instrument. Tetranitromethane, 4-methoxystyrene, *trans*-1-(4'-methoxyphenyl)-1-propene and 4-methoxycinnamionitrile were purchased from Aldrich.

**WARNING.** Mixtures of tetranitromethane with hydrocarbons are detonative within certain concentration limits.<sup>13</sup>

*General procedure for the photonitration of the 4-methoxystyrene (2a) with tetranitromethane.* A solution of **2a** (500 mg, 0.47 mol dm<sup>-3</sup>) and tetranitromethane (0.94 mol dm<sup>-3</sup>) in dichloromethane or acetonitrile was irradiated with filtered light ( $\lambda_{\text{cutoff}}$  435 nm). After the reaction mixture changed colour from red to yellow the volatile material was removed under reduced pressure at  $\leq 0^\circ\text{C}$ , and the product composition of each sample determined by NMR spectral analysis.

*Photochemistry of 4-methoxystyrene (2a) in dichloromethane and the identification of 2-(4'-methoxyphenyl)-1-nitro-2-trinitromethylethane (1).* Reaction of **2a**-tetranitromethane in dichloromethane, as above, for 30 min resulted in complete conversion into essentially pure 2-(4'-methoxyphenyl)-1-nitro-2-trinitromethylethane (**1**). This material was unstable, either on column chromatography on silica gel or on a silica gel Chromatotron plate (see below), and was characterized after the removal of all more volatile substances under reduced pressure at  $\leq 0^\circ\text{C}$ . 2-(4'-Methoxyphenyl)-1-nitro-2-trinitromethylethane (**1**), an oil in pure form (Found:  $M^+$  330.0442.  $\text{C}_{10}\text{H}_{10}\text{N}_4\text{O}_9$  requires 330.0448).  $\nu_{\text{max}}$  (liquid film) 1605, 1595, 1567, 1560 cm<sup>-1</sup>.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.26 (d,  $J_{\text{H,H}}$  8.8 Hz, H2', H6'), 6.92 (d,  $J_{\text{H,H}}$  8.8 Hz, H3', H5'), 5.34 (dd,  $J_{\text{H}_2,\text{H}_{1A}}$  9.6 Hz,  $J_{\text{H}_2,\text{H}_{1B}}$  2.9 Hz, H2), 5.14 (dd,  $J_{\text{H}_{1A},\text{H}_{1B}}$  14.1 Hz,  $J_{\text{H}_{1A},\text{H}_2}$  9.6 Hz, H1A), 5.05 (dd,  $J_{\text{H}_{1B},\text{H}_{1A}}$  14.1 Hz,  $J_{\text{H}_{1B},\text{H}_2}$  2.9 Hz, H1B), 3.82 (s, OMe).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  161.9 (C4'), 131.4 (C2', C6'), 119.5 (C1'), 115.8 (C3', C5'), 76.1 (C1), 55.8 (OMe), 47.9 (C2). The above assignments were confirmed by double irradiation and heteronuclear correlation (HETCOR) spectra.

*Photochemistry of 4-methoxystyrene (2a) in acetonitrile.* Reaction of **2a**-tetranitromethane in acetonitrile, as above, for 15 min resulted in complete conversion into a mixture of 2-(4'-methoxyphenyl)-1-nitro-2-trinitromethylethane (**1**) (66%) and a complex mixture (34%) exhibiting  $^1\text{H}$  NMR resonances in the regions  $\delta$  4.62–4.65 and 3.75–3.85. Because of the instability of the major component (**1**) of the mixture to chromatography it was not possible to examine the complex mixture further.

*Chromatography of 2-(4'-methoxyphenyl)-1-nitro-2-trinitromethylethane (1) on silica gel.* The nitro-trinitromethyl compound (**1**) (125 mg) in dichloromethane

(1 ml) was adsorbed onto a silica (20 g) chromatographic column and allowed to stand for 2 h. Elution with dichloromethane afforded a yellow solid (67 mg) on evaporation of the solvent, which was identified as (*E*)-4'-methoxy-2-nitrostyrene (**3**), m.p. 87–87.5  $^\circ\text{C}$  (lit.<sup>7</sup> m.p. 86–87  $^\circ\text{C}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.00 (d,  $J_{\text{H}_2,\text{H}_1}$  13.6 Hz, H2), 7.54 (d,  $J_{\text{H}_1,\text{H}_2}$  13.6 Hz, H1), 7.52 (d,  $J_{\text{H,H}}$  8.9 Hz, H2', H6'), 6.97 (d,  $J_{\text{H,H}}$  8.9 Hz, H3', H5'), 3.89 (s, OMe).

