

# Photochemical Nitration by Tetranitromethane. Part XLIII.† Photolysis of Some Styrene Derivatives with Tetranitromethane: Mechanism of Isoxazolidine Formation

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The photochemical reaction of tetranitromethane in dichloromethane or acetonitrile with 4-methylstyrene (**2a**), styrene (**2b**), 4-chlorostyrene (**2c**), 3-chlorostyrene (**2d**) or 4-acetoxystyrene (**2e**) gives two stereoisomeric isoxazolidines, 2-(2'-nitro-1'-X-phenyl)ethoxy-3,3-dinitro-5-(X-phenyl)isoxazolidine (**3** and **4**, X = 4-Me, H, 4-Cl, 3-Cl or 4-AcO), a nitro ketone, nitromethyl X-phenyl ketone (**5**, X = 4-Me, H, 4-Cl, 3-Cl or 4-AcO) and a nitronic ester, 3-nitro-5-(X-phenyl)-2-isoxazoline N-oxide (**6**, X = 4-Me, H, 4-Cl or 4-AcO). In each case, the (*RS,RS*)-stereoisomer **4** is the major isoxazolidine formed.

The first step of the reaction is the photogeneration of the triad [**2**<sup>+</sup> NO<sub>2</sub> (NO<sub>2</sub>)<sub>3</sub>C<sup>-</sup>]. In the formation of isoxazolidines **3** and **4**, and of the nitronic esters **6**, the key intermediate is assumed to be the substituted aminoxy, 3,3-dinitro-4-(X-phenyl)isoxazolidin-N-oxyl (**8**, X = 4-Me, H, 4-Cl, 3-Cl or 4-AcO) formed by reaction of the substituted styrene radical cation (**2**<sup>+</sup>) with trinitromethanide ion followed by cyclization of the resulting carbon radical **7**. Loss of nitrogen dioxide from **8** gives nitronic esters **6**, and trapping of the 1-(X-phenyl)-2-nitroethyl radical, formed by addition of NO<sub>2</sub> at the β-carbon of **2**, by aminoxy **8**, gives the isoxazolidines **3** and **4** directly.

Isoxazolidines (**1**) have been reported as products of the long-term (up to 5 days) reactions of 4-methylstyrene (**2a**),<sup>2</sup> styrene (**2b**),<sup>3</sup> 4-chlorostyrene (**2c**)<sup>2</sup> and 3-chlorostyrene (**2d**)<sup>2</sup> with tetranitromethane in diethyl ether at ca. 20 °C under undefined conditions of illumination. Subsequently Mathew *et al.*<sup>4</sup> reported the single-crystal X-ray structure of an isoxazolidine (**3a**), m.p. 114 °C, obtained in 5% yield from 4-methylstyrene (**2a**)-tetranitromethane on irradiation of the charge transfer band in acetonitrile solution. The isoxazolidine obtained earlier by Ratsino *et al.*<sup>2</sup> from 4-methylstyrene (**2b**) had a reported m.p. 122 °C and was isolated in 62% yield, but unfortunately no NMR data were given to allow comparison with the material isolated by Mathew *et al.*<sup>4</sup> In contrast, apparently identical isoxazolidine products were isolated by Altukhov *et al.*<sup>3</sup> (m.p. 104–105 °C) and Mathew *et al.*<sup>4</sup> (m.p. 104 °C) from reactions of styrene and tetranitromethane under their respective reaction conditions (see above).

† Part XLII, See Ref. 1.

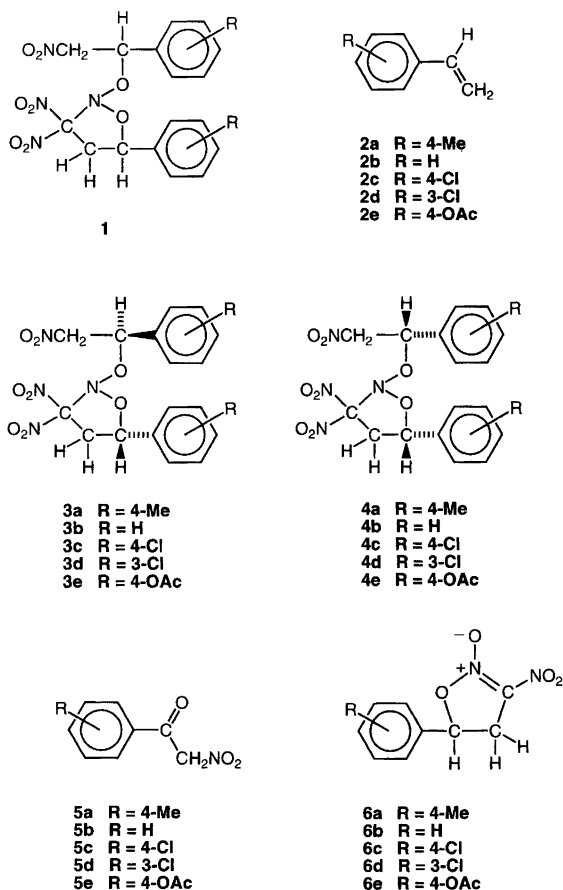
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The reported<sup>2–4</sup> reactions of styrene derivatives with tetranitromethane suffer from some deficiencies. First, the reactions conducted in diethyl ether<sup>2,3</sup> were carried out under uncertain conditions of illumination. Second, in all studies<sup>2–4</sup> the focus was almost exclusively on the apparent major product of reaction, only passing reference<sup>4</sup> being made to a second product. Finally, the clearly photochemical reactions of 4-methylstyrene (**2a**) and styrene (**2b**) with tetranitromethane were conducted only in acetonitrile, a solvent notable for inducing secondary reactions of initially formed products.<sup>5</sup> We now report the results of photochemical reactions of styrene derivatives (**2a–2e**) with tetranitromethane in both dichloromethane and acetonitrile. In the event, the isoxazolidine (**3a**) reported earlier<sup>4</sup> as the major product from the photochemical reaction of 4-methylstyrene (**2a**) with tetranitromethane in acetonitrile was found to be the minor isoxazolidine formed in reactions in both dichloromethane and acetonitrile.

## Results

**General.** The photochemical experiments were performed with filtered light (cut-off at 435 nm, 5 cm water IR filter, with a 300 W incandescent lamp) as described before.<sup>6</sup> The temperature of the solution was kept at 15 °C. The work-up procedure, involving evaporation of solvent and excess tetranitromethane, was conducted at a temperature of  $\leq 0$  °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-methylstyrene (2a) with tetranitromethane in dichloromethane.** A solution of **2a** and tetranitromethane in dichloromethane was irradiated, and its composition monitored with time. After 1.5 h **2a** was converted into a mixture of isoxazolidines **3a** (18.3%) and **4a** (45.5%), nitro ketone **5a** (14.2%), minor adduct **6a** (10.9%) and unidentified adducts (total 11.0%). Crystallization of this mixture from dichloromethane-methanol gave the pure nitro ketone **5a**, which was identified from a consideration of its NMR spectra

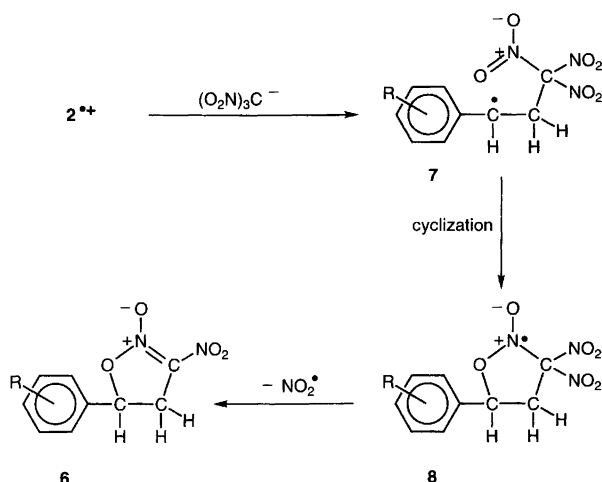


(Experimental section). A second crop of crystals was a mixture of isoxazolidines **3a** (53.5%) and **4a** (17.8%), nitro ketone **5a** (18.7%), minor adduct **6a** (9.7%), which on chromatography on a Chromatotron silica gel plate followed by further crystallization yielded isoxazolidine

