Photochemistry of Charge Transfer Complexes of Styrene Derivatives with Tetranitromethane. X-Ray Crystal Structure of a Novel Dimeric Adduct from *p*-Methylstyrene

Lizamma Mathew,[a] **Babu Varghese**[b] **and S. Sankararaman** *[,a]
[a] *Department of Chemistry, Indian Institute of Technology, Madras 600 036, India*
[b] *Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Madras 600 036, India*

Styrene and its derivatives form coloured charge transfer complexes with tetranitromethane as the acceptor. These complexes are stable in acetonitrile under neutral conditions in the dark for several days. Photochemistry of these complexes was found to be highly dependent on the structure and substituent effects on the styrene. The structure of the dimeric adduct **2b** from *p*-methylstyrene is determined by X-ray crystallography and it clearly establishes the ambident reactivity of the trinitromethide anion to act as an oxygen nucleophile in the present case, which is in contrast to its well known reactivity as a carbon nucleophile in the previously reported adducts from other aromatic substrates.

Tetranitromethane (TNM) is a strong electron acceptor and forms coloured charge transfer (CT) complexes with a variety of donors like amines, aromatic hydrocarbons, olefins and sulfides.[1] The stability of the CT complexes is dependent on several factors such as the structural properties and ionization potential of the donors, and solvent polarity. The photochemistry of the CT complexes of aromatic compounds with TNM is well established.[2] Similarly the chemistry of the thermally labile complexes of reactive olefins such as 1,1-bis(*p*-methoxyphenyl)-ethene,[3] *N*-vinylcarbazole, and vinylanthracene is also well characterised.[4] However, considerable ambiguity exists in the literature over the stability and chemistry associated with the CT complexes of simple olefins.[5] In this study we have focussed our attention on the thermal stability and photochemistry of the CT complexes of styrene and its derivatives.

Results and Discussion

When *p*-methylstyrene (**1b**) was added to a colourless solution of TNM in acetonitrile, the mixture turned bright yellow instantaneously due to the formation of the CT complex. The solution when protected from light was stable for several days as evidenced from the persistence of the colour and also from the analysis of the mixture by TLC. However, upon irradiation with visible light the colour of the solution turned to pale yellow within 4–6 h and the TLC of the photolysate showed the disappearance of *p*-methylstyrene and formation of a single major product. Work-up of the reaction mixture yielded an orange slurry from which the product was obtained in 85% yield as a colourless crystalline solid by recrystallization from a mixture of dichloromethane and methanol. Based on the spectroscopic data and elemental analysis the product was identified as 3,3-dinitro-2-[1-(4-methylphenyl)-2-nitroethoxy]-5-(4-methylphenyl)isoxazolidine (**2b**), Scheme 1. The structure was further confirmed by X-ray crystallography (Fig. 1 and Tables 1 and 2). The 'envelope' conformation of the isoxazolidine ring is clearly evident from the crystal structure [Fig. 1(*a*)]. The high resolution ^{1}H NMR spectrum of the crude product showed the formation of **2b** as a mixture of diastereoisomers in the ratio 8:1. The crystal structure given in Fig. 1 is that of the major isomer. The methylene protons in **2b** are diastereotopic and they appeared as four distinct, well resolved double doublets and the methine protons appeared as an overlapping multiplet. The coupling pattern was deduced from proton double resonance and COSY spectra. The crystal structure of **2b** is unique in that the trinitromethyl group is bonded through both the carbon and the oxygen. A similar structure has been recently reported in which one nitro of the trinitromethyl group forms part of the

