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Photochemical Nitration by Tetranitromethane. Part XLIV.† Some Reactions of 2-Phenylpropene and 2,4,6-Trimethylstyrene with Tetranitromethane: Competition Between the Radical Chain Addition Reaction and Isoxazolidine Formation: Nitrogen Inversion in Some Isoxazolidines

Ulf Berg,[a] Craig P. Butts,[b] Lennart Eberson,[a,*] Michael P. Hartshorn[c,*] and Ola Persson[a]

[a]Department of Chemistry, Lund University, PO Box 124, S-221 00 Lund, Sweden, [b]School of Chemistry, Bristol University, Bristol BS8 1TS, UK and [c]Department of Chemistry, University of Canterbury, Christchurch, New Zealand

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Reaction of 2-phenylpropene with tetranitromethane in dichloromethane occurs either slowly in the dark or more rapidly photochemically to give 1-nitro-2-phenyl-2-trinitromethylpropane (**1**) and the two diastereomers of 5-methyl-2-(2′-nitro-1′-phenyl)ethoxy-3,3-dinitro-5-phenylisoxazolidine (**5** and **6**). In diethyl ether solution these products are also formed, but the yields of **5** and **6** are increased at the expense of the nitro-trinitromethyl adduct **1**. At 23 °C in [^{2}H]chloroform solution each isoxazolidine **5** and **6** exists as two *N*-invertimers. Variable temperature ^{1}H NMR studies of **5** and **6** revealed band broadening and coalescence of all signals in the temperature range 50–100 °C; the rate constants and corresponding free energies of activation were identical for the two isoxazolidines **5** and **6**, $\Delta G^{\ddagger} = 74.7(5)$ kJ mol^{-1} at 353 K. A single-crystal X-ray analysis of isoxazolidine **5** is reported.

Photolysis of 2,4,6-trimethylstyrene with tetranitromethane in either dichloromethane or acetonitrile gives the nitro-trinitromethyl adduct, 2-(2′,4′,6′-trimethylphenyl)-1-nitro-2-trinitromethylethane (**9**), and nitromethyl 2,4,6-trimethylphenyl ketone (**10**).

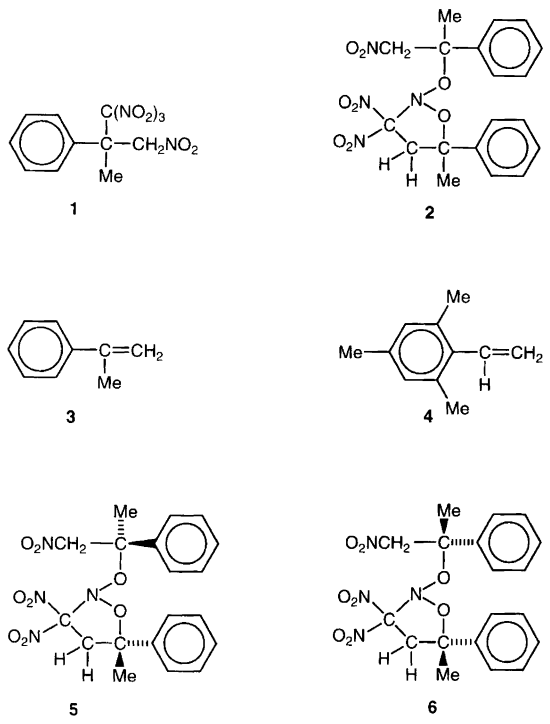
Base-catalysed eliminations of nitroform from adducts **1** and **9** give the corresponding (*E*)-nitro alkenes **7** and **11**, respectively, kinetic studies showing that the rate of elimination from the secondary but sterically more compressed trinitromethyl compound **9** was greater (× 15) than for the tertiary trinitromethyl compound **1**.

The modes of formation of adducts **1** and **9**, isoxazolidines **5** and **6**, and nitro ketone **10** are discussed.

Ratsino *et al.*[2] reported the formation of the nitro-trinitromethyl adduct **1** (42%) and the isoxazolidine **2** (31.5%) on reaction of 2-phenylpropene (**3**) with tetranitromethane for 24 h in dichloromethane under uncertain conditions of illumination. Further, variation of the solvent employed resulted in a change in the relative yields of these two products, a more polar solvent favouring the formation of the nitro-trinitromethyl adduct **1**. The isoxazolidine **2**, m.p. 114 °C, was apparently a pure single compound, but its stereochemistry was not determined, nor was evidence presented of other stereoisomers for a structure in which there are two stereogenic carbon centres and the potential for *N*-invertimers at the central nitrogen atom of the structure.[3]

As part of a continuing study[1] of the reactions of unsaturated systems with tetranitromethane we have examined the reactions of 2-phenylpropene (**3**) and 2,4,6-trimethylstyrene (**4**). In our hands, reaction of tetranitromethane with 2-phenylpropene in dichloromethane in the dark for 24 h gave the nitro-trinitromethyl adduct **1** (44%) and two stereoisomeric isoxazolidines **5** (26.6%)

† Part XLIII, see Ref. 1.
* To whom correspondence should be addressed.



and **6** (29.4%); isoxazolidine **5** was crystalline, m.p. 117–118 °C, most probably identical with the material isolated earlier by Ratsino *et al.*[2] Both isoxazolidines **5** and **6** exhibited inversion at the central nitrogen atom, with an energy barrier to inversion which resulted in each case in discrete ^{1}H NMR spectra for the two *N*-invertimers in [^{2}H]chloroform at 23 °C. We now report the results of our study of the reactions of 2-phenylpropene (**3**) with tetranitromethane, including the X-ray crystal structure of isoxazolidine **5**, and also some analogous reactions of 2,4,6-trimethylstyrene (**4**).

Results

Reaction of 2-phenylpropene (**3**) *with tetranitromethane in dichloromethane in the dark at 20 °C.* A mixture of **3** (2.02 mol dm^{-3}) and tetranitromethane (2.02 mol dm^{-3}) in dichloromethane was stored in the dark at 20 °C for 24 h, and the solvent and excess tetranitromethane were removed under reduced pressure at $\leqslant$0 °C to give a residue which was shown by ^{1}H NMR spectroscopy to be a mixture of the nitro-trinitromethyl adduct (**1**) (44.0%) and isoxazolidines (**5**) (26.6%) and (**6**) (29.4%). These materials were separated by chromatography on a silica gel Chromatotron plate.

Eluted first was 1-nitro-2-phenyl-2-trinitromethylpropane (**1**), m.p. 54–55 °C (lit.[2] m.p. 53 °C) which was identified from a consideration of its NMR spectra (Experimental section). The CH_2–NO_2 function was characterized by ^{1}H NMR signals at δ 5.80 (dq, $J_{H1a,H1b}$ 12.7 Hz, $J_{H1a,Me}$ 0.6 Hz, H1a) and 5.32 (d, $J_{H1b,H1a}$ 12.7 Hz, H1b), and a ^{13}C NMR signal at δ 79.5. The ^{13}C NMR chemical shift for C2 (δ 51.4) pointed to the attachment of the trinitromethyl group at that carbon atom.