**3a**, m.p. 128–129 °C (lit. m.p. 122 °C,<sup>3</sup> m.p. 114 °C<sup>4</sup>). The NMR data for isoxazolidine **3a** (Experimental section) were essentially identical with those reported by Mathew *et al.*<sup>4</sup> for the material for which a single-crystal X-ray structure analysis was given. In terms of the NMR data for isoxazolidine **3a** we were able to resolve the 2H-multiplet at  $\delta$  5.74 reported by Mathew *et al.*<sup>4</sup> for the two protons, CH-CH<sup>a</sup>H<sup>b</sup>NO<sub>2</sub> and CH-CH<sup>c</sup>H<sup>d</sup>C(NO<sub>2</sub>)<sub>3</sub> into separate signals at  $\delta$  5.81 (dd,  $J_{H,H^a}$  7.6 Hz,  $J_{H,H^b}$  5.7 Hz) and  $\delta$  5.79 [dd,  $J_{H,H^c}$  8.1 Hz,  $J_{H,H^d}$  7.3 Hz] respectively; consequently, from heteronuclear correlation (HETCOR) spectra the following assignments were made:  $-\delta$  84.4 [CH-CH<sub>2</sub>C(NO<sub>2</sub>)<sub>3</sub>], and  $\delta$  81.7 (CH-CH<sub>2</sub>NO<sub>2</sub>), which are interchanged from what appear to be arbitrary assignments earlier.<sup>4</sup>

Although the minor adduct could not be isolated from any of the mixtures in which it was present, it was identified tentatively as the nitronic ester **6a** on the basis of its NMR data. In particular, the <sup>13</sup>C NMR resonances for C1 ( $\delta$  84.3) and C2 ( $\delta$  39.4) pointed to the attachment respectively of an oxygen atom and a carbon atom at these positions; for comparison the <sup>13</sup>C NMR resonance for [-O-CH-CH<sub>2</sub>C(NO<sub>2</sub>)<sub>3</sub>] was  $\delta$  84.3 for isoxazolidine **3a** and  $\delta$  84.6 for isoxazolidine **4a**. As there was no evidence suggesting the presence of a second molecular unit derived from 4-methylstyrene (**2a**), the nitronic ester structure **6a** was assigned to this minor adduct. Such nitronic esters are envisaged as being formed as shown in Scheme 1. Reaction of trinitromethanide ion at the  $\beta$ -carbon of the substituted styrene radical cation (**3<sup>+</sup>**) would give the carbon radical **7**. Subsequent carbon-oxygen bond formation in radical **7** would yield the substituted cyclic aminoxyl **8**, a species which while relatively stable, could lose nitrogen dioxide, leading to the formation of nitronic esters **6** (Scheme 1).

The residue, after the removal of much of isoxazolidine **3a** and nitro ketone **5a**, consisted mainly of the isoxazolidine **4a**. This material could not be separated from its impurities either by crystallization or chromatography,



Scheme 1.

but isoxazolidine **4a** was characterized from the NMR spectra of this impure material. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra for isoxazolidine **4a** were closely similar to those of its stereoisomer **3a**. The  $^1\text{H}$  NMR chemical shifts for the two protons,  $\text{CH}-\text{CH}^a\text{H}^b\text{NO}_2$  and  $\text{CH}-\text{CH}^c\text{H}^d\text{C}(\text{NO}_2)_3$ , were marginally different (Experimental section), but the significant distinguishing feature between the two  $^1\text{H}$  NMR spectra lay in the different chemical shifts, and to a lesser extent the coupling constants for  $\text{H}^a$  and  $\text{H}^b$  in the respective  $\text{CH}-\text{CH}^a\text{H}^b\text{NO}_2$  functions. For the minor isoxazolidine **3a** the chemical shifts are:  $\text{H}^a$   $\delta$  5.12 ( $J_{\text{H}^a,\text{H}}$  7.6 Hz,  $J_{\text{H}^a,\text{H}^b}$  13.5 Hz) and  $\text{H}^b$   $\delta$  4.57 ( $J_{\text{H}^b,\text{H}}$  5.7 Hz,  $J_{\text{H}^b,\text{H}^a}$  13.5 Hz) and for the major isoxazolidine **4a** the corresponding data are:  $\text{H}^a$   $\delta$  4.86 ( $J_{\text{H}^a,\text{H}}$  9.7 Hz,  $J_{\text{H}^a,\text{H}^b}$  13.6 Hz) and  $\text{H}^b$   $\delta$  4.61 ( $J_{\text{H}^b,\text{H}}$  4.0 Hz,  $J_{\text{H}^b,\text{H}^a}$  13.5 Hz). This pattern of  $^1\text{H}$  NMR chemical shifts and coupling constants persists throughout the stereoisomeric pairs of isoxazolidines **3** and **4** (Table 1) and, on the apparently reasonable assumption that the single-crystal X-ray analysis<sup>4</sup> was indeed for isoxazolidine **3a**, allows the assignment of relative stereochemistry to all isoxazolidines **3** and **4**.

*Photolysis of 4-methylstyrene (2a) with tetranitromethane in acetonitrile.* A solution of **2a** and tetranitromethane in acetonitrile was irradiated, and its composition monitored with time. After 45 min **2a** was converted into a mixture of isoxazolidines **3a** (16.8%) and **4a** (26.8%), nitro ketone **5a** (30.2%), nitronic ester **6a** (7.8%) and unidentified adducts (total 18.4%). After 5 min the corresponding product yields were **3a** (19.1%), **4a** (46.7%), **5a** (15.6%), **6a** (9.5%) and unidentified adducts (total 9.0%). These data indicate clearly that isoxazolidine **4a**, and to a lesser extent isoxazolidine **3a**, are converted into the nitro ketone **5a** during the photolysis reaction in acetonitrile.

*Photolysis of styrene (2b) with tetranitromethane in dichloromethane.* A solution of **2b** and tetranitromethane in dichloromethane was irradiated, and its composition monitored with time. After 2.45 h **2b** was converted into a mixture of isoxazolidines **3b** (31.2%) and **4b** (49.0%), nitro ketone **5b** (11.9%), nitronic ester **6b** (4.2%) and

unidentified adducts (total 3.5%). Chromatography of this material on a silica gel Chromatotron plate gave first a fraction consisting mainly (ca. 90%) of isoxazolidine **4b**, containing traces of isoxazolidine **3b** and the nitronic ester **6b**. The major component could not be crystallized from this mixture; whereas the minor stereoisomers **3** appear to crystallize, and indeed co-crystallize with other compounds, the major stereoisomers **4** appear most resistant to crystallization. Isoxazolidine **4b** was characterized from its NMR data (Experimental section and Table 1). The assignment of structure to nitronic ester **6b** was again based entirely on a consideration of its NMR spectra (Experimental section).

A later fraction eluted from the Chromatotron plate was also a mixture consisting of isoxazolidines **3b** (55.2%) and **4b** (10.6%), nitro ketone **5b** (24.6%) and nitronic ester **6b** (9.6%). The structures of isoxazolidine **3b** and nitro ketone **5b** were assigned on the basis of the NMR data derived from this mixture (Experimental section). The NMR data for isoxazolidine **3b** were closely similar to those reported earlier,<sup>4</sup> except that again we were able to distinguish the signals for the two protons,  $\text{CH}-\text{CH}^a\text{H}^b\text{NO}_2$  and  $\text{CH}-\text{CH}^c\text{H}^d\text{C}(\text{NO}_2)_3$  into separate signals at  $\delta$  5.86 (dd,  $J_{\text{H},\text{H}^a}$  7.7 Hz,  $J_{\text{H},\text{H}^b}$  5.5 Hz) and  $\delta$  5.82 [dd,  $J_{\text{H},\text{H}^c}$  8.1 Hz,  $J_{\text{H},\text{H}^d}$  7.3 Hz], respectively; consequently, from heteronuclear correlation (HETCOR) spectra the following assignments were made:  $\delta$  84.4 [ $\text{CH}-\text{CH}_2\text{C}(\text{NO}_2)_3$ ], and  $\delta$  81.9 ( $\text{CH}-\text{CH}_2\text{NO}_2$ ), which are interchanged from what appear to be the earlier arbitrary assignments.<sup>4</sup>

*Photolysis of 4-methylstyrene (2b) with tetranitromethane in acetonitrile.* A solution of **2b** and tetranitromethane in acetonitrile was irradiated, and its composition monitored with time. After 2.45 h **2b** was converted into a mixture a mixture of isoxazolidines **3b** (25.0%) and **4b** (34.2%), nitro ketone **5b** (32.0%) and nitronic ester **6b** (8.7%). After 30 min the corresponding product yields were **3b** (33.6%), **4b** (39.4%), **5b** (16.6%) and **6b** (10.4%). As for the analogous reaction of 4-methylstyrene (**2a**), these data indicate that isoxazolidines **3b** and **4b** are

Table 1.  $^1\text{H}$  NMR data for the  $\text{CH}_2\text{NO}_2$  group in isoxazolidines **3** and **4**.