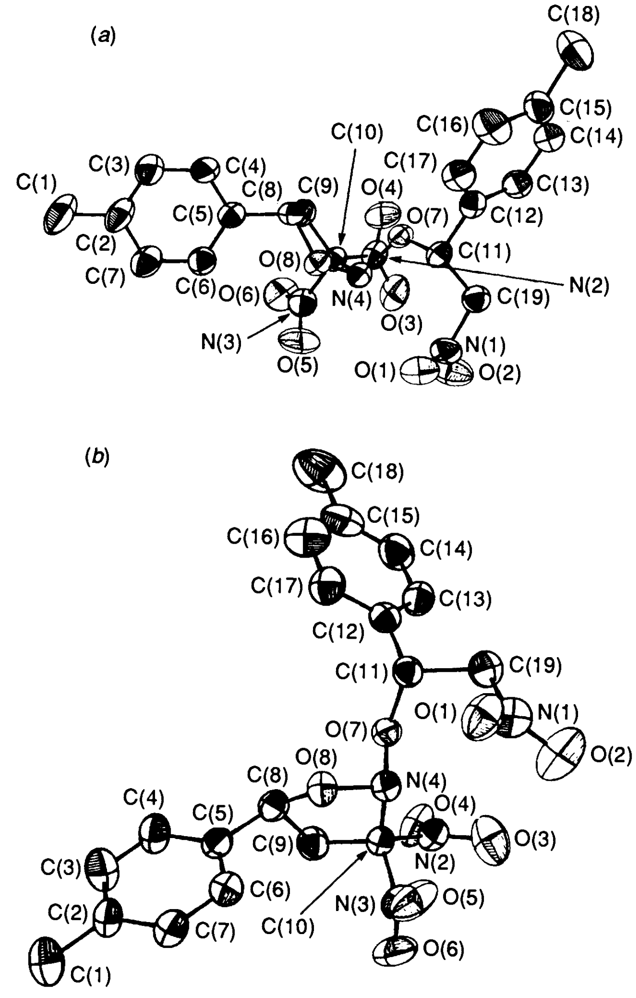
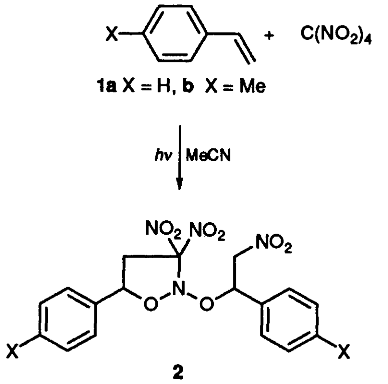


Fig. 1 (*a*) ORTEP diagram of the molecular structure of **2b** showing the 'envelope' conformation of the isoxazolidine ring; (*b*) another perspective view of **2b** showing the trinitromethyl as part of the isoxazolidine ring

Table 1 Selected bond distances in **2b**

Bond	d/Å[a]
C(5)–C(8)	1.506(4)
C(8)–C(9)	1.535(4)
C(8)–O(8)	1.468(3)
C(9)–C(10)	1.498(4)
C(10)–N(2)	1.514(4)
C(10)–N(3)	1.524(4)
C(10)–N(4)	1.474(4)
C(11)–C(12)	1.497(4)
C(11)–C(19)	1.505(4)
C(11)–O(7)	1.458(3)
C(19)–N(1)	1.500(4)
N(1)–O(1)	1.207(3)
N(1)–O(2)	1.217(3)
N(2)–O(3)	1.208(3)
N(2)–O(4)	1.207(3)
N(3)–O(5)	1.205(4)
N(3)–O(6)	1.214(4)
N(4)–O(7)	1.442(3)
N(4)–O(8)	1.407(3)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.



Scheme 1

1,3,2-dioxazolidine ring.[6] In all the previously reported photoadducts of TNM the trinitromethyl is bonded only through the carbon.[7]

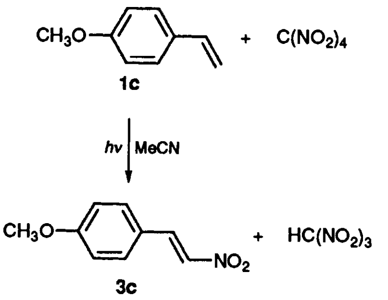
Photolysis of the styrene (**1a**) complex in acetonitrile also yielded the corresponding isoxazolidine derivative **2a** in 85% yield as a mixture of diastereoisomers in the ratio of 6:1, Scheme 1.