The structure of the second material eluted was determined by single-crystal X-ray analysis as (*RS,SR*)-isoxazolidine (**5**), $C_{19}H_{20}N_4O_8$, m.p. 117–118 °C. A perspective drawing of **5** is presented in Fig. 1, and the corresponding atomic coordinates in Table 1. The structure consists of two crystallographically independent molecules in the asymmetric unit. The two molecules retain the same stereochemistry at the two stereogenic carbon atoms and also at the central nitrogen atom. The minor conformational differences between them are illustrated in Fig. 2; these differences are not significant chemically and presumably arise as a result of crystal packing. In the discussion of the structure which follows the data will be for molecule 1. In the five-membered ring the substituents at C(1) and C(2) are close to eclipsed, torsional angles: C(3)–C(2)–C(1)–H(1B) −13.9(3)°, C(21)–C(2)–C(1)–H(1A) −7.4(4)°, but the envelope conformation of the ring system is indicated by the stereochemical relationship between the two C(11)–NO_2 bonds and the N(1)–O(11) bond, torsional angles: O(11)–N(1)–C(11)–N(2) −170.5(2)°, O(11)–N(1)–C(11)–N(3) −57.8(3)°. The N(1)–O(11) and C(2)–C(21) bonds are *syn* in this structure. In the connection between the five-membered ring and C(2A) the molecular conformation is such that the O(11)–N(1) bond is staggered with respect to the C(2A)–C(3A) and C(2A)–C(1A) bonds, torsional angles: N(1)–O(11)–C(2A)–C(3A) −68.1(3)°, N(1)–O(11)–C(2A)–C(1A) 56.2(4)°, and necessarily close to *anti* to the C(2A)–C(21A) bond, torsional angle: N(1)–O(11)–C(2A)–C(21A) 168.6(2)°. The conformation of the molecule about the second stereogenic carbon atom, C(2A), is indicated by the following torsional angles. First, the plane of the phenyl group is close to eclipsed with the C(2A)–C(3A) bond, torsional angle: C(26A)–C(21A)–C(2A)–C(3A) 15.1(6)°. Second, the orientation of the CH_2–NO_2 structural unit, relative to the remainder of the molecule, is indicated by the tor-

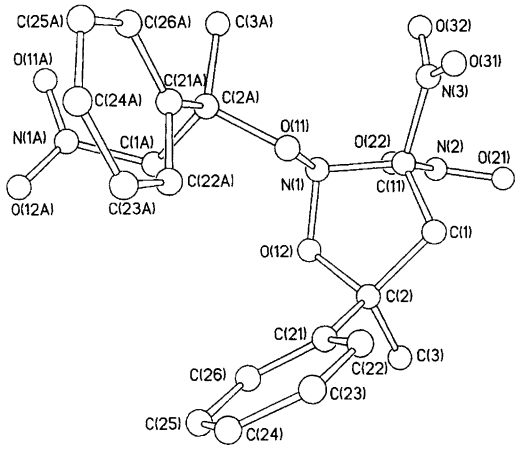


Fig. 1. Perspective drawing of compound **5**.

Table 1. Fractional coordinates for atoms in isoxazolidine (**5**).

Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	$10^3U/Å^2$ [a]
Molecule 1				
O(11)	3421(3)	4637(3)	3724(1)	19(1)
O(12)	5383(3)	4190(3)	2981(1)	22(1)
O(21)	3967(3)	8336(5)	2581(1)	31(1)
O(22)	3590(4)	6558(4)	2204(1)	43(1)
O(31)	1967(3)	7938(3)	3994(1)	33(1)
O(32)	1035(3)	7977(4)	3203(1)	37(1)
O(11A)	2030(4)	1060(4)	3321(2)	48(1)
O(12A)	4101(4)	−96(4)	3718(1)	43(1)
N(1)	3773(3)	5016(4)	3142(1)	20(1)
N(2)	3763(3)	7196(5)	2605(1)	22(1)
N(3)	2084(3)	7589(4)	3496(1)	24(1)
N(1A)	3232(4)	980(5)	3466(1)	28(1)
C(1)	5033(4)	6388(5)	3502(1)	22(1)
C(2)	6265(4)	4790(5)	3297(1)	19(1)
C(3)	7522(4)	4855(5)	2847(2)	30(1)
C(1A)	3659(4)	2258(6)	3338(1)	21(1)
C(2A)	2641(4)	3633(5)	3748(1)	19(1)
C(3A)	1031(4)	4493(5)	3570(2)	27(1)
C(11)	3686(4)	6535(5)	3205(1)	18(1)
C(21)	6954(3)	3716(5)	3766(1)	19(1)
C(22)	6923(4)	4232(5)	4309(1)	25(1)
C(23)	7563(4)	3194(5)	4732(2)	33(1)
C(24)	8246(4)	1664(5)	4610(2)	31(1)
C(25)	8315(4)	1147(5)	4965(2)	32(1)
C(26)	7675(4)	2171(5)	3644(2)	27(1)
C(21A)	2675(4)	3101(5)	4363(1)	19(1)
C(22A)	4074(4)	2546(5)	4595(1)	22(1)
C(23A)	4160(4)	1945(5)	5139(1)	28(1)
C(24A)	2869(5)	1908(5)	5456(2)	30(1)
C(25A)	148(5)	2463(5)	5230(2)	33(1)
C(26A)	1382(4)	3070(5)	4685(2)	29(1)
Molecule 2				
O(11')	6903(2)	819(3)	1322(1)	22(1)
O(12')	8001(3)	1331(3)	2052(1)	22(1)
O(21')	9242(3)	−2945(4)	2556(1)	36(1)
O(22')	7432(4)	−798(4)	2893(1)	47(1)
O(31')	8586(4)	−2496(4)	1100(1)	45(1)
O(32')	6833(4)	−2318(4)	1807(1)	40(1)
O(11B)	2212(3)	3985(4)	2044(1)	46(1)
O(12B)	2639(4)	5145(4)	1290(1)	51(1)
N(1')	7159(3)	528(4)	1913(1)	21(1)
N(2')	8317(4)	−1630(4)	2512(1)	26(1)
N(3')	7890(4)	−2054(4)	1571(1)	29(1)
N(1B)	3074(4)	4202(4)	1658(1)	33(1)
C(1')	9896(4)	−1045(5)	1679(2)	29(1)
C(2')	9627(4)	600(5)	1761(1)	21(1)
C(3')	10603(4)	758(6)	2190(2)	32(1)
C(1B)	4778(4)	3225(5)	1639(1)	24(1)
C(2B)	5224(4)	1775(5))	1281(1)	21(1)
C(3B)	4312(4)	907(5)	1494(2)	31(1)
C(11')	8353(4)	−1037(5)	1902(1)	21(1)
C(21')	9771(4)	1446(5)	1218(1)	21(1)
C(22')	9090(5)	3009(5)	1238(2)	31(1)
C(23')	9182(5)	3838(6)	754(2)	37(1)
C(24')	9988(5)	3073(6)	243(2)	35(1)
C(25')	10686(5)	1527(6)	220(2)	35(1)
C(26')	10592(4)	700(5)	707(2)	27(1)
C(21B)	5261(4)	2117(5)	645(1)	24(1)
C(22B)	6298(4)	2645(5)	379(2)	28(1)
C(23B)	6291(5)	3038(5)	−192(2)	37(1)
C(24B)	5241(5)	2879(6)	−501(2)	42(2)
C(25B)	4223(6)	2349(6)	−245(2)	47(2)
C(26B)	4221(5)	1954(6)	328(2)	38(1)

[a] The equivalent isotropic temperature factor in Table 1 is defined as one-third of orthogonalized U_{ij} tensor in Å^2.