Compound	Chemical shifts $\delta$ /ppm, and coupling constants/Hz				$\Delta\delta$ /Hz
	$\text{H}_a$		$\text{H}_b$		
<b>3a</b>	5.12	7.6, 13.5	4.57	5.7, 13.5	0.55
<b>3b</b>	5.12	7.7, 13.6	4.59	5.5, 13.6	0.53
<b>3c</b>	5.10	7.8, 13.7	4.56	5.5, 13.7	0.54
<b>3d</b>	5.05	8.0, 13.8	4.57	5.1, 13.8	0.48
<b>3e</b>	5.06	7.8, 13.8	4.55	5.3, 13.8	0.51
<b>4a</b>	4.86	9.7, 13.6	4.61	4.0, 13.6	0.25
<b>4b</b>	4.88	9.7, 13.7	4.64	3.8, 13.7	0.24
<b>4c</b>	4.83	9.8, 13.8	4.62	3.8, 13.8	0.21
<b>4d</b>	4.83	9.8, 13.9	4.63	3.7, 13.9	0.20
<b>4e</b>	4.815	9.8, 13.85	4.60	3.7, 13.85	0.215

converted into the nitro ketone **5b** during the photolysis reaction in acetonitrile.

**Photolysis of 4-chlorostyrene (2c) with tetranitromethane in dichloromethane.** A solution of **2c** and tetranitromethane in dichloromethane was irradiated, and its composition monitored with time. After 3 h **2c** was converted into a mixture of isoxazolidines **3c** (17.9%) and **4c** (45.5%), nitro ketone **5c** (26.8%), nitronic ester **6c** (7.8%) and unidentified adducts (total 2.0%). After 30 min the corresponding product yields were **3c** (27.4%), **4c** (50.8%), **5c** (14.4%) and **6c** (7.4%). Chromatography of the final product on a silica gel Chromatotron plate gave first a fraction consisting essentially of isoxazolidine **4c** containing small amounts of isoxazolidine **3c** and nitronic ester **6c**. The second fraction consisted mainly of isoxazolidine **3c** containing small amounts of isoxazolidine **4c** and nitronic ester **6c**. The NMR data for these isoxazolidines **3c** and **4c** (Experimental section) were determined from these mixtures, and were consistent with the emerging pattern for isoxazolidines **3** and **4**. Finally, a small sample of impure nitro ketone **5c** was eluted from the Chromatotron plate.

**Photolysis of 4-chlorostyrene (2c) with tetranitromethane in acetonitrile.** A solution of **2c** and tetranitromethane in acetonitrile was irradiated, and its composition monitored with time. After 3 h **2c** was converted into a mixture a mixture of isoxazolidines **3c** (10.6%) and **4c** (27.6%), nitro ketone **5c** (51.7%) and unidentified material (10.1%). After 30 min the product yields were isoxazolidines **3c** (10.6%) and **4c** (34.3%), nitro ketone **5c** (44.5%) and unidentified material (10.6%).

**Photolysis of 3-chlorostyrene (2d) with tetranitromethane in dichloromethane.** A solution of **2d** and tetranitromethane in dichloromethane was irradiated, and its composition monitored with time. After 7 h **2d** was converted into a mixture of isoxazolidines **3d** (12.9%) and **4d** (45.2%), nitro ketone **5d** (22.6%) and unidentified adducts (total 19.3%). Chromatography of the final product on a silica gel Chromatotron plate gave first a fraction containing mainly isoxazolidine **4d** with only minor amounts of isoxazolidine **3d** and unidentified products. The structure of **4d** was established from a consideration of its NMR spectra determined from this mixture (Experimental section).

The second material eluted was a mixture (ca. 3:2) of the nitro ketone **5d** and isoxazolidine **3d**. The pure nitro ketone **5d** was separated by crystallization of this mixture and identified from its NMR spectra. The NMR spectra for isoxazolidine **3d** were determined from that of the mixture prior to the crystallization. Again, the NMR spectra of isoxazolidines **3d** and **4d** were consistent with the remaining data for isoxazolidines **3** and **4** (Experimental section and Table 1).

**Photolysis of 3-chlorostyrene (2d) with tetranitromethane in acetonitrile.** A solution of **2d** and tetranitromethane in

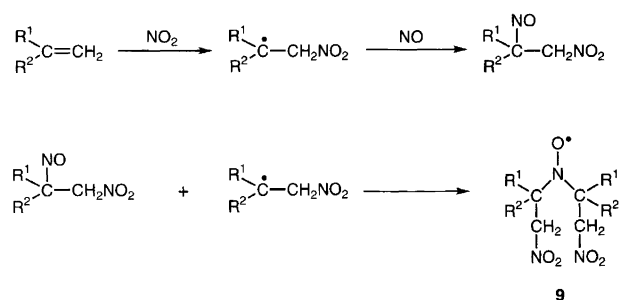
acetonitrile was irradiated, and its composition monitored with time. After 6 h **2d** was converted partially (ca. 80%) into a mixture of isoxazolidines **3d** (8.5%) and **4d** (27.4%), nitro ketone **5d** (47.5%) and unidentified material (16.6%). After 2 h the product yields were isoxazolidines **3d** (10.1%) and **4d** (27.8%), nitro ketone **5d** (46.5%) and unidentified material (15.6%).

**Photolysis of 4-acetoxystyrene (2e) with tetranitromethane in dichloromethane.** A solution of **2e** and tetranitromethane in dichloromethane was irradiated, and its composition monitored with time. After 2 h **2e** was converted into a mixture of isoxazolidines **3e** (27.9%) and **4e** (53.4%), nitro ketone **5e** (5.9%), nitronic ester **6e** (8.4%) and unidentified adducts (total 4.4%). Chromatography of this material on a silica gel Chromatotron plate gave first the pure nitro ketone **5e**, the structure of which was determined from a consideration of its NMR spectra. The second material eluted was a mixture of isoxazolidines **3e** and **4e**, nitronic ester **6e** and a small amount of unidentified adducts. The identities of the three products, **3e**, **4e** and **6e** were determined from their respective NMR spectra in the spectra of this mixture.

In each case, the spectroscopic data paralleled data for the related compounds, above.

**EPR spectral search for aminoxyl intermediate 8.** The aminoxyl radical **8** of Scheme 1 might in principle be persistent enough for EPR spectral detection. Alkyl alkoxy aminoxyls, with the general structure fragment of  $-\text{CH}_2-\text{N}(\text{O}^\bullet)-\text{O}-\text{CH}_2-$ , are known<sup>7</sup> both in acyclic and cyclic form, and are characterized by a large coupling to nitrogen (1.4–2.4 mT) and smaller couplings to hydrogens in the  $\text{CH}_2$  and  $\text{O}-\text{CH}_2$  groups, the former being the larger one. In **8**, the critical structure is  $-\text{C}(\text{NO}_2)_2-\text{N}(\text{O}^\bullet)-\text{O}-\text{CH}(\text{Ar})$  which then should give rise to an EPR spectrum consisting of a triplet (N) of doublets [CH(Ar)], possibly further split by weak coupling to the nitrogens of the nitro groups.

However, the photolysis of **2a–2e** or 4-methoxystyrene<sup>1</sup> with tetranitromethane in dichloromethane (light of  $\lambda > 400$  nm) only gave weak spectra of diastereomeric aminoxyl radicals **9**, known<sup>8</sup> to result from the reaction between a styrene **2**,  $\text{NO}_2$  and  $\text{NO}$  according to Scheme 2. EPR spectral parameters of these radicals are given in Table 2. These are quite different from those expected



Scheme 2.

Table 2. EPR spectra of radicals **9** obtained by irradiation of a solution of  $R^1R^2C=CH_2$  and tetranitromethane in dichloromethane ( $\lambda > 400$  nm).

$R^1$	$R^2$	$a^N/mT$	$a^H/mT^a$
4-MeC <sub>6</sub> H <sub>4</sub> ( <b>2a</b> ) <sup>b</sup>	H	1.52	1.18
		1.44	0.72
C <sub>6</sub> H <sub>5</sub> ( <b>2b</b> ) <sup>c</sup>	H	1.51	1.18
		1.46	0.70
4-ClC <sub>6</sub> H <sub>4</sub> ( <b>2c</b> ) <sup>d</sup>	H	1.49	1.11
		1.47	0.64
3-ClC <sub>6</sub> H <sub>4</sub> ( <b>2d</b> )	H	1.46	1.04
		1.44	0.64
4-AcOC <sub>6</sub> H <sub>4</sub> ( <b>2e</b> )	H	1.49	1.10
		1.44	0.70
4-MeOC <sub>6</sub> H <sub>4</sub>	H	1.49	1.18
		1.46	0.73

<sup>a</sup>Coupling to two hydrogens. <sup>b</sup>Lit.<sup>7</sup> in benzene:  $a^N$  1.50,  $a^H$  1.20;  $a^N$  1.43,  $a^H$  0.70 mT. <sup>c</sup>Lit.<sup>7</sup> in benzene:  $a^N$  1.49,  $a^H$  1.14;  $a^N$  1.45,  $a^H$  0.66 mT. <sup>d</sup>Lit.<sup>7</sup> in benzene:  $a^N$  1.46,  $a^H$  1.15;  $a^N$  1.42,  $a^H$  0.65 mT.

for the EPR spectrum of **8**. In an experiment with styrene (**2b**) it could be shown that the level of **9** changed abruptly with the onset of irradiation (Fig. 1, triangles) and that the concentration of **9** decreased to a lower level when irradiation is discontinued. Thus **9** presumably can be used as a marker for the progress of the main reaction, since it must reflect the concentration of NO<sub>2</sub> in the reaction mixture. The reaction between tetranitromethane and styrene also gave radicals **9** without illumination, although at a lower concentration (Fig. 1, squares).