It must be mentioned that the thermal reaction of styrene with TNM has been reported to give **2a** in 60% yield after 60 h at room temperature[8] which might have been due to the photolysis of the CT complex by adventitious room light, since in our control experiments in the dark we did not observe any thermal reaction of styrene and TNM. In sharp contrast to the behaviour of styrene and *p*-methylstyrene, a very slow thermal reaction (in the dark) was observed with *p*-methoxystyrene (**1c**) and the product was identified as 1,1,1,3-tetranitro-2-(4-methoxyphenyl)propane, which is consistent with the previously reported results.[3,9] However, by comparison under identical experimental conditions we found that the photoreaction of *p*-methoxystyrene in acetonitrile was much more efficient and yielded *p*-methoxy-β-nitrostyrene (**3c**) as the only product, Scheme 2. The photoreaction was complete within 2 h whereas under identical conditions the thermal dark reaction had proceeded only to an extent of about 10% in 2 h. Thermal reaction in the presence of pyridine has been reported to give **3c** in good yield.[10]

Table 2 Selected bond angles in **2b**

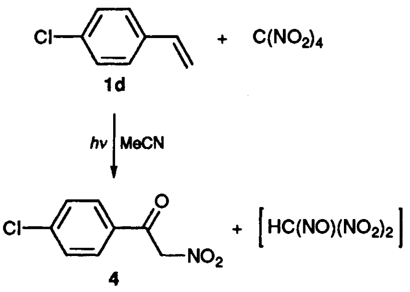
Atoms	Angle/°[a]
O(1)–N(1)–O(2)	124.8(3)
O(1)–N(1)–C(19)	118.4(3)
O(2)–N(1)–C(19)	116.7(3)
O(3)–N(2)–O(4)	126.4(3)
O(3)–N(2)–C(10)	115.4(3)
O(4)–N(2)–C(10)	118.2(3)
O(5)–N(3)–O(6)	125.4(3)
O(5)–N(3)–C(10)	120.1(3)
O(6)–N(3)–C(10)	114.5(3)
O(7)–N(4)–O(8)	107.4(2)
O(7)–N(4)–C(10)	102.8(2)
O(8)–N(4)–C(10)	100.6(2)
C(5)–C(8)–C(9)	115.0(3)
C(5)–C(8)–O(8)	108.4(2)
C(9)–C(8)–O(8)	103.8(2)
C(8)–C(9)–C(10)	102.8(2)
C(9)–C(10)–N(2)	116.7(3)
C(9)–C(10)–N(3)	112.1(3)
C(9)–C(10)–N(4)	107.8(2)
N(2)–C(10)–N(3)	104.0(2)
N(2)–C(10)–N(4)	108.9(2)
N(3)–C(10)–N(4)	106.9(2)
N(4)–O(7)–C(11)	107.5(2)
C(8)–O(8)–N(4)	109.5(2)
O(7)–C(11)–C(12)	105.9(2)
O(7)–C(11)–C(19)	111.5(3)
C(12)–C(11)–C(19)	113.2(3)
C(11)–C(19)–N(1)	113.3(3)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.



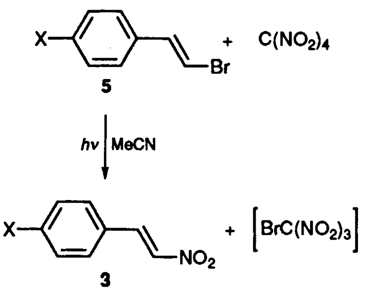
Scheme 2

The CT complex of *p*-chlorostyrene (**1d**) and TNM was found to be stable for several days when protected from room light. When the mixture was photolysed deliberately using visible light the bleaching of the CT band was observed. Upon work-up of the reaction mixture *p*-chloro-α-nitroacetophenone (**4**) was obtained in 90% yield, Scheme 3. The product was thoroughly characterised by various spectroscopic and elemental analysis data.