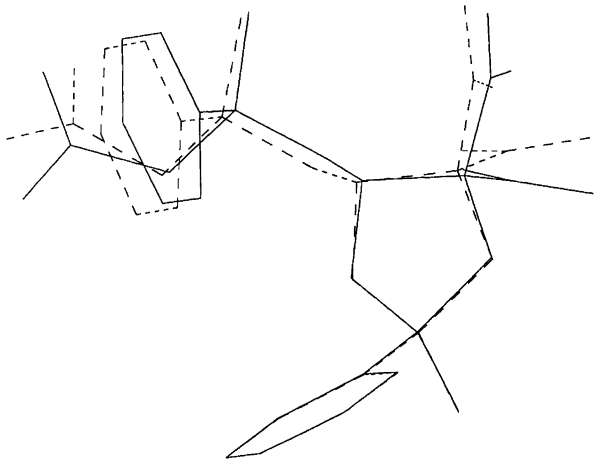


Fig. 2. Superposition of molecule 1 and and molecule 2 of compound **5**.

sional angle: N(1A)–C(1A)–C(2A)–O(11) 162.4(3)°, i.e. with the C(1A)–N(1A) bond close to *anti* to the C(2A)–O(11) bond. Third, the orientation of the N(1A) nitro group is such that its plane is close to perpendicular to the C(1A)–C(2A) bond, torsional angle: O(11A)–N(1A)–C(1A)–C(2A) 74.8(4)°.

On dissolution in [^{2}H]chloroform at 23 °C solid isoxazolidine **5**, m.p. 117–118 °C, gave ^{1}H and ^{13}C NMR spectra (Experimental section) consistent with a mixture (ca. 1:1) of two *N*-invertimers **A** and **B**; the assignments of these spectra to the two *N*-invertimers **A** and **B** were based on the results of double irradiation, difference NOE, and long- and short-range heteronuclear correlation (HETCOR) spectra.

The third material eluted was the pure (*RR,SS*)-isoxazolidine **5** isolated as an oil. The ^{1}H and ^{13}C NMR spectra in [^{2}H]chloroform at 23 °C (Experimental section) of this material were consistent with it being a mixture (ca. 1.7:1) of two *N*-invertimers; the assignments of these spectra to the two *N*-invertimers were again based on the results of double irradiation, difference NOE, and long- and short-range heteronuclear correlation (HETCOR) spectra.

Reaction of 2-phenylpropene (**3**) *with tetranitromethane in diethyl ether in the dark at 20 °C.* A mixture of **3** (0.42 mol dm^{-3}) and tetranitromethane (0.42 mol dm^{-3}) in diethyl ether were stored in the dark for 24 h, and the solvent and excess tetranitromethane were removed under reduced pressure at ≤0 °C to give a residue which was shown by ^{1}H NMR spectroscopy to be a mixture of the nitro-trinitromethyl adduct **1** (27.8%) and isoxazolidines **5** (35.6%) and **6** (36.6%). Earlier in a similar reaction Ratsino *et al.*[2] reported the formation of isoxazolidine(s) (83%), but the absence of nitro-trinitromethyl adduct **1** from among the products.

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.[4] The temperature of the reaction mixture was kept at 15 °C, unless otherwise stated. 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 (^{1}H NMR spectroscopy, see Experimental section) as soon as possible.

Photochemistry of 2-phenylpropene (**3**) *with tetranitromethane in dichloromethane.* Reaction of **3**–tetranitromethane, as above, for 3.5 h resulted in complete conversion into a mixture of nitro-trinitromethyl adduct **1** (47.1%) and isoxazolidines **5** (25.0%) and **6** (27.9%).

Reaction of 1-nitro-2-phenyl-2-trinitromethylpropane (**1**) *with 2,6-lutidine in (^{2}H)chloroform.* Reaction of a solution of **1** and 2,6-lutidine in (^{2}H)chloroform at 23 °C gave (*E*)-1-nitro-2-phenylpropene (**7**), identified by a comparison of the 1H NMR spectrum of the reaction mixture with literature data for nitroalkenes **7** and **8** (Fig. 3.).[5]

Variable-temperature ^{1}H NMR spectroscopic studies of isoxazolidines **5** *and* **6**. The ^{1}H NMR spectra in ($^2H_3$)nitromethane of isoxazolidines **5** and **6** showed band-broadening and coalescence of all signals in the temperature range 50–100 °C. The coalescence resulted in a change of the spectral features from an averaged diastereomer above coalescence temperature instead of two species at ambient temperatures for each compound **5** and **6**. For each compound the four methyl signals merged to two singlets and the four AB quartets merged to two AB quartets.

Bandshape analysis of the methyl region as well as of the region of the low-field CH_2–$C(NO_2)_2$ AB quartets was performed by visual fitting of calculated to experimental spectra. The temperature drift of the chemical shifts were taken into account in the simulations, but hampered the analysis of the low-field AB quartet of isoxazolidine **5**, due to merging signals at the coalescence temperature. The rate constants and corresponding free energies of activation were identical for the **5** and **6** within experimental error, i.e. $\Delta G^{\ddagger} = 74.7(5)$ kJ mol^{-1} at 353 K.

The barriers are ca. 15 kJ mol^{-1} higher than for the nitrogen inversion in *N*-benzyl-5-ethoxyisoxazolidines.[3] This is in agreement with earlier observations that electronegative substituents on nitrogen increase the inversion barrier.[6] Although we cannot rule out unequivocally slow rotation around either the N(1)–O(11) or C(2A)–O(11) bonds as the origin of the dynamic NMR features, all information such as NMR, X-ray and barrier height indicate nitrogen inversion as the most likely process.

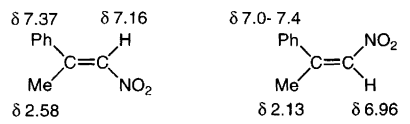
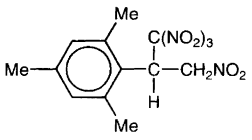


Fig. 3. ^{1}H NMR data [(^{2}H)chloroform, δ] for nitro alkenes **7** and **8**.