## Discussion

Isoxazolidines **3** and **4** as products from the photolysis of styrene derivatives **2** with tetranitromethane. In spite of

the relatively broad spread of melting points recorded for the various samples of isoxazolidine **3a** (Refs. 3 and 4, and in the present study), there appears little doubt that these samples are in fact stereoisomer **3a** (a compound which is remarkably more readily crystallizable than the stereoisomer **4a**) and that the single-crystal X-ray analysis reported by Mathew *et al.*<sup>4</sup> is of compound **3a**. If that assumption is made, the <sup>1</sup>H NMR data reported in Table 1 clearly relate the various substituted derivatives of compounds **3**. Further, the <sup>1</sup>H NMR data for the various substituted derivatives of compounds **4** follow a distinct but different pattern.

It is notable that for each substituted styrene substrate (**2**) the major product of photolysis with tetranitromethane is stereoisomer **4** (Tables 3 and 4), and not stereoisomer **3** as claimed by Mathew *et al.*<sup>4</sup> In our hands, the photolysis reactions in dichloromethane solution gave high yields (45–53%) of isoxazolidines **4**, and only for styrene itself (**2b**) did the yield of isoxazolidine **3b** exceed 30% (Table 3).

For photolysis reactions in both dichloromethane and acetonitrile solution some decomposition of the isoxazoli-

Table 3. Overview of relative yields of products from the photolyses of styrenes (**2**) with tetranitromethane in dichloromethane at 15 °C.

Styrene	Product yield (%) of				
	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	Unidentified
<b>2a</b>	18.3	45.5	14.2	10.9	11.0
<b>2b</b>	31.2	49.0	11.9	4.2	3.5
<b>2c</b>	17.9	45.5	26.8	7.8	2.0
<b>2d</b>	12.9	45.2	22.6	—	19.3
<b>2e</b>	27.9	53.4	5.9	8.4	4.4

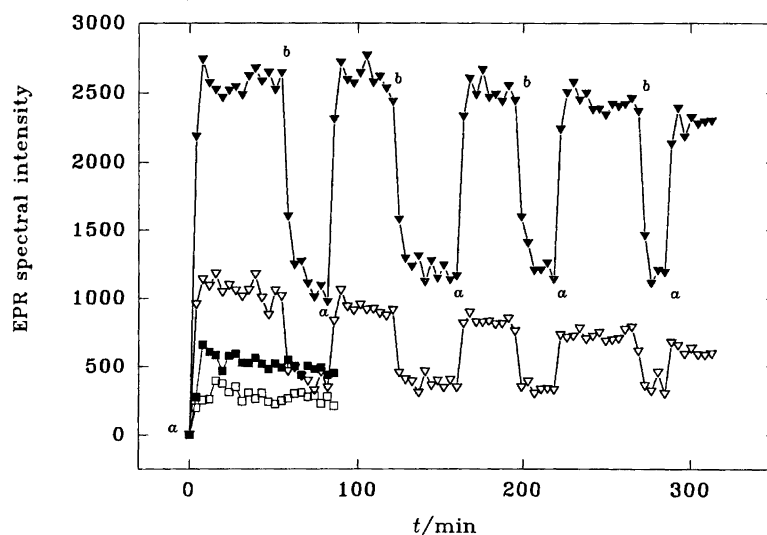


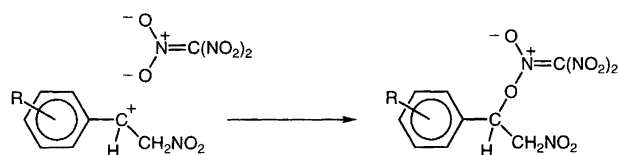
Fig. 1. Intensities of one line of each of the EPR spectra of the diastereomers of **9** (filled triangles correspond to the major isomer, empty triangles to the minor one), during irradiation by light of  $\lambda > 400$  nm (at each *a*) and discontinuation of irradiation (at each *b*) of a solution of styrene (0.50 mol dm<sup>-3</sup>) and tetranitromethane (0.60 mol dm<sup>-3</sup>) in dichloromethane at 26 °C. Filled and empty squares represent the same two EPR spectral lines monitored from a spontaneously reacting solution under the same conditions.

**Table 4.** Overview of relative yields of products from the photolyses of styrenes (**2**) with tetranitromethane in acetonitrile at 15 °C at short and long reaction times.

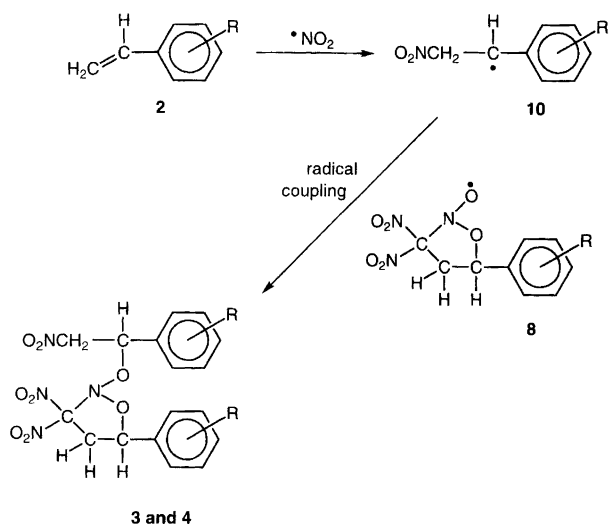
Styrene	Reaction time/min	Product yield (%) of				
		<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	Unidentified
<b>2a</b>	5	19.1	46.7	15.6	9.5	9.0
	45	16.8	26.8	30.2	7.8	18.4
<b>2b</b>	30	33.6	39.4	16.6	10.4	—
	165	25.0	34.2	32.0	8.7	—
<b>2c</b>	30	10.6	34.3	44.5	—	10.6
	180	10.6	27.6	51.7	—	10.1
<b>2d</b>	120	10.1	27.8	46.5	—	15.6
	360	8.5	27.4	47.6	—	16.6

dines **3** and **4** to give the corresponding nitro ketone **5** was evident; this is documented for reactions in acetonitrile in Table 4, where relative yields of products at short and long reaction times are recorded for substituted styrene substrates (**2a–2d**). It is a matter for conjecture as to whether the photochemical decompositions of isoxazolidines **3** and **4** are the exclusive origin of the nitro ketones **5**, but there is no doubt that these reaction pathways are a contributory origin.

The mode of formation of the isoxazolidines **3** and **4** suggested in the literature,<sup>3,4</sup> involving carbon–oxygen bond formation in the attack of the *aci*-form of trinitromethane ion on carbocations (Scheme 3), remains unsupported by any direct experimental evidence. A clear alternative reaction mechanism now emerges which accommodates the established facts in terms for which there is adequate precedent. The substituted aminoxyl **8** is proposed, above, as a relatively stable intermediate in the formation of the minor adducts, the nitronic esters **6**, in the photochemical reactions of substituted styrenes **2** with tetranitromethane (Scheme 1). This substituted aminoxyl **8** will also be capable of acting as a radical trap and on reaction with the carbon radical **10**, formed in the reaction of nitrogen dioxide with the substituted styrene **2**, would lead directly to the observed isoxazolidines **3** and **4** (Scheme 4). Unfortunately, no EPR spectral evidence for the presence of **8** could be obtained under the reaction conditions employed, presumably due to a combination of several factors: radical **8** has at least two facile pathways for disappearance to stable products (Schemes 1 and 4) and any EPR signal from **8** might be obscured by the spectra of aminoxyls **9**. The latter are considered to be unreactive bystanders to the major reaction, but have diagnostic value for indicating the



**Scheme 3.**



**Scheme 4.**

presence of NO<sub>2</sub> and NO (Scheme 2) and the intermediacy of radical **10**, common to Schemes 2 and 4.

## Experimental

Melting points are uncorrected. Infrared spectra were recorded on a Perkin Elmer 298 spectrophotometer; <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker 400 spectrometer. Mass spectrometry was performed on a JEOL JMS SX-102 instrument. Tetranitromethane, styrene, 4-methylstyrene and 4-acetoxystyrene were purchased from Aldrich, and 3-chlorostyrene from Lancaster Chemicals.