Scheme 3

The photo-behaviour of the CT complexes of β-bromostyrene and its *para*-substituted derivatives with TNM was markedly different from the above mentioned styrene derivatives, in that the β-bromostyrene derivatives (**5a–d**) underwent nitrodebromination reaction upon CT excitation to give the corresponding β-nitrostyrene derivatives (**3a–d**) in good yields, Scheme 4. The



a X = H, **b** X = Me, **c** X = OMe, **d** X = Cl

Scheme 4

time resolved spectroscopy of the CT complexes of aromatic compounds is well established.[11] The CT excitation of the CT complexes of TNM leads to electron transfer from the donor to TNM in accordance with the Mulliken's theory[12] of CT to yield the donor radical cation, NO_2, and trinitromethide anion. The solvent effects on the dynamics of these triad of intermediates is such that in non polar solvents such as dichloromethane in-cage ion-pair annihilation leading to the formation of trinitromethylated product predominates whereas in polar solvents such as acetonitrile out-of-cage radical pair collapse leading to the formation of nitration products is the major pathway.[11b] The wide variety of products obtained from styrene and its derivatives (*vide infra*) can be explained on the same mechanistic lines [Scheme 5(*a*) and (*b*)],through the formation of a common intermediate, the benzyl cation **7**, initially formed by radical pair collapse of the styrene radical cation and NO_2 in acetonitrile at the terminal vinylic carbon as shown [Scheme 5(*c*)]. Such a regiospecific radical pair collapse at the terminal position is dictated by the high electron spin density at that position in the radical cation of styrene, as evident from the large hyperfine coupling constant observed with the protons attached to the terminal carbon in the EPR spectrum.[13] Formation of the observed final products can be explained by the effect of substituents X and Y on the stability and reactivity of **7** as shown in Schemes 6–9.

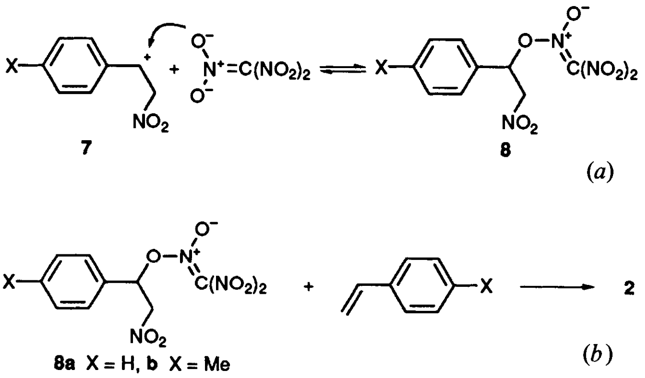
$$p\text{-XC}_6\text{H}_4\text{CH{=}CHY} + \text{C(NO}_2)_4 \rightleftharpoons [p\text{-XC}_6\text{H}_4\text{CH{=}CHY, C(NO}_2)_4] \quad (a)$$

$$[p\text{-XC}_6\text{H}_4\text{CH{=}CHY, C(NO}_2)_4] \xrightarrow[\text{MeCN}]{h\nu_{\text{CT}}} p\text{-XC}_6\text{H}_4\text{CH{=}CHY}^{\bullet+} + {}^{\bullet}\text{NO}_2 + \text{C(NO}_2)_3^- \quad (b)$$

$$\underset{\mathbf{6}}{p\text{-XC}_6\text{H}_4\text{CH{=}CHY}^{\bullet+}} + {}^{\bullet}\text{NO}_2 \longrightarrow \underset{\mathbf{7}}{p\text{-XC}_6\text{H}_4\overset{+}{\text{C}}\text{H-CH(Y)NO}_2} \quad (c)$$