The populations of the inverting diastereomers were slightly different in ($^2H_3$)nitromethane [55:45 (±1) for both **5** and **6**] compared with (^{2}H)chloroform [**5** (ca. 1:1), **6** (ca. 65:35)], indicating that polar effects are involved and that steric and stereoelectronic effects are either negligible or cancel out in determining the position of equilibrium.

Photochemistry of 2,4,6-trimethylstyrene (**4**) *with tetranitromethane in dichloromethane.* Reaction of **4**–tetranitromethane, as above, for 45 min resulted in complete conversion into a mixture of 2-(2′,4′,6′-trimethylphenyl)-1-nitro-2-trinitromethylethane (**9**) (58.0%), nitro ketone **10** (24.5%) and some unidentified adducts (total 17.5%).



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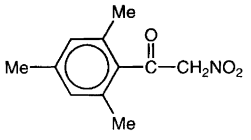

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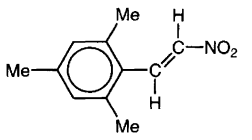

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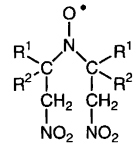

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Chromatography of this mixture on a silica gel Chromatotron plate gave first 2-(2′,4′,6′-trimethylphenyl)-1-nitro-2-trinitromethylethane (**9**), which was identified from its spectroscopic data. In particular, the connectivity in **9** followed from the ^{1}H and ^{13}C NMR data for the CH_2–NO_2 function [δ 5.32 (dd, $J_{H1a,H1b}$ 13.7 Hz, $J_{H1a,H2}$ 9.6 Hz, H1a), 5.20 (dd, $J_{H1b,H1a}$ 13.7 Hz, $J_{H1b,H2}$ 3.6 Hz, H1b), and δ 74.4], and the –CH–$C(NO_2)_3$ function [δ 6.40 (dd, $J_{H2,H1a}$ 9.6 Hz, $J_{H2,H1b}$ 3.6 Hz, H2), and δ 43.8].

The second material eluted was the pure nitro ketone **10**, with a mass spectrum indicating the molecular formula, $C_{11}H_{13}NO_3$, which in the solid state gave an infrared spectrum (1710, 1560 cm^{-1}) consistent with its formulation as a nitro ketone. In (^{2}H)chloroform solution the ^{1}H NMR spectrum (Experimental section) indicated clearly that **10** was substantially enolized.[7]

Photochemistry of 2,4,6-trimethylstyrene (**4**) *with tetranitromethane in acetonitrile.* Reaction of **4**–tetranitromethane, as above, for 30 min resulted in complete conversion into a mixture of 2-(2′,4′,6′-trimethylphenyl)-1-nitro-2-trinitromethylethane (**9**) (56.8%), nitro ketone **10** (9.7%) and some unidentified adducts (total 33.5%).

Table 2. Rates of 3,5-lutidine-induced elimination from nitro-trinitromethyl adducts **1** and **9** in dichlormethane at 23 °C.

Compound	[3,5-lutidine]/ mol dm^{-3}	k/s^{-1}	k_2/dm^3 mol^{-1} s^{-1}	Rel. rate
1	0.117	1.23×10^{-3}	0.0105	
	0.234	2.55×10^{-3}	0.0109	
	0.293	3.03×10^{-3}	0.0103	
			Ave: 0.0106	1.0
9	0.117	0.0186	0.159	
	0.117	0.0191	0.163	
	0.234	0.0368	0.157	
			Ave: 0.160[a]	15

[a] With 2,6-di-*tert*-butylpyridine as the base the rate constant was 6.1×10^{-4} dm^3 mol^{-1} s^{-1}.

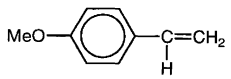
Reaction of 2-(2',4',6'-trimethylphenyl)-1-nitro-2-trinitromethylethane (**9**) *with 2,6-lutidine in* (^2H)*chloroform.* Reaction of a solution of **9** and 2,6-lutidine in (^{2}H)-chloroform for 18 min at 23 °C gave (*E*)-2-(2',4',6'-trimethylphenyl-1-nitropropene (**11**), identified by a comparison of the ^{1}H NMR spectrum of the reaction mixture with literature data.[8]

Kinetics of elimination of nitroform from nitro-trinitromethyl adducts **3** *and* **8.** The nitro-trinitromethyl adducts (**3**) and (**8**) were treated with excess 3,5-lutidine in dichloromethane at 23 °C and the appearance of the 350 nm maximum of trinitromethanide ion monitored vs. time by UV spectroscopy. The reactions obeyed first-order kinetics and runs at different 3,5-lutidine concentrations gave satisfactory second-order rate constants (Table 2).

EPR spectral search for possible radical intermediates. The photochemical reactions between tetranitromethane and **3** or **4** in dichloromethane solution were monitored by EPR spectroscopy in order to detect radical intermediates. However, only the EPR spectra of aminoxyl radicals **12** formed by the known[9] reaction of styrenes with NO_2 and NO were detected, as was found for other styrenes in the preceding paper.[1] The EPR spectrum of radical **12** obtained from **3** was a triplet (a^N 1.50 mT) and from **4** a triplet of triplets [a^N 1.51, a^H 1.99 (2 H) mT; lit.[9] in benzene: a^N 1.51, a^H 1.99 (2 H) mT].

Discussion

The mode of formation of **1**, **5** *and* **6** *on reaction of tetranitromethane with 2-phenylpropene* (**3**). Reaction of tetranitromethane with 2-phenylpropene (**3**) in either dichloromethane or diethyl ether solution in the dark at 20 °C both give the nitro-trinitromethyl adduct **1** and the two isoxazolidines **5** and **6**, but with different adduct: isoxazolidine ratios. In dichloromethane solution these products were formed in essentially the same ratios, irrespective of whether the reaction was conducted photochemically (3.5 h) or in the dark (24 h).



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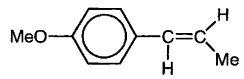

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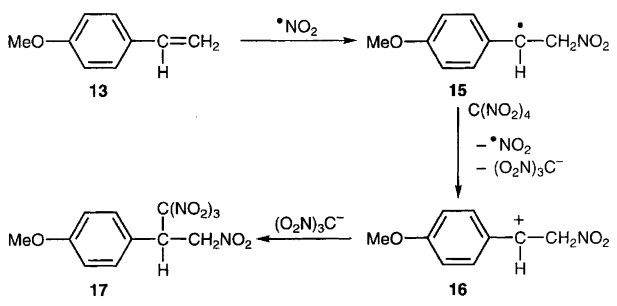
The regiochemistry of addition of the elements of tetranitromethane to 2-phenylpropene (**3**) to form adduct **1** is the same as that for the analogous additions to the 4-methoxystyrenes **13** and **14**,[10] the trinitromethyl group being located at the benzylic position. Nitro-trinitromethyl adduct formation from 4-methoxystyrene **13** proceeds via a radical chain reaction[11] initiated by attack of nitrogen dioxide to give the benzylic radical **15** (Scheme 1). Subsequent oxidation of this benzylic radical by tetranitromethane yields the carbocation **16**, trinitromethanide ion and nitrogen dioxide; reaction of the carbocation **16** with trinitromethanide ion completes the formation of the nitro-trinitromethyl adduct **17**. The formation of nitro-trinitromethyl adduct **1** is assumed to occur similarly.