**WARNING.** It should be noted that mixtures of tetranitromethane with hydrocarbons are detonative within certain concentration limits.<sup>9</sup>

**EPR spectroscopy.** 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 light from the 50 W high-pressure Hg lamp from Bruker (ER 202). The filter (Schott AG) had λ<sub>cut-off</sub> at 400 nm. The EPR experiments were performed at a 100 kHz modulation frequency, microwave effect 0.4–1.6 mW and modulation amplitude 0.01–0.04 mT.

**General procedure for the photonitration of 4-methylstyrene (2a) with tetranitromethane.** A solution of **2a** (500 mg, 0.53 mol dm<sup>-3</sup>) and tetranitromethane (1.06 mol dm<sup>-3</sup>) in dichloromethane or acetonitrile at 15 °C was irradiated with filtered light (λ<sub>cut-off</sub> 435 nm). After the reaction mixture changed colour from orange to yellow the volatile material was removed under reduced pressure at ≤0 °C, and the relative product composition of each sample determined by NMR spectral analysis.

**Photochemistry of 4-methylstyrene (2a) in dichloromethane.** Reaction of **2a**-tetranitromethane in dichlorometh-

ane, as above, for 1.5 h resulted in complete conversion into a mixture of isoxazolidines **3a** (18.3%) and **4a** (45.5%), nitro ketone **5a** (14.2%), nitronic ester **6a** (10.9%) and unidentified adducts (total 11.0%).

Crystallization of this mixture from dichloromethane-methanol gave first the pure nitro ketone **5a**, m.p. 123–125 °C. (Found:  $M^+$  179.0585.  $C_9H_9NO_3$  requires 179.0583).  $^1H$  NMR ( $CDCl_3$ )  $\delta$  7.79 (d,  $J_{H,H}$  8.3 Hz, H2', H6'), 7.35 (d,  $J_{H,H}$  8.3 Hz, H3', H5'), 5.88 (s,  $CH_2NO_2$ ), 2.47 (Me).  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  190.3 (C=O), 146.9 (C4'), 131.4 (C1'), 130.4 (C3', C5'), 128.8 (C2', C6'), 81.7 ( $CH_2NO_2$ ), 22.3 (Me). These assignments were confirmed by heteronuclear correlation (HETCOR) spectra.

The second crop of crystals was a mixture of isoxazolidine **3a** (53.5%), isoxazolidine **4a** (17.8%), nitro ketone **5a** (18.7%) and an adduct tentatively assigned the nitronic ester structure **6a** (9.7%). Chromatography of this material on a silica gel Chromatotron plate gave a major fraction which, on crystallization from dichloromethane-methanol, yielded isoxazolidine **3a**, m.p. 128–129 °C (lit. m.p. 122 °C,<sup>3</sup> m.p. 114 °C<sup>4</sup>).  $^1H$  NMR ( $CDCl_3$ )  $\delta$  7.21 (s, ArH), 7.18 (d,  $J_{H,H}$  8.1 Hz, ArH), 7.07 (d,  $J_{H,H}$  8.1 Hz, ArH), 5.81 (dd,  $J_{H,H^a}$  7.6 Hz,  $J_{H,H^b}$  5.7 Hz,  $CH-CH^aH^bNO_2$ ), 5.79 [dd,  $J_{H,H^c}$  8.1 Hz,  $J_{H,H^d}$  7.3 Hz,  $CH-CH^cH^dC(NO_2)_3$ ], 5.12 (dd,  $J_{H^a,H}$  7.6 Hz,  $J_{H^a,H^b}$  13.5 Hz,  $CH-CH^aH^bNO_2$ ), 4.57 (dd,  $J_{H^b,H}$  5.7 Hz,  $J_{H^b,H^a}$  13.5 Hz,  $CH-CH^aH^bNO_2$ ), 4.14 [dd,  $J_{H^c,H}$  8.1 Hz,  $J_{H^c,H^d}$  15.6 Hz,  $CH-CH^cH^dC(NO_2)_3$ ], 3.04 [dd,  $J_{H^d,H}$  7.3 Hz,  $J_{H^d,H^c}$  15.6 Hz,  $CH-CH^cH^dC(NO_2)_3$ ], 2.38 (s, Me), 2.37 (s, Me).  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  140.7, 140.5, 131.4, 130.9, 130.3, 130.2, 127.9, 127.2, 84.4 [ $CH-CH_2C(NO_2)_3$ ], 81.7 ( $CH-CH_2NO_2$ ), 77.5 ( $CH_2NO_2$ ), 41.7 [ $CH_2C(NO_2)_3$ ], 21.7 (Me), 21.6 (Me). The above assignments were confirmed by double irradiation and heteronuclear correlation (HETCOR) spectra.

The minor adduct, nitronic ester **6a**, could not be separated from **3a** and **4a**, but its structure was assigned tentatively from its partial NMR spectra in mixtures,  $^1H$  NMR ( $CDCl_3$ )  $\delta$  5.41 (dd,  $J_{H1,H2a}$  9.6 Hz,  $J_{H1,H2b}$  6.9 Hz, H1), 3.76 (dd,  $J_{H2a,H2b}$  14.9 Hz,  $J_{H2a,H1}$  9.6 Hz, H2a), 3.58 (dd,  $J_{H2b,H2a}$  14.9 Hz,  $J_{H2b,H1}$  6.9 Hz, H2b); the remainder of the spectrum was obscured.  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  84.3 (C1), 39.4 (C2); the remainder of the spectrum was obscured. The above assignments were confirmed by double irradiation and heteronuclear correlation (HETCOR) spectra.

The residue, after the removal of much of the isoxazolidine **3a** and nitro ketone **5a**, consisted mainly of the isoxazolidine **4a** which could not be separated from its impurities by chromatography or crystallization, but was assigned the isoxazolidine (**4a**) structure, stereoisomeric with isoxazolidine **3a**, on the basis of its NMR spectra:  $^1H$  NMR ( $CDCl_3$ )  $\delta$  7.23–7.11 (m, ArH), 5.79 (dd,  $J_{H,H^a}$  9.7 Hz,  $J_{H,H^b}$  4.0 Hz,  $CH-CH^aH^bNO_2$ ), 5.77 [dd,  $J_{H,H^c}$  8.2 Hz,  $J_{H,H^d}$  7.3 Hz,  $CH-CH^cH^dC(NO_2)_3$ ], 4.86 (dd,  $J_{H^a,H}$  9.7 Hz,  $J_{H^a,H^b}$  13.6 Hz,  $CH-CH^aH^bNO_2$ ), 4.61 (dd,  $J_{H^b,H}$  4.0 Hz,  $J_{H^b,H^a}$  13.6 Hz,  $CH-CH^aH^bNO_2$ ), 4.175

[dd,  $J_{H^c,H}$  8.2 Hz,  $J_{H^c,H^d}$  15.6 Hz,  $CH-CH^cH^dC(NO_2)_3$ ], 3.04 [dd,  $J_{H^d,H}$  7.3 Hz,  $J_{H^d,H^c}$  15.6 Hz,  $CH-CH^cH^dC(NO_2)_3$ ], 2.37 (s, Me), 2.36 (s, Me).  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  140.6, 130.3, 130.2, 127.6, 127.5, 84.6 [ $CH-CH_2C(NO_2)_3$ ], 81.6 ( $CH-CH_2NO_2$ ), 77.7 ( $CH_2NO_2$ ), 41.5 [ $CH_2C(NO_2)_3$ ], 21.74 (Me), 21.68 (Me). The above assignments were confirmed by double irradiation and heteronuclear correlation (HETCOR) spectra.

#### *Photochemistry of 4-methylstyrene (2a) in acetonitrile.*

Reaction of **2a**-tetranitromethane in acetonitrile, as above, for 45 min resulted in complete conversion into a mixture of isoxazolidines **3a** (16.8%) and **4a** (26.8%), nitro ketone **5a** (30.2%), nitronic ester **6a** (7.8%) and unidentified adducts (total 18.4%). After 5 min the corresponding product yields were **3a** (19.1%), **4a** (46.7%), **5a** (15.6%), **6a** (9.5%) and unidentified adducts (total 9.0%). These data indicate clearly that isoxazolidine **4a**, and to a lesser extent isoxazolidine **3a**, are converted into the nitro ketone **5a** during the photolysis reaction in acetonitrile.

#### *General procedure for the photonitration of styrene (2b) with tetranitromethane.*

A solution of **2b** (500 mg, 0.6 mol  $dm^{-3}$ ) and tetranitromethane (1.2 mol  $dm^{-3}$ ) in dichloromethane or acetonitrile at 15 °C was irradiated with filtered light ( $\lambda_{cut-off}$  435 nm). After the colour of the reaction mixture faded from yellow to nearly colourless the volatile material was removed under reduced pressure at  $\leq 0$  °C, and the product composition of each sample determined by NMR spectral analysis.