X = H, Me, OMe, Cl; Y = H, Br

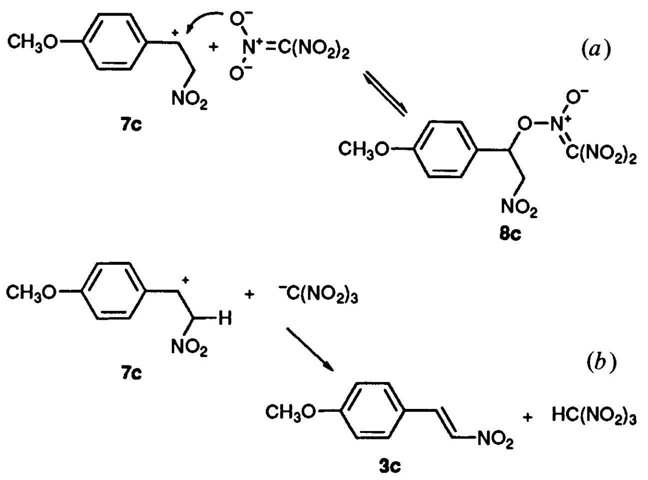
Scheme 5



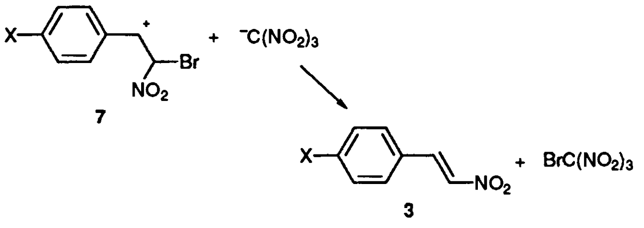
Scheme 6

When X = H and Me and Y = H (Scheme 6) intermediate **7** undergoes ion pair annihilation with trinitromethide anion. The trinitromethide anion is an ambident nucleophile and can either undergo O- or C-alkylation. The ambident reactivity of the trinitromethide anion can be compared with that of the anion from 2-methyl-2-nitropropane, studied in detail by Kornblum.[14] The fate of the O-alkylated intermediate **8** depends on the rates of the further reactions such as those in Schemes 6(*b*) and 9. In the absence of any further reaction the O-alkylation, which is subject to kinetic control,[14] might be reversible [Schemes 6(*a*) and 7(*a*)] and competing deprotonation [Scheme 7(*b*)] and C-alkylation can occur. In the present case formation of **2a** and **b** clearly indicates initial O-alkylation to give a 1,3-dipolar intermediate species **8** [Scheme 6(*a*)], followed by a regiospecific 1,3-dipolar cycloaddition with another molecule of styrene [Scheme 6(*b*)] as suggested earlier by Perekalin and co-workers.[8,15] The observed stereoselectivity in the formation of **2a** and **b** could arise from the stereoselective nature of the 1,3-dipolar cycloaddition step.[16]

When X = OMe and Y = H (Scheme 7) the resulting benzylic cation **7c** is relatively more stable and hence deprotonation [Scheme 7(*b*)] to give **3c** effectively competes with O-alkylation which might be reversible, Scheme 7(*a*). Similarly when X = H, Me, OMe and Cl and Y = Br (Scheme 8), debromination competes with alkylation to yield the corresponding nitrostyrenes **3a–d** as the product. Such a nitrodebromination mechanism is similar to the mechanism proposed for the debromination of α-bromo-α-nitrobenzyl cation and the corresponding benzyl radical intermediates involved in the nitration of β-bromostyrene to β-nitrostyrene.[17] Nitrodebromination is also commonly observed in aromatic nitration involving an ipso Wheland intermediate with bromine as the electrofuge.[18]

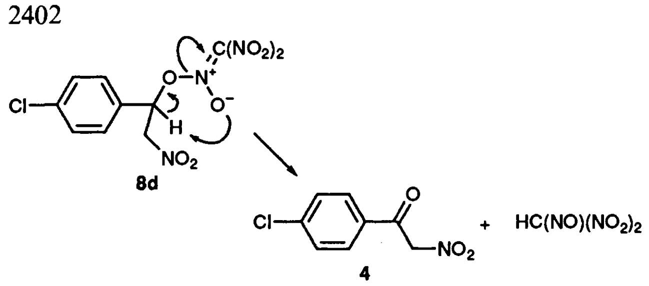


Scheme 7



Scheme 8

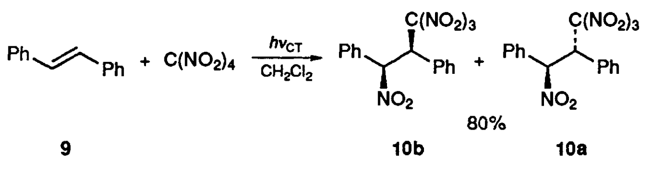
p-Chloro-α-nitroacetophenone **4** from *p*-chlorostyrene (**1d**) arises, presumably, from the decomposition of the O-alkylated product **8d**, Scheme 9. Since **4** is formed in very good yield the



Scheme 9

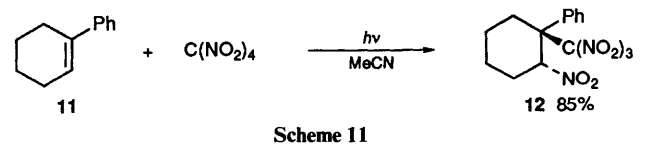
decomposition of the O-alkylated intermediate **8d** must compete effectively with the 1,3-dipolar cycloaddition and the deprotonation reactions. At present we are unable to find a satisfactory explanation for the unusual behaviour of *p*-chlorostyrene.