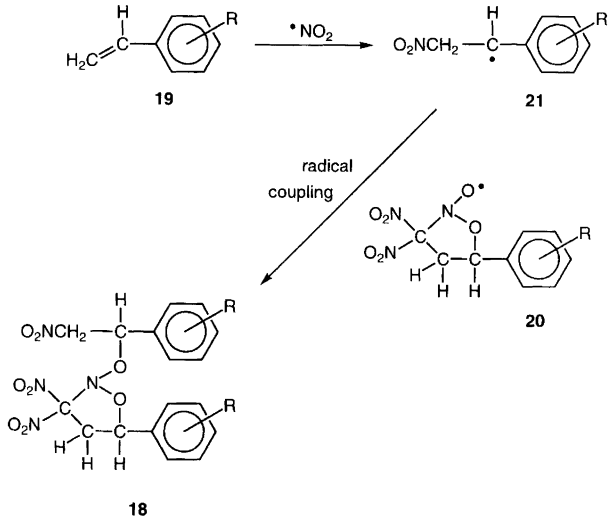
Isoxazolidines **18** are the major products of the reactions of substituted styrenes (**19**) with tetranitromethane,[1,12] either on long-term (several days) reaction with no deliberate illumination or more rapidly (1.5–7 h) under photochemical conditions. The isoxazolidines are assumed to be formed by reaction of the substituted aminoxyl radical **20** with the benzylic radical **21**, the latter arising from the reaction of nitrogen dioxide with the substituted styrene **19** (Scheme 2).[1] The aminoxyl **20** is formed by reaction of trinitromethanide ion with the substituted styrene radical cation (**19**$^{\cdot+}$), followed by cyclization of the benzylic radical **22** (Scheme 3).[1] Isoxazolidines **5** and **6** are assumed to be formed in an analogous manner from 2-phenylpropene (**3**).

Mode of formation of **9** *and* **10** *on reaction of tetranitromethane with 2',4',6'-trimethylstyrene* (**4**). The nitro-trinitromethyl adduct **9** is presumably formed via the radical chain mechanism suggested for the formation of **1** and **17** (Scheme 1). The mode of formation of the nitro ketone **10** is less certain. However, it appears that, under the conditions employed to form them, the isoxazolidines **18** partially fragment to give nitro ketones **23**,[1] for example by proton abstraction from C' and cleavage of the adjacent N–O bond. Given the greater degree of

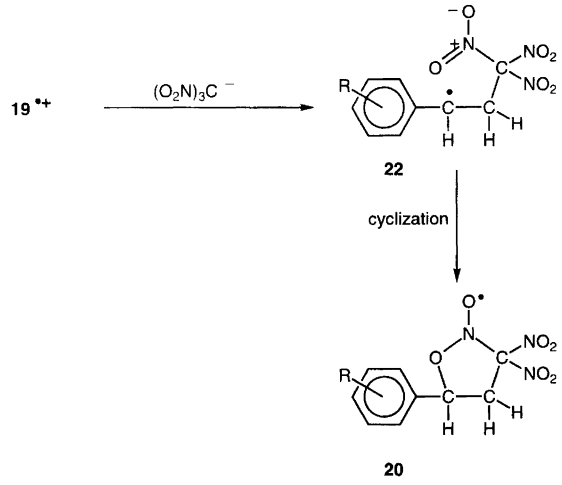


13 **15** **17** **16**

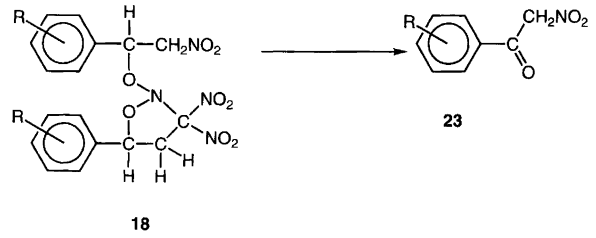
Scheme 1.



Scheme 2.

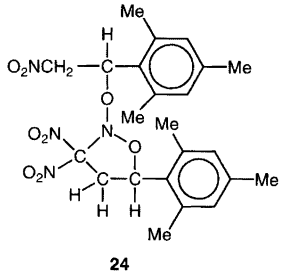


Scheme 3.



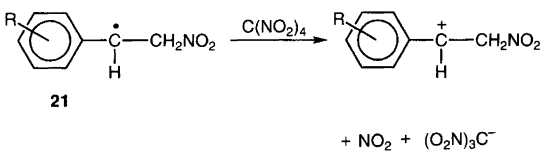
steric compression in the putative isoxazolidine **24** compared with isoxazolidines **18**, it could be expected that **24** might be significantly more labile and be converted completely into nitro ketone **10**.

Summarizing remarks. The various mechanisms discussed above and earlier[1,10] for the formation of products from the reaction between tetranitromethane and styrenes depend critically on the redox properties of the participating reagents and intermediates. To begin with the mode of formation of nitro-trinitromethyl adducts, the chain



mechanism exemplified in Scheme 1 has the electron transfer between radical **21** and tetranitromethane as the critical step (Scheme 4). No accurate value of the reversible potential of tetranitromethane is known, but a limited kinetic study, in combination with a treatment based on the Marcus theory of outer-sphere electron transfer, gave a preliminary value of $E°[C(NO_2)_4/C(NO_2)_4^{\cdot -}] \approx 0.2$ V vs. Ag/AgCl.[13] Redox potentials for the oxidation of two series of benzylic radicals have been determined[14] (relevant examples, see Table 3); these are located in the range of 0.30–0.84 V for benzylic radicals and 0.4–0.6 V lower for cumyl radicals. The presence of the nitro group in the β-position of radical **21** probably shifts the redox potentials somewhat upwards in relation to the benzylic radicals, but still the endergonicity of the electron transfer step would be in a range corresponding to fast or relatively fast reactions. Thus the kinetic requirements for an efficient chain reaction are satisfied.

The second problem concerns the mechanism of isoxazolidine and nitronic ester formation under dark conditions. In order to form the critical intermediate, aminoxyl radical **20**, the radical cation of the styrene **19**$^{\cdot +}$ must somehow be generated in a thermal reaction and be attacked by trinitromethanide ion forming radical **22** and eventually **20** by cyclization. Since styrenes are difficult to oxidize (for redox potentials of interest in this context, see Table 4),[15] a strong electron-transfer oxidant must be present in the reaction mixture. The most probable



Scheme 4.