#### *Photochemistry of styrene (2b) in dichloromethane.*

Reaction of **2b**-tetranitromethane in dichloromethane, as above, for 2.45 h resulted in complete conversion into a mixture of isoxazolidines **3b** (31.2%) and **4b** (49.0%), nitro ketone **5b** (11.9%), nitronic ester **6b** (4.2%) and unidentified adducts (total 3.5%). Chromatography on a silica gel Chromatotron plate gave first a fraction consisting mainly (ca. 90%) of isoxazolidine **4b** containing traces of isoxazolidine **3b** and the nitronic ester **6b**. Unfortunately the major product could not be induced to crystallize from this mixture and the NMR spectra of compound **4b** reported below are derived from this mixture. Isoxazolidine **4b**:  $^1H$  NMR ( $CDCl_3$ )  $\delta$  7.45–7.41 (m, ArH), 7.28–7.26 (m, ArH), 5.865 (dd,  $J_{H,H^a}$  9.7 Hz,  $J_{H,H^b}$  3.8 Hz,  $CH-CH^aH^bNO_2$ ), 5.835 [dd,  $J_{H,H^c}$  8.25 Hz,  $J_{H,H^d}$  7.2 Hz,  $CH-CH^cH^dC(NO_2)_3$ ], 4.88 (dd,  $J_{H^a,H}$  9.7 Hz,  $J_{H^a,H^b}$  13.7 Hz,  $CH-CH^aH^bNO_2$ ), 4.64 (dd,  $J_{H^b,H}$  3.8 Hz,  $J_{H^b,H^a}$  13.7 Hz,  $CH-CH^aH^bNO_2$ ), 4.21 [dd,  $J_{H^c,H}$  8.25 Hz,  $J_{H^c,H^d}$  15.6 Hz,  $CH-CH^cH^dC(NO_2)_3$ ], 3.06 [dd,  $J_{H^d,H}$  7.2 Hz,  $J_{H^d,H^c}$  15.6 Hz,  $CH-CH^cH^dC(NO_2)_3$ ].  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  134.4, 133.5, 130.5, 130.4, 129.7, 129.6, 127.7, 127.4, 84.6 [ $CH-CH_2C(NO_2)_3$ ], 81.8 ( $CH-CH_2NO_2$ ), 77.7 ( $CH_2NO_2$ ), 41.5 [ $CH_2C(NO_2)_3$ ]. The above assignments were confirmed by double irradiation and heteronuclear correlation (HETCOR) spectra.

The structure of the nitronic ester **6b** was assigned on the basis of the following spectroscopic data:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.45 (dd,  $J_{\text{H1,H2a}}$  9.5 Hz,  $J_{\text{H1,H2b}}$  7.0 Hz, H1), 3.79 (dd,  $J_{\text{H2a,H2b}}$  14.9 Hz,  $J_{\text{H2a,H1}}$  9.5 Hz, H2a), 3.62 (dd,  $J_{\text{H2b,H2a}}$  14.9 Hz,  $J_{\text{H2b,H1}}$  7.0 Hz, H2b); the remainder of the spectrum was obscured.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  84.6 (C1), 39.5 (C2); the remainder of the spectrum was obscured. The above assignments were confirmed by double irradiation and heteronuclear correlation (HETCOR) spectra.

A later fraction eluted from the Chromatotron plate was a mixture of isoxazolidines **3b** (55.2%) and **4b** (10.6%), nitro ketone **5b** (24.6%) and nitronic ester **6b** (9.6%). Based on the NMR spectra of this mixture, isoxazolidine **3b** had:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.86 (dd,  $J_{\text{H,H}^a}$  7.7 Hz,  $J_{\text{H,H}^b}$  5.5 Hz,  $\text{CH}-\text{CH}^a\text{H}^b\text{NO}_2$ ), 5.82 [dd,  $J_{\text{H,H}^c}$  8.1 Hz,  $J_{\text{H,H}^d}$  7.3 Hz,  $\text{CH}-\text{CH}^c\text{H}^d\text{C}(\text{NO}_2)_3$ ], 5.12 (dd,  $J_{\text{H}^a,\text{H}}$  7.7 Hz,  $J_{\text{H}^a,\text{H}^b}$  13.6 Hz,  $\text{CH}-\text{CH}^a\text{H}^b\text{NO}_2$ ), 4.59 (dd,  $J_{\text{H}^b,\text{H}}$  5.5 Hz,  $J_{\text{H}^b,\text{H}^a}$  13.6 Hz,  $\text{CH}-\text{CH}^a\text{H}^b\text{NO}_2$ ), 4.18 [dd,  $J_{\text{H}^c,\text{H}}$  8.1 Hz,  $J_{\text{H}^c,\text{H}^d}$  15.6 Hz,  $\text{CH}-\text{CH}^c\text{H}^d\text{C}(\text{NO}_2)_3$ ], 3.06 [dd,  $J_{\text{H}^d,\text{H}}$  7.3 Hz,  $J_{\text{H}^d,\text{H}^c}$  15.6 Hz,  $\text{CH}-\text{CH}^c\text{H}^d\text{C}(\text{NO}_2)_3$ ].  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  84.4 [ $\text{CH}-\text{CH}_2\text{C}(\text{NO}_2)_3$ ], 81.9 ( $\text{CH}-\text{CH}_2\text{NO}_2$ ), 77.7 ( $\text{CH}_2\text{NO}_2$ ), 41.7 [ $\text{CH}_2\text{C}(\text{NO}_2)_3$ ]. The above assignments were confirmed by double irradiation and heteronuclear correlation (HETCOR) spectra.

Correspondingly, the nitro ketone **6b** had data:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.90 (dd,  $J_{\text{H,H}}$  8.4 Hz,  $J_{\text{H,H}}$  1.2 Hz, H2', H6'), 7.71 (dd,  $J_{\text{H,H}} = J_{\text{H,H}} \approx 7.5$  Hz, H4'), 7.56 (dd,  $J_{\text{H,H}} = J_{\text{H,H}} \approx 7.5$  Hz, H3', H5'), 5.90 (s,  $\text{CH}_2\text{NO}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  186.2 (C=O), 81.8 ( $\text{CH}_2\text{NO}_2$ ). These assignments were confirmed by heteronuclear correlation (HETCOR) spectra.

**Photochemistry of styrene (2b) in acetonitrile.** Reaction of **2b**-tetranitromethane in acetonitrile, as above, for 2.45 h resulted in complete conversion into a mixture of isoxazolidines **3b** (25.0%) and **4b** (34.2%), nitro ketone **5b** (32.0%) and nitronic ester **6b** (8.7%). After 30 min the corresponding product yields were **3b** (33.6%), **4b** (39.4%), **5b** (16.6%) and **6b** (10.4%). These data indicate clearly that isoxazolidines **3b** and **4b** are converted into the nitro ketone **5b** during the photolysis reaction in acetonitrile.

**General procedure for the photolysis of 4-chlorostyrene (2c) with tetranitromethane.** A solution of **2c** (500 mg,  $0.45 \text{ mol dm}^{-3}$ ) and tetranitromethane ( $0.9 \text{ mol dm}^{-3}$ ) in dichloromethane or acetonitrile was irradiated with filtered light ( $\lambda_{\text{cut-off}}$  435 nm). After the colour of the reaction mixture faded from yellow to nearly colourless 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-chlorostyrene (2c) in dichloromethane.** Reaction of **2c**-tetranitromethane in dichloromethane, as above, for 3 h resulted in complete conversion

into a mixture of isoxazolidines **3c** (17.9%) and **4c** (45.5%), nitro ketone **5c** (26.8%), nitronic ester **6c** (7.8%) and unidentified adducts (total 2.0%). After 30 min the corresponding product yields were **3c** (27.4%), **4c** (50.8%), **5c** (14.4%) and **6c** (7.4%).