Due to the poor solubility of *trans*-stilbene (**9**) in acetonitrile the CT photochemistry was carried out in dichloromethane. The orange solution of a mixture of stilbene and TNM in dichloromethane was stable for several days when left in the dark. Upon photolysis of the mixture bleaching of the orange colour was observed and analysis of the reaction mixture by TLC indicated the complete disappearance of stilbene and formation of products. After work-up, the crude product was chromatographed over silica gel and two products were isolated, purified and identified as *threo* and *erythro* isomers of 2,3-diphenyl-1,1,1,3-tetranitropropane (**10a,b**), Scheme 10. The structure of the diastereoisomers was assigned on the basis of elemental analysis and spectroscopic data. In the ^{13}C NMR spectra of **10a** and **b** the carbon bearing the $C(NO_2)_3$ group appeared at δ 52.3 and 55.3, respectively indicating that the group is attached through the carbon (C-alkylation) and not the oxygen, in which case these resonances are expected around δ 80 ppm.[19] The relative stereochemistry of **10a** and **b** is assigned on the basis of the vicinal coupling constant of the two methine hydrogens.[20] In isomer **10a** the coupling constant is 11.4 Hz and in **10b** it is 5.8 Hz. Based on the relative stabilities of the conformers in these two diastereoisomers it is expected that in **10a** the average dihedral angle between the two hydrogens will be much larger than that in **10b**.[20] Accordingly we assign **10a** (m.p. 147 °C) to be the *threo* and **10b** (m.p. 96 °C) to be the *erythro* isomer.



Scheme 10

Photolysis of a mixture of 1-phenylcyclohexene (**11**) and TNM yielded a single diastereoisomer of 2-nitro-1-phenyl-1-trinitromethylcyclohexane (**12**) in 85% yield as a colourless crystalline solid, Scheme 11. The elemental analysis and spectroscopic data are consistent with the structure of **12**. The addition of NO_2 and $C(NO_2)_3$ is regiospecific. In the ^1H NMR spectrum of **12**, 2-H appeared at 5.6 ppm as a double doublet (J = 11.2 and 3.9) due to coupling with the diastereotopic protons on the adjacent carbon and C-2 itself appeared at 88.8 ppm as a doublet in the ^{13}C NMR off resonance spectrum, consistent with NO_2 being attached to C-2. From the coupling constants we infer that the nitro group is in the equatorial position.[19] The resonance of C-1 appeared at 58.1 ppm consistent with the C-alkylation product. The relative stereochemistry on C-1 is assigned only based on the assumption that the bulkier trinitromethyl group would tend to occupy the equatorial position, and the phenyl, the axial position. In the case of stilbene and 1-phenylcyclohexene the absence of dimeric products similar to **2** may be due to steric hindrance which prevent the 1,3-dipolar cycloaddition step of the initial O-alkylation product. Formation of dinitroisoxazolidine derivative similar to **2** has been reported in case of **11** when the reaction was carried out in the presence of another sterically unhindered alkene which acts as the 1,3-dipolarophile to trap the intermediate nitronic ester of trinitromethane (O-alkylated product similar to **8**).[21] Thus in the absence of any competing reactions the O-alkylated 1,3-dipolar intermediate could revert to the more stable C-alkylated product, Scheme 7(*a*). The photoinitiated thermal nitration of **11** has been reported to give a nondescript oily mass of unstable material after 2 days.[4] A radical initiated chain reaction mechanism has been proposed and radical addition and oxidative cleavage of the double bond leads to a mixture of products which are not identified. Compared to the reactive olefins such as *N*-vinylcarbazole which yielded a well defined and stable TNM adduct in good yield under radical initiated reaction, the less reactive olefins such as cyclohexene and 1-phenylcyclohexene (**11**) failed to undergo photoinitiated reaction with TNM efficiently presumably because of inefficient chain mechanism. These limitations are overcome in the present study by continuous photolysis and thus adduct **12** has been obtained in good yield from **11**. Though the radical initiated chain mechanism may be operative it is very slow and non-selective compared to the stoichiometric reaction which is very selective towards the formation of **12**. Thus the photoinitiated thermal reaction of TNM with olefins which gives a mixture of products differs from the continuous CT excitation which is very selective and gives well defined and isolable products in short duration.