Table 3. Redox potentials for the oxidation of some benzylic radicals.[14]

R	$E_{1/2}$/V vs. Ag/AgCl	R	$E_{1/2}$/V vs. Ag/AgCl
4-MeO	0.30	4-MeO	−0.10
4-Me	0.55	H	0.20
H	0.77		
4-Cl	0.84		

Table 4. Redox potentials for the oxidation of various styrenes.[15]

3-Chlorostyrene	2.26[a]	4-Acetoxystyrene	1.88[a]
Styrene	2.09	2,4,6-Trimethylstyrene	1.75[a]
4-Chlorostyrene	2.09	4-Methoxystyrene	1.53
4-Methylstyrene	1.91	β-Methyl-4-methoxystyrene	1.37
α-Methylstyrene (**3**)	1.89, 1.91[a]		

[a] E_p-Values determined by Osteryoung square-wave voltammetry in acetonitrile–Bu_4NPF_6 (0.15 mol dm^{-3}).

candidate is the nitrosonium ion, a strong electron transfer oxidant [$E°(NO^+/NO) = 1.3$ V],[16] shown[17] to be formed from N_2O_4 via its equilibrium with NO_2O–NO.

Experimental

Melting points are uncorrected. Infrared spectra were recorded on a Perkin Elmer 298 spectrophotometer; ^1H and ^{13}C NMR spectra were recorded on a Bruker 400 spectrometer. Mass spectrometry was performed on a JEOL JMS SX-102 instrument. Square wave voltammetry was performed by the BAS-100 instrument. Tetranitromethane was purchased from Aldrich, 2,4,6-trimethylstyrene from Lancaster Chemicals, and 2-phenylpropene from Fluka AG.

WARNING. It should be noted that mixtures of tetranitromethane with hydrocarbons are detonative within certain concentration limits.[18]

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 $\lambda_{cut\text{-}off}$ 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.

Reaction of 2-phenylpropene (**3**) *with tetranitromethane in dichloromethane.* A mixture of tetranitromethane (2.61 g; 2.02 mol dm^{-3}) and **3** (1.57 g; 2.02 mol dm^{-3}) in dichloromethane was stored in the dark for 24 h. The solvent was removed under reduced pressure at $\leqslant 0$ °C to give a residue the composition of which was shown by ^1H NMR spectroscopy to be nitro-trinitromethyl adduct **1** (44.0%), and isoxazolidines **5** (26.6%) and **6** (29.4%). Chromatography on a silica gel Chromatotron plate gave first *1-nitro-2-phenyl-2-trinitromethylpropane* (**1**), m.p. 54–55 °C (lit.[2] m.p. 53 °C). IR (KBr) 1615, 1595 (sh), 1585, 1572, 1555 cm^{-1}. ^1H NMR δ 7.53–7.51 (m, 2 H, ArH), 7.47–7.43 (m, 3 H, ArH), 5.80 (dq, $J_{H1a,H1b}$ 12.7 Hz, $J_{H1a,Me}$ 0.6 Hz, H1a), 5.32 (d, $J_{H1b,H1a}$ 12.7 Hz, H1b), 2.33 (d, $J_{Me,H1a}$ 0.6 Hz, Me). ^{13}C NMR δ 131.5, 130.9, 129.7, 129.0, 79.5 (C1), 51.4 (C2), 22.5 (Me). The above assignments were confirmed by double irradiation and heteronuclear correlation (HETCOR) experiments.

The next fraction eluted, after crystallization from dichloromethane–pentane, gave the pure (*RS,SR*)-isoxazolidine **5**, m.p. 117–118 °C (lit.[2] m.p. 114 °C) (X-ray crystal structure determined, below). In solution this compound exists as two *N*-invertimers in a ratio (1:1): ^1H NMR ($CDCl_3$) δ 7.56–7.21 (m, ArH), 7.14–7.10 (m, ArH), 6.61 (dd, $J_{H,H}$ 8.5 Hz, $J_{H,H}$ 1.2 Hz, ArH). ***N*-invertimer A:** 5.12 (d, $J_{Ha,Hb}$ 11.8 Hz, $C_{HaHb}NO_2$), 4.81 (d, $J_{Hb,Ha}$ 11.8 Hz, $CHaHbNO_2$), 4.04 [d, $J_{Hc,Hd}$ 15.0 Hz, $CHcHdC(NO_2)_2$], 3.65 [d, $J_{Hd,Hc}$ 15.0 Hz, $CHcHdC(NO_2)_2$], 2.18 (s, **Me**–C–CH_2NO_2), 1.88 [s, **Me**–C–CH_2–$C(NO_2)_2$]. ***N*-invertimer B:** 5.04 (d, $J_{Ha,Hb}$ 11.4 Hz, $CHaHbNO_2$), 4.78 (d, $J_{Hb,Ha}$ 11.4 Hz, $CHaHbNO_2$), 4.42 [d, $J_{Hc,Hd}$ 14.9 Hz, $CHcHdC(NO_2)_2$], 3.57 [d, $J_{Hd,Hc}$ 14.9 Hz, $CHcHdC(NO_2)_2$], 1.89 (s, **Me**–C–CH_2NO_2), 1.58 [s, **Me**–C–CH_2–$C(NO_2)_2$]. ^{13}C NMR ($CDCl_3$) δ ***N*-invertimer A:** 82.7 (CH_2–NO_2), 46.2 [CH_2–$C(NO_2)_2$], 32.3 [**Me**–C–CH_2–$C(NO_2)_2$], 22.9 (**Me**–C–CH_2NO_2). ***N*-invertimer B:** 83.15 (CH_2–NO_2), 42.7 [CH_2–$C(NO_2)_2$], 31.2 [**Me**–C–CH_2–$C(NO_2)_2$], 20.885 (**Me**–C–CH_2NO_2). The above assignments were made on the basis of double irradiation, difference NOE, long- and short-range heteronuclear correlation (HETCOR) experiments.

The next fraction eluted was the pure (*RR,SS*)-isoxazolidine **6**, an oil. In solution this compound exists as two *N*-invertimers in a ratio (1.7:1). ^1H NMR ($CDCl_3$) δ 7.43–7.14 (m, ArH), 6.84 (d, $J_{H,H}$ 8.6 Hz, ArH). **Major *N*-invertimer:** 5.22 (d, $J_{Ha,Hb}$ 13.5 Hz, $CHaHbNO_2$), 5.08 (d, $J_{Hb,Ha}$ 13.5 Hz, $CHaHbNO_2$), 4.13 [d, $J_{Hc,Hd}$ 15.0 Hz, $CHcHdC(NO_2)_2$], 3.68 [d, $J_{Hd,Hc}$ 15.0 Hz, $CHcHdC(NO_2)_2$], 1.97 [s, **Me**–C–CH_2–$C(NO_2)_2$], 1.88 (s, **Me**–C–CH_2NO_2). **Minor *N*-invertimer:** 4.90 (d, $J_{Ha,Hb}$ 12.95 Hz, $CHaHbNO_2$), 4.83 (d, $J_{Hb,Ha}$ 12.95 Hz, $CHaHbNO_2$), 4.39 [d, $J_{Hc,Hd}$ 15.0 Hz, $CHcHdC(NO_2)_2$], 3.60 [d, $J_{Hd,Hc}$ 15.0 Hz, $CHcHdC(NO_2)_2$], 1.93 (s, **Me**–C–CH_2NO_2), 1.54 [s, **Me**–C–CH_2–$C(NO_2)_2$]. ^{13}C NMR ($CDCl_3$) δ **Major *N*-invertimer:** 81.4 (CH_2–NO_2), 46.1 [CH_2-$C(NO_2)_2$], 32.3 [**Me**–C–CH_2–$C(NO_2)_2$], 23.8 (**Me**–C–CH_2NO_2). **Minor *N*-invertimer:** 81.0 (CH_2–NO_2), 43.6 [CH_2-$C(NO_2)_2$], 30.8 [**Me**–C–CH_2–$C(NO_2)_2$], 23.8 (**Me**–C–CH_2NO_2). The above assignments were made on the basis of double irradiation, difference NOE, long- and short-range heteronuclear correlation (HETCOR) experiments.