*Reaction of 2-(4'-methoxyphenyl)-1-nitro-2-trinitromethylethane (1) with 2,6-lutidine in ( $^2\text{H}$ )chloroform.* A solution of **1** (50 mg) and 2,6-lutidine (50 mg) in ( $^2\text{H}$ )chloroform (0.7 ml) after 3 min gave a  $^1\text{H}$  NMR spectrum which revealed that **1** had been converted essentially quantitatively into the nitroalkene **3**.

*General procedure for the photonitration of the trans-1-(4'-methoxyphenyl)-1-propene (2b) with tetranitromethane.* A solution of **2b** (500 mg, 0.42 mol dm<sup>-3</sup>) and tetranitromethane (0.84 mol dm<sup>-3</sup>) in dichloromethane or acetonitrile was irradiated with filtered light ( $\lambda_{\text{cut-off}}$  435 nm). After the reaction mixture changed colour from red to yellow the volatile material was removed under reduced pressure at  $\leq 0^\circ\text{C}$ , and the product composition of each sample determined by NMR spectral analysis.

*Photochemistry of trans-1-(4'-methoxyphenyl)-1-propene (2b) in dichloromethane and the identification of the stereoisomeric 1-(4'-methoxyphenyl)-2-nitro-1-trinitromethylpropanes 6 and 7.* Reaction of **2b**-tetranitromethane in dichloromethane, as above, for 10 min resulted in complete conversion into a mixture of the stereoisomeric 1-(4'-methoxyphenyl)-2-nitro-1-trinitromethylpropanes (**6**) (29%) and (**7**) (71%). Chromatography of this mixture on a silica gel Chromatotron plate gave in elution order:

(1RS,2SR)-1-(4'-methoxyphenyl)-2-nitro-1-trinitromethylpropane (**6**), m.p. 81–82  $^\circ\text{C}$  (Found:  $M^+$  344.0601.  $\text{C}_{11}\text{H}_{12}\text{N}_4\text{O}_9$  requires 344.0605).  $\nu_{\text{max}}$  (KBr) 1600, 1590, 1560, 1552 cm<sup>-1</sup>.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.19 (d,  $J_{\text{H,H}}$  8.9 Hz, H2', H6'), 6.89 (d,  $J_{\text{H,H}}$  8.9 Hz, H3', H5'), 5.45 (dq,  $J_{\text{H}_2,\text{H}_1}$  9.6 Hz,  $J_{\text{H}_2,\text{Me}}$  6.8 Hz, H2), 5.13 (d,  $J_{\text{H}_1,\text{H}_2}$  9.6 Hz, H1), 3.81 (s, OMe), 1.725 (d,  $J_{\text{Me},\text{H}_2}$  6.8 Hz, Me).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  161.7 (C4'), 131.5 (C2', C6'), 120.5 (C1'), 115.6 (C3', C5'), 86.5 (C2), 55.8 (OMe), 52.3 (C1), 18.4 (Me). The above assignments were confirmed by double irradiation and heteronuclear correlation (HETCOR) experiments.

(1RS,2RS)-1-(4'-methoxyphenyl)-2-nitro-1-trinitromethylpropane (**7**), m.p. 61–62  $^\circ\text{C}$  (Found:  $M^+$  344.0605.  $\text{C}_{11}\text{H}_{12}\text{N}_4\text{O}_9$  requires 344.0605).  $\nu_{\text{max}}$  (KBr) 1610, 1595, 1585, 1555 cm<sup>-1</sup>.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.31 (d,  $J_{\text{H,H}}$  8.9 Hz, H2', H6'), 6.94 (d,  $J_{\text{H,H}}$  8.9 Hz, H3', H5'), 5.31 (dq,  $J_{\text{H}_2,\text{H}_1}$  5.5 Hz,  $J_{\text{H}_2,\text{Me}}$  6.8 Hz, H2), 5.37 (d,  $J_{\text{H}_1,\text{H}_2}$  5.5 Hz, H1), 3.84 (s, OMe), 1.43 (d,  $J_{\text{Me},\text{H}_2}$  6.8 Hz, Me).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  161.5 (C4'), 132.2 (C2', C6'), 120.3 (C1'), 115.6 (C3', C5'), 82.9 (C2), 55.8 (OMe), 52.9 (C1), 19.75 (Me). The above assignments were confirmed by

double irradiation and heteronuclear correlation (HETCOR) experiments.

*Photochemistry of trans-1-(4'-methoxyphenyl)-1-propene (2b) in acetonitrile.* Reaction of **2b**-tetranitromethane in acetonitrile, as above, for 10 min resulted in complete conversion into a mixture of the stereoisomeric 1-(4'-methoxyphenyl)-2-nitro-1-trinitromethylpropanes **6** (6%) and **7** (64%) and a complex mixture (30%) exhibiting <sup>1</sup>H NMR resonances in the region δ 4.02–5.10 and 3.75–3.85.