Chromatography of the final product on a silica gel Chromatotron plate gave a first fraction consisting essentially of isoxazolidine **4c** containing small amounts of isoxazolidine **3c** and nitronic ester **6c**. The NMR spectra of isoxazolidine **4c** were:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.43–7.39 (m, ArH), 7.22–7.19 (m, ArH), 5.84 (dd,  $J_{\text{H,H}^a}$  9.8 Hz,  $J_{\text{H,H}^b}$  3.8 Hz,  $\text{CH}-\text{H}^a\text{H}^b\text{NO}_2$ ), 5.79 [dd,  $J_{\text{H,H}^c}$  8.2 Hz,  $J_{\text{H,H}^d}$  7.2 Hz,  $\text{CH}-\text{CH}^c\text{H}^d\text{C}(\text{NO}_2)_3$ ], 4.83 (dd,  $J_{\text{H}^a,\text{H}}$  9.8 Hz,  $J_{\text{H}^a,\text{H}^b}$  13.8 Hz,  $\text{CH}-\text{CH}^a\text{H}^b\text{NO}_2$ ), 4.62 (dd,  $J_{\text{H}^b,\text{H}}$  3.8 Hz,  $J_{\text{H}^b,\text{H}^a}$  13.8 Hz,  $\text{CH}-\text{CH}^a\text{H}^b\text{NO}_2$ ), 4.19 [dd,  $J_{\text{H}^c,\text{H}}$  8.2 Hz,  $J_{\text{H}^c,\text{H}^d}$  15.6 Hz,  $\text{CH}-\text{CH}^c\text{H}^d\text{C}(\text{NO}_2)_3$ ], 3.02 [dd,  $J_{\text{H}^d,\text{H}}$  7.2 Hz,  $J_{\text{H}^d,\text{H}^c}$  15.6 Hz,  $\text{CH}-\text{CH}^c\text{H}^d\text{C}(\text{NO}_2)_3$ ].  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  84.1 [ $\text{CH}-\text{CH}_2\text{C}(\text{NO}_2)_3$ ], 81.0 ( $\text{CH}-\text{CH}_2\text{NO}_2$ ), 77.2 ( $\text{CH}_2\text{NO}_2$ ), 40.6 [ $\text{CH}_2\text{C}(\text{NO}_2)_3$ ]; the remainder of the signals were uncertain in a weak spectrum. The above assignments were confirmed by double irradiation and heteronuclear correlation (HETCOR) spectra.

The second fraction eluted consisted mainly of the isoxazolidine **3c** with minor amounts of isoxazolidine **4c** and nitronic ester **6c**. The NMR spectra of isoxazolidine **3c** were as follows:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.42–7.36 (m, ArH), 7.28 (d,  $J_{\text{H,H}}$  8.5 Hz, ArH), 7.14 (d,  $J_{\text{H,H}}$  8.5 Hz, ArH), 5.81 (dd,  $J_{\text{H,H}^a}$  7.8 Hz,  $J_{\text{H,H}^b}$  5.5 Hz,  $\text{CH}-\text{CH}^a\text{H}^b\text{NO}_2$ ), 5.78 [dd,  $J_{\text{H,H}^c}$  8.1 Hz,  $J_{\text{H,H}^d}$  7.3 Hz,  $\text{CH}-\text{CH}^c\text{H}^d\text{C}(\text{NO}_2)_3$ ], 5.10 (dd,  $J_{\text{H}^a,\text{H}}$  7.8 Hz,  $J_{\text{H}^a,\text{H}^b}$  13.7 Hz,  $\text{CH}-\text{CH}^a\text{H}^b\text{NO}_2$ ), 4.56 (dd,  $J_{\text{H}^b,\text{H}}$  5.5 Hz,  $J_{\text{H}^b,\text{H}^a}$  13.7 Hz,  $\text{CH}-\text{CH}^a\text{H}^b\text{NO}_2$ ), 4.16 [dd,  $J_{\text{H}^c,\text{H}}$  8.1 Hz,  $J_{\text{H}^c,\text{H}^d}$  15.6 Hz,  $\text{CH}-\text{CH}^c\text{H}^d\text{C}(\text{NO}_2)_3$ ], 3.02 [dd,  $J_{\text{H}^d,\text{H}}$  7.3 Hz,  $J_{\text{H}^d,\text{H}^c}$  15.6 Hz,  $\text{CH}-\text{CH}^c\text{H}^d\text{C}(\text{NO}_2)_3$ ].  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  83.6 [ $\text{CH}-\text{CH}_2\text{C}(\text{NO}_2)_3$ ], 82.3 ( $\text{CH}-\text{CH}_2\text{NO}_2$ ), 77.3 ( $\text{CH}_2\text{NO}_2$ ), 40.5 [ $\text{CH}_2\text{C}(\text{NO}_2)_3$ ]; the remainder of the signals were uncertain in a weak spectrum. The above assignments were confirmed by double irradiation and heteronuclear correlation (HETCOR) spectra.

The next fraction contained an impure sample of the nitro ketone **5c**,  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  7.88 (d,  $J_{\text{H,H}}$  8.9 Hz, ArH), 7.58 (d,  $J_{\text{H,H}}$  8.9 Hz, ArH), 6.09 (s,  $\text{COCH}_2\text{NO}_2$ ); insufficient for a  $^{13}\text{C}$  NMR spectrum.

**Photochemistry of 4-chlorostyrene (2c) in acetonitrile.** Reaction of **2c**-tetranitromethane in acetonitrile, as above, for 3 h resulted in complete conversion into a mixture of isoxazolidines **3c** (10.6%) and **4c** (27.6%), nitro ketone **5c** (51.7%) and unidentified material (10.1%). After 30 min the product yields were isoxazolidines **3c** (10.6%) and **4c** (34.3%), nitro ketone **5c** (44.5%) and unidentified material (10.6%).

**General procedure for the photolysis of 3-chlorostyrene (2d) with tetranitromethane.** A solution of **2d** (500 mg,  $0.45 \text{ mol dm}^{-3}$ ) and tetranitromethane ( $0.9 \text{ mol dm}^{-3}$ )



in dichloromethane or acetonitrile was irradiated with filtered light ( $\lambda_{\text{cut-off}}$  435 nm). After the colour of the reaction mixture faded from yellow to nearly colourless 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 3-chlorostyrene (2d) in dichloromethane.** Reaction of **2d**-tetranitromethane in dichloromethane, as above, for 7 h resulted in complete conversion into a mixture of isoxazolidines **3d** (12.9%) and **4d** (45.2%), nitro ketone **5d** (22.6%) and unidentified adducts (total 19.3%). Chromatography on a silica gel Chromatotron plate allowed a partial separation of the major components of this mixture. The first material eluted was substantially the isoxazolidine **4d** with minor amounts of isoxazolidine **3d** and unidentified products. Isoxazolidine **4d** gave the following NMR spectra:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.43–7.34 (m, ArH), 7.29–7.26 (m, ArH), 7.17–7.14 (m, ArH), 5.84 (dd,  $J_{\text{H,H}^a}$  9.8 Hz,  $J_{\text{H,H}^b}$  3.7 Hz, CH–CH<sup>a</sup>H<sup>b</sup>NO<sub>2</sub>), 5.79 [dd,  $J_{\text{H,H}^c}$  8.2 Hz,  $J_{\text{H,H}^d}$  7.2 Hz, CH–CH<sup>c</sup>H<sup>d</sup>C(NO<sub>2</sub>)<sub>3</sub>], 4.83 (dd,  $J_{\text{H}^a,\text{H}}$  9.8 Hz,  $J_{\text{H}^a,\text{H}^b}$  13.9 Hz, CH–CH<sup>a</sup>H<sup>b</sup>NO<sub>2</sub>), 4.63 (dd,  $J_{\text{H}^b,\text{H}}$  3.7 Hz,  $J_{\text{H}^b,\text{H}^a}$  13.9 Hz, CH–CH<sup>a</sup>H<sup>b</sup>NO<sub>2</sub>), 4.21 [dd,  $J_{\text{H}^c,\text{H}}$  8.2 Hz,  $J_{\text{H}^c,\text{H}^d}$  15.6 Hz, CH–CH<sup>c</sup>H<sup>d</sup>C(NO<sub>2</sub>)<sub>3</sub>], 3.03 [dd,  $J_{\text{H}^d,\text{H}}$  7.2 Hz,  $J_{\text{H}^d,\text{H}^c}$  15.6 Hz, CH–CH<sup>c</sup>H<sup>d</sup>C(NO<sub>2</sub>)<sub>3</sub>].  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  136.3, 135.2, 131.04, 130.96, 130.8, 130.6, 127.9, 127.4, 125.8, 125.3, 83.9 [CH–CH<sub>2</sub>C(NO<sub>2</sub>)<sub>3</sub>], 81.0 (CH–CH<sub>2</sub>NO<sub>2</sub>), 77.3 (CH<sub>2</sub>NO<sub>2</sub>), 41.45 [CH<sub>2</sub>C(NO<sub>2</sub>)<sub>3</sub>]. The above assignments were confirmed by double irradiation and heteronuclear correlation (HETCOR) spectra.