Reaction of 2-phenylpropene (**3**) *with tetranitromethane in diethyl ether.* A mixture of tetranitromethane (166 mg; 0.42 mol dm^{-3}) and 2-phenylpropene (**3**) (100 mg; 0.42 mol dm^{-3}) in diethyl ether was stored at 23 °C in

the dark for 29.5 h. The solvent was removed under reduced pressure at $\leqslant 0$ °C to give a residue the composition of which was shown by ^{1}H NMR spectroscopy to be nitro-trinitromethyl adduct **1** (27.8%), and isoxazolidines **5** (35.6%) and **6** (36.6%).

Photochemistry of 2-phenylpropene (**3**) *with tetranitromethane in dichloromethane.* A solution of **3** (500 mg, 0.53 mol dm^{-3}) and tetranitromethane (1.66 g, 1.06 mol dm^{-3}) in dichloromethane was irradiated with filtered light ($\lambda_{cut\text{-}off}$ 435 nm). After 3.5 h, when the colour of the reaction mixture had faded from yellow to nearly colourless, the volatile material was removed under reduced pressure at $\leqslant 0$ °C. The product composition determined by NMR spectroscopic analysis was nitro-trinitromethyl adduct **1** (47.1%), and isoxazolidines **5** (25.0%) and **6** (27.9%).

Reaction of 1-nitro-2-phenyl-2-trinitromethylpropane (**1**) *with 2,6-lutidine in (*^{2}*H)chloroform.* A solution of **1** (39 mg) and 2,6-lutidine (40 mg) in (^{2}H)chloroform (0.7 ml) was stored at 22 °C and its ^{1}H NMR spectrum was monitored until the complete disappearance (after 3 h) of **1**. The exclusive product of reaction was (*E*)-1-nitro-2-phenylpropene (**7**), ^{1}H NMR ($CDCl_3$) δ 7.41 (s, ArH), 7.28 (q, $J_{H,Me}$ 1.4 Hz, H1), 2.61 (d, $J_{Me,H}$ 1.4 Hz, Me) [lit.[5] quote for **7**: ^{1}H NMR ($CDCl_3$) δ 7.37 (s, ArH), 7.16 [d (!), $J_{H,Me} \leqslant 1.5$ Hz, H1], 2.58 (d, $J_{Me,H} \leqslant 1.5$ Hz, Me) and for **8**: δ 7.4–7.0 (m, ArH), 6.96 [d (!), $J_{H,Me} \leqslant 1.5$ Hz, H1], 2.13 (d, $J_{Me,H} \leqslant 1.5$ Hz, Me)].

Variable temperature studies on isoxazolidines **5** *and* **6**. Variable temperature ^{1}H NMR spectra were recorded on a Varian XL-300 using the solvent peak of ($^2H_3$)nitromethane as the internal shift standard. The dynamic NMR experiment is described by Sandström.[19] Temperature calibration of the NMR spectrometer was performed with methanol according to the method described by van Geet.[20] The rate constants were evaluated by visual fitting of the experimental spectra to spectra calculated by the McConnell classical formalism,[21] or by DNMR5.[22] The evaluations of T_2 and δν values for bandshape calculations were performed as described previously.[23] Errors in activation parameters have been given with the assumption that the temperature could be determined with the accuracy of ±1 K.

General procedure for the photonitration of 2,4,6-trimethylstyrene (**4**) *with tetranitromethane.* A solution of **4** (500 mg, 0.43 mol dm^{-3}) and tetranitromethane (0.86 mol dm^{-3}) in dichloromethane or acetonitrile at 15 °C was irradiated with filtered light ($\lambda_{cut\text{-}off}$ 435 nm). After the colour of the reaction mixture had changed from orange to pale yellow the volatile material was removed under reduced pressure at $\leqslant 0$ °C, and the product composition of each sample determined by NMR spectral analysis.

Photochemistry of 2,4,6-trimethylstyrene (**4**) *in dichloromethane.* Reaction of **4**–tetranitromethane in dichloromethane, as above, for 45 min resulted in complete conversion into a mixture of 2-(2′,4′,6′-trimethylphenyl)-1-nitro-2-trinitromethylethane (**9**) (58.0%), nitro ketone **10** (24.5%) and some unidentified adducts (total 17.5%). Chromatography of this mixture on a silica gel Chromatotron plate gave first *2-(2′,4′,6′-trimethylphenyl)-1-nitro-2-trinitromethylethane* (**9**), m.p. 76–77 °C (Found: M^+ 342.0811. $C_{12}H_{14}N_4O_8$ requires 342.0814). IR (KBr) 1600, 1577, 1558 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 6.91, 6.90 (each s, ArH), 6.40 (dd, $J_{H2,H1a}$ 9.6 Hz, $J_{H2,H1b}$ 3.6 Hz, H2), 5.32 (dd, $J_{H1a,H1b}$ 13.7 Hz, $J_{H1a,H2}$ 9.6 Hz, H1a), 5.20 (dd, $J_{H1b,H1a}$ 13.7 Hz, $J_{H1b,H2}$ 3.6 Hz, H1b), 2.34 (Me), 2.25 (Me), 2.19 (Me). ^{13}C NMR ($CDCl_3$) δ 132.85, 131.5, 74.4 (C1), 43.8 (C2); the remainder of the spectrum was not visible in a weak spectrum. The above assignments were confirmed by heteronuclear correlation (HETCOR) spectra.

The second material eluted was pure *nitro ketone* **10**, m.p. 65–66 °C (Found: M^+ 207.0899. $C_{11}H_{13}NO_3$ requires 207.0897). IR (KBr) 1710, 1560 cm^{-1}. In (^{2}H)chloroform solution this material exists substantially in enolized form in solution[4] and the ^{1}H NMR spectrum reflected this, signals being observed as follows: δ 6.94 (relative integral 0.73), 6.91 (1.05), 6.84 (0.27), 5.50 (1.00), 2.33 (1.06), 2.32 (3.80), 2.305 (3.27).