*Attempted reaction of (1RS,2SR)-1-(4'-methoxyphenyl)-2-nitro-1-trinitromethylpropane (6) with 2,6-lutidine in (<sup>2</sup>H)chloroform.* A solution of **6** (23 mg) and 2,6-lutidine (19 mg) in (<sup>2</sup>H)chloroform (0.7 ml) was stored at 22 °C, and its <sup>1</sup>H NMR spectrum was monitored for 24 h. During this period no reaction of **6** was detected.

*Attempted reaction of (1RS,2RS)-1-(4'-methoxyphenyl)-2-nitro-1-trinitromethylpropane (7), with 2,6-lutidine in (<sup>2</sup>H)chloroform.* A solution of **7** (40 mg) and 2,6-lutidine (26 mg) in (<sup>2</sup>H)chloroform (0.7 ml) was stored at 22 °C, and its <sup>1</sup>H NMR spectrum was monitored for 24 h. During this period no reaction of **7** was detected.

*Reaction of (1RS,2SR)-1-(4'-methoxyphenyl)-2-nitro-1-trinitromethylpropane (6), with (<sup>2</sup>H<sub>5</sub>)-pyridine in (<sup>2</sup>H)chloroform.* A solution of **6** (40 mg) and (<sup>2</sup>H<sub>5</sub>)pyridine (40 mg) in (<sup>2</sup>H)chloroform (0.7 ml) was stored at 22 °C, and its <sup>1</sup>H NMR spectrum was monitored until the complete disappearance (after 4.25 h) of **6**. The exclusive product of this reaction was (*E*)-1-(4'-methoxyphenyl)-2-nitro-1-propene (**8**), <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.03 (br s, H1), 7.38 (d, *J*<sub>H,H</sub> 8.8 Hz, H2', H6'), 6.94 (d, *J*<sub>H,H</sub> 8.8 Hz, H3', H5'), 3.82 (s, OMe), 2.43 (d, *J*<sub>Me,H</sub> 0.9 Hz, Me). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 161.5 (C4'), 146.1 (C2), 134.0 (C1), 132.5 (C2', C6'), 125.1 (C1'), 114.9 (C3', C5'), 55.8 (OMe), 14.5 (Me). The above assignments were confirmed by heteronuclear correlation (HETCOR) experiments.

*Reaction of (1RS,2RS)-1-(4'-methoxyphenyl)-2-nitro-1-trinitromethylpropane (7) with (<sup>2</sup>H<sub>5</sub>)pyridine in (<sup>2</sup>H)chloroform.* A solution of **7** (22 mg) and (<sup>2</sup>H<sub>5</sub>)pyridine (40 mg) in [<sup>2</sup>H]chloroform (0.7 ml) was stored at 22 °C, and its <sup>1</sup>H NMR spectrum was monitored until the complete disappearance (after 2.5 h) of **7**. No nitroalkene (**11**) was detected during the course of the reaction, but the product was characterized by <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.34 (d, *J*<sub>H,H</sub> 9.0 Hz, H2', H6'), 6.93 d, *J*<sub>H,H</sub> 8.8 Hz, H3', H5'), 3.80 (s, OMe), 2.39 (s, Me). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 150.3 (C4'), 130.9 (C2', C6'), 114.9 (C3', C5'), 16.8 (Me); signals could not be assigned to C1', C1 and C2.

*Photochemistry of a mixture (1.6:1) of cis- and trans-4-methoxycinnamonnitrile (2d) with tetranitromethane in*

*dichloromethane at 15 °C.* A solution of **2d** (500 mg, 0.39 mol dm<sup>-3</sup>) and tetranitromethane (0.78 mol dm<sup>-3</sup>) in dichloromethane at 15 °C was irradiated with filtered light (λ<sub>cut-off</sub> 435 nm) for 6 h. The volatile material was removed under reduced pressure at ≤0 °C to give a residue shown (<sup>1</sup>H NMR spectra) to be exclusively a mixture (1:1.7) of *cis*- and *trans*-4-methoxycinnamonnitrile **2d**.

*Kinetics of the elimination reactions of nitro-trinitromethyl adducts 1, 6, 7 and 12.* The kinetics of elimination from each of nitro-trinitromethyl adducts **1**, **6**, **7** and **12** was monitored at 350 nm, the maximum of the emerging trinitromethanide ion, by UV spectroscopy (HP-8452 diode array spectrometer) at 23 °C. The appropriate amount of 3,5-lutidine was added to a 1 cm cell containing a dichloromethane solution of the nitro-trinitromethyl adduct (ca. 0.1 mmol dm<sup>-3</sup>) and 50–200 absorbance vs. time points were collected, using the Hewlett-Packard 89532K UV-Visible Kinetics Software package. The rate constants were calculated by the Sigmaplot® program.

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