The second material eluted was a mixture (ca. 3:2) of the nitro ketone **5d** and isoxazolidine **3d**. Crystallization of this material from dichloromethane–pentane gave pure nitro ketone **5d**, m.p. 94–95 °C (Found:  $M^+$  199.0037. C<sub>8</sub>H<sub>6</sub>ClNO<sub>3</sub> requires 199.0036). IR (KBr) 1682 cm<sup>-1</sup>.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.88 (m, ArH), 7.76 (m, ArH), 7.68 (m, ArH), 7.52 (dd,  $J_{\text{H,H}}$   $\approx$  8.0 Hz, ArH), 5.88 (CO–CH<sub>2</sub>NO<sub>2</sub>).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  185.1 (C=O), 136.2, 135.5, 135.3, 131.1, 130.9, 128.8, 126.7, 81.5 (CH<sub>2</sub>NO<sub>2</sub>). The NMR spectra of isoxazolidine **3d** determined from this mixture were as follows:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.82 (dd,  $J_{\text{H,H}^a}$  8.0 Hz,  $J_{\text{H,H}^b}$  5.1 Hz, CH–CH<sup>a</sup>H<sup>b</sup>NO<sub>2</sub>), 5.80 [dd,  $J_{\text{H,H}^c}$  8.1 Hz,  $J_{\text{H,H}^d}$  7.3 Hz, CH–CH<sup>c</sup>H<sup>d</sup>C(NO<sub>2</sub>)<sub>3</sub>], 5.05 (dd,  $J_{\text{H}^a,\text{H}}$  8.0 Hz,  $J_{\text{H}^a,\text{H}^b}$  13.8 Hz, CH–CH<sup>a</sup>H<sup>b</sup>NO<sub>2</sub>), 4.57 (dd,  $J_{\text{H}^b,\text{H}}$  5.1 Hz,  $J_{\text{H}^b,\text{H}^a}$  13.8 Hz, CH–CH<sup>a</sup>H<sup>b</sup>NO<sub>2</sub>), 4.19 [dd,  $J_{\text{H}^c,\text{H}}$  8.1 Hz,  $J_{\text{H}^c,\text{H}^d}$  15.7 Hz, CH–CH<sup>c</sup>H<sup>d</sup>C(NO<sub>2</sub>)<sub>3</sub>], 3.05 [dd,  $J_{\text{H}^d,\text{H}}$  7.3 Hz,  $J_{\text{H}^d,\text{H}^c}$  15.7 Hz, CH–CH<sup>c</sup>H<sup>d</sup>C(NO<sub>2</sub>)<sub>3</sub>]; the remainder of the spectrum was obscured.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  83.6 [CH–CH<sub>2</sub>C(NO<sub>2</sub>)<sub>3</sub>], 81.5 (CH–CH<sub>2</sub>NO<sub>2</sub>), 77.2 (CH<sub>2</sub>NO<sub>2</sub>), 41.5 [CH<sub>2</sub>C(NO<sub>2</sub>)<sub>3</sub>]. The above assignments were confirmed by double irradiation and heteronuclear correlation (HETCOR) spectra.

**Photochemistry of 3-chlorostyrene (2d) in acetonitrile.** Reaction of **2d**-tetranitromethane in acetonitrile, as

above, for 6 h resulted in partial conversion (ca. 80%) into a mixture of isoxazolidines **3d** (8.5%) and **4d** (27.4%), nitro ketone **5d** (47.5%) and unidentified material (16.6%). After 2 h the product yields were isoxazolidines **3d** (10.1%) and **4d** (27.8%), nitro ketone **5d** (46.5%) and unidentified material (15.6%).

**General procedure for the photolysis of 4-acetoxystyrene (2e) with tetranitromethane.** A solution of **2e** (500 mg, 0.39 mol dm<sup>-3</sup>) and tetranitromethane (0.78 mol dm<sup>-3</sup>) in dichloromethane was irradiated with filtered light ( $\lambda_{\text{cut-off}}$  435 nm). After the colour of the reaction mixture faded from yellow to nearly colourless 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-acetoxystyrene (2e) in dichloromethane.** Reaction of **2e**-tetranitromethane in dichloromethane, as above, for 2 h resulted in complete conversion into a mixture of isoxazolidines **3e** (27.9%) and **4e** (53.4%), nitro ketone **5e** (5.9%), nitronic ester **6e** (8.4%) and unidentified adducts (total 4.4%).

Chromatography of this material on a silica gel Chromatotron plate gave first the nitro ketone **5e**, m.p. 103–104 °C (Found:  $M^+$  223.0482. C<sub>10</sub>H<sub>9</sub>NO<sub>5</sub> requires 223.0481).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.92 (d,  $J_{\text{H,H}}$  8.9 Hz, H2', H6'), 7.30 (d,  $J_{\text{H,H}}$  8.9 Hz, H3', H5'), 5.87 (CH<sub>2</sub>NO<sub>2</sub>), 2.35 (s, OCOCH<sub>3</sub>).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  184.9 (CO–CH<sub>2</sub>NO<sub>2</sub>), 168.9 (CO–Me), 156.3 (C4'), 131.35 (C1'), 130.4 (C2', C6'), 123.0 (C3', C5'), 21.5 (Me). The above assignments were confirmed by heteronuclear correlation (HETCOR) spectra.

The second material eluted was an inseparable mixture of isoxazolidines **3e** and **4e**, nitronic ester **6e** and a small amount of unidentified adducts. The three identifiable products had NMR spectra as follows:

**Isoxazolidine 3e:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.06 (dd,  $J_{\text{H}^a,\text{H}}$  7.8 Hz,  $J_{\text{H}^a,\text{H}^b}$  13.8 Hz, CH–CH<sup>a</sup>H<sup>b</sup>NO<sub>2</sub>), 4.55 (dd,  $J_{\text{H}^b,\text{H}}$  5.3 Hz,  $J_{\text{H}^b,\text{H}^a}$  13.8 Hz, CH–CH<sup>a</sup>H<sup>b</sup>NO<sub>2</sub>), 4.13 [dd,  $J_{\text{H}^c,\text{H}}$  8.1 Hz,  $J_{\text{H}^c,\text{H}^d}$  15.7 Hz, CH–CH<sup>c</sup>H<sup>d</sup>C(NO<sub>2</sub>)<sub>3</sub>], 3.02 [dd,  $J_{\text{H}^d,\text{H}}$  7.2 Hz,  $J_{\text{H}^d,\text{H}^c}$  15.7 Hz, CH–CH<sup>c</sup>H<sup>d</sup>C(NO<sub>2</sub>)<sub>3</sub>]; the remainder of the spectrum was obscured.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  169.5, 152.3, 152.1, 129.2, 128.45, 122.9, 122.8, 83.9 [CH–CH<sub>2</sub>C(NO<sub>2</sub>)<sub>3</sub>], 81.3 (CH–CH<sub>2</sub>NO<sub>2</sub>), 77.3 (CH<sub>2</sub>NO<sub>2</sub>), 41.6 [CH<sub>2</sub>C(NO<sub>2</sub>)<sub>3</sub>], 21.45 (Me), 21.43 (Me). The above assignments were confirmed by double irradiation and heteronuclear correlation (HETCOR) spectra.

**Isoxazolidine 4e:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  4.815 (dd,  $J_{\text{H}^a,\text{H}}$  9.8 Hz,  $J_{\text{H}^a,\text{H}^b}$  13.85 Hz, CH–CH<sup>a</sup>H<sup>b</sup>NO<sub>2</sub>), 4.60 (dd,  $J_{\text{H}^b,\text{H}}$  3.7 Hz,  $J_{\text{H}^b,\text{H}^a}$  13.85 Hz, CH–CH<sup>a</sup>H<sup>b</sup>NO<sub>2</sub>), 4.16 [dd,  $J_{\text{H}^c,\text{H}}$  8.2 Hz,  $J_{\text{H}^c,\text{H}^d}$  15.7 Hz, CH–CH<sup>c</sup>H<sup>d</sup>C(NO<sub>2</sub>)<sub>3</sub>], 3.02 [dd,  $J_{\text{H}^d,\text{H}}$  7.2 Hz,  $J_{\text{H}^d,\text{H}^c}$  15.7 Hz, CH–CH<sup>c</sup>H<sup>d</sup>C(NO<sub>2</sub>)<sub>3</sub>].  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  169.55, 152.3, 152.2, 129.0, 128.7, 122.9, 122.8, 84.1 [CH–CH<sub>2</sub>C(NO<sub>2</sub>)<sub>3</sub>], 81.1 (CH–CH<sub>2</sub>NO<sub>2</sub>), 77.5 (CH<sub>2</sub>NO<sub>2</sub>), 41.4 [CH<sub>2</sub>C(NO<sub>2</sub>)<sub>3</sub>], 21.47 (Me), 21.44

(Me). The above assignments were confirmed by double irradiation and heteronuclear correlation (HETCOR) spectra.

*Nitronic ester 6e*:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.40 (dd,  $J_{\text{H1,H2a}}$  9.3 Hz,  $J_{\text{H1,H2b}}$  7.3 Hz, H1), 3.72 (dd,  $J_{\text{H2a,H2b}}$  15.0 Hz,  $J_{\text{H2a,H1}}$  9.3 Hz, H2a), 3.63 (dd,  $J_{\text{H2b,H2a}}$  15.0 Hz,  $J_{\text{H2b,H1}}$  7.3 Hz, H2b); the remainder of the spectrum was obscured.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  84.1 (C1), 39.0 (C2); the remainder of the spectrum was obscured. The above assignments were confirmed by double irradiation and heteronuclear correlation (HETCOR) spectra.

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