Photochemistry of 2,4,6-trimethylstyrene (**4**) *in acetonitrile.* Reaction of **4**–tetranitromethane in acetonitrile, as above, for 30 min resulted in complete conversion into a mixture of 2-(2′,4′,6′-trimethylphenyl)-1-nitro-2-trinitromethylethane (**9**) (56.8%), nitro ketone **10** (9.7%) and a large number of unidentified adducts (total 33.5%).

Reaction of 2-(2′,4′,6′-trimethylphenyl)-1-nitro-2-trinitromethylethane (**9**)*with 2,6-lutidine in (*^{2}*H)chloroform.* A solution of **9** (28 mg) and 2,6-lutidine (30 mg) in (^{2}H)chloroform (0.7 ml) was stored at 22 °C and its ^{1}H NMR spectrum was monitored until the complete disappearance (after 18 min) of **9**. The exclusive product of reaction was (E)-*2-(2′,4′,6′-trimethylphenyl)-1-nitropropene* (**11**), ^{1}H NMR ($CDCl_3$) δ 8.26 (d, $J_{H1,H2}$ 13.9 Hz, H1), 7.28 (d, $J_{H2,H1}$ 13.9 Hz, H2), 6.93 (s, 2 H, ArH), 2.37 (s, 6 H, 2′-, 6′- Me), 2.29 (s, 4′-Me) [lit.[8] quote for **11**: ^{1}H NMR ($CDCl_3$) δ 8.26 (d, $J_{H1,H2}$ 13.9 Hz, H1), 7.28 (d, $J_{H2,H1}$ 13.9 Hz, H2), 6.94 (s, 2 H, ArH), 2.38 (s, 6 H, 2′-, 6′-Me), 2.30 (s, 4′-Me).

Kinetics of elimination of nitroform from nitro-trinitromethyl adducts **1** *and* **9**. The kinetics of elimination from **1** and **9** were 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^{-3}) 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.

Crystallography.

Crystal data for isoxazolidine **5**, $C_{19}H_{20}N_4O_8$, M 432.39, triclinic, $P\bar{1}$, $a=9.6356(12)$, $b=9.7619(14)$, $c=23.710(5)$ Å, $a=87.91(2)$, $b=82.49(2)$, $g=64.631(9)°$; $V=1997.4(5)$ Å^3, $Z=4$, $D_c=1.438$ g cm^{-3}, $\lambda=0.710\,73$, graphite monochromated Mo-Kα X-radiation, μ(Mo Kα) 1.14 cm^{-1}, $F(000)=904$, $T=173$ K. Data were collected on a Siemens SMART Area Detector diffractometer for a hemisphere of reciprocal space for $1.73>2\theta>27.50°$. The crystal was colourless and of approximate dimensions $0.48\times0.42\times0.20$ mm. The structure was solved by direct methods and refined by full-matrix least-squares methods (563 parameters) against all 4916 unique data with $I>2\sigma(I)$ to a final $R1=0.0527$ for the 4916 reflections with $I>2\sigma(I)$. Atomic coordinates, bond lengths and angles, and thermal parameters for isoxazolidine **5** have been deposited at the Cambridge Crystallographic Centre.

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References

1. Eberson, L., Hartshorn, M. P. and Persson, O. *Acta Chem. Scand. 52* (1998) 751.
2. Ratsono, E. V., Altukhov, K. V. and Perekalin, V. V. *Zhur. Org. Khim. 9* (1973) 58.
3. Hassan, A., Wazeer, M. I. M., Perzonowski, H. P. and Ali, S. A. *J. Chem. Soc., Perkin Trans. 2* (1997) 411.
4. Butts, C. P., Eberson, L., Hartshorn, M. P., Persson, O. and Robinson, W. T. *Acta. Chem. Scand. 49* (1995) 253.
5. Miller, D. B., Flanagan, P. W. and Schechter, H. *J. Org. Chem. 41* (1976) 2112.
6. Eliel, E. L. and Wilen, S. H. *Stereochemistry of Organic Compounds*, Wiley, New York 1994, p. 57.
7. For a general review of such enolization phenomena, see: Nielsen, A.T. In Feuer, H., Ed., *The Chemistry of the Nitro and Nitroso Groups*, Part 1, Interscience, New York, 1969, p. 349.
8. Van Eijk, P. J. S. S., Overkempe, C., Trompenaars, W. P., Reinhoudt, D. N., Manninen, L. M., van Hummel, G. J. and Harkema, S. *Recl. Trav. Chim Pays-Bas. 107* (1988) 27.
9. Jonkman, L., Muller, H., Kiers, H. and Kommandeur, J. *J. Phys. Chem. 74* (1970) 1650; Jonkman, L., Muller, H. and Kommandeur, J. *J. Am. Chem. Soc. 93* (1971) 5833.
10. Eberson, L., Hartshorn, M. P. and Persson, O. *Acta Chem. Scand. 52* (1998) 745.
11. Masnovi, J. M. and Kochi, J. K. *Recl. Trav. Chim. Pays-Bas 105* (1986) 286.
12. Altukhov, K. V., Tartakovskii, V. A. and Perekalin, V. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* (1967) 197; Ratsino, E. V. and Altukhov, K. V. *Zhur. Org. Khim. 8* (1972) 2281; Mathew, L., Varghese, B. and Sankararaman, S. *J. Chem. Soc.., Perkin Trans. 2* (1993) 2399.
13. Eberson, L. and Radner, F. *J. Am. Chem. Soc. 113* (1991) 5825.
14. Sim, B. A., Milne, P. H., Griller, D. and Wayner, D. D. M. *J. Am. Chem. Soc. 112* (1990) 6635.
15. Schepp, N. P. and Johnston, L. J. *J. Am. Chem. Soc. 118* (1996) 2872.
16. Lee, K. Y., Amatore, C. and Kochi, J. K. *J. Phys. Chem. 95* (1991) 1285; Lee, K. Y., Kuchynka, D. J. and Kochi, J. K. *Inorg. Chem. 29* (1990) 4196; Boughriet, A. and Wartel, M. *J. Chem. Soc., Chem. Commun.* (1989) 809; Bontempelli, G., Mazzocchin, G.-A. and Magno, F. *J. Electroanal. Chem. 55* (1974) 91.
17. Bosch, E. and Kochi, J. K. *J. Org. Chem. 59* (1994) 3314.
18. Tschinkel, J. G. *Ind. Eng. Chem. 48* (1965) 732.
19. Sandström, J. *Dynamic NMR Spectroscopy*, Academic Press, London 1982, p. 66.
20. van Geet, A. L. *Anal. Chem. 40* (1968) 2227; *42* (1970) 679.
21. McConnell, H. M. *J. Chem. Phys. 28* (1958) 430.
22. Stephensen, D. S. and Binsch, G. *Quantum Chemistry Program Exchange 11* (1978) 365.
23. Berg, U. and Sjöstrand, U. *Org. Magn. Reson. 11* (1978) 557.

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