Scheme 11

Experimental

Materials.—Styrene (Aldrich), *p*-methylstyrene (Aldrich), *p*-methoxystyrene (Aldrich), *trans*-stilbene (Fluka) and *p*-chlorostyrene (Aldrich) were used as received. 1-Phenylcyclohexene was prepared from cyclohexanone by the addition of phenyl magnesium bromide followed by dehydration with 85% H_3PO_4. β-Bromostyrene and its *para*-substituted derivatives were prepared by a literature reported procedure[22] and were purified and thoroughly characterised by spectroscopic methods before use. Tetranitromethane was prepared from acetic anhydride and fuming nitric acid according to a literature procedure[23] and stored in a freezer. Acetonitrile and dichloromethane were distilled from P_2O_5.

Instrumentation.—M.p.s were determined on a microscope heating unit of Toshniwal (India) melting point apparatus and are uncorrected. IR spectra were recorded on a Shimadzu IR-470 spectrometer. High resolution NMR spectra were recorded on a JEOL GSX 400NB FT spectometer operating at 400 for ^1H and at 100.5 MHz for ^{13}C. The NMR spectra were recorded with Me_4Si as the internal standard. In the ^{13}C NMR data the signal multiplicity from the off-resonance spectra is given in parentheses. *J*-Values in Hz. MS data were obtained from a Finnigan-Mat 8230 mass spectrometer (EI, 70 eV). The elemental analysis were done using a Heraeus-CHN analysis instrument. (The Kinetics and Catalysis Division, Department of Chemistry, Indian Institute of Technology, Madras.) The

UV–VIS spectra were recorded on a Shimadzu UV240 spectrometer. The photoreactions were performed using a focussed beam from a 150 W xenon arc lamp source (Applied Photophysics) using a blue filter (cut-off wavelength $340 < \lambda > 480$ nm).

General Procedure for Photolysis of CT Complexes.—A mixture of the styrene donor (0.5 g) and TNM (1–2.0 equiv.) in CH_3CN (10 cm^3) was kept in a pyrex tube that was immersed in ice-cold water contained in a dewar flask fitted with quartz windows. The solution was deaerated for 10 min by passing argon. A focussed beam from a 150 W xenon arc lamp passing through a blue filter was used to photolyse the mixture and the blue filter ensured the irradiation of only the CT band. Photolysis was carried out until the disappearance of the CT band or the disappearance of the styrene donors analysed by TLC. The photolysate was diluted with CH_2Cl_2 (25 cm^3), washed with ice-cold 10% aq. sodium hydrogen carbonate and then washed with ice-cold water. The organic layer was separated, dried (anhyd. sodium sulfate) and then solvent was removed at a rotary evaporator to give the crude product. The products were separated and purified either by column chromatography over silica gel or by recrystallization from a suitable solvent as discussed in the individual cases.

p-*Methylstyrene* (**1b**). A solution containing **1b** (0.5 g, 3.8 mmol) and TNM (0.75 g, 3.8 mmol) in CH_3CN (10 cm^3) was photolysed for 4 h. After workup the crude product was obtained as a solid. From the high resolution ^{1}H NMR spectral peak integration of the crude product we inferred that **2b** was formed as a mixture of diastereoisomers in the ratio 8:1. The crude was dissolved in minimum amount of CH_2Cl_2 and CH_3OH was added until turbidity appeared and then the solution was left in the freezer to afford 0.7 g (85%) of a single diastereoisomer of **2b** as a colourless crystalline solid: m.p. 114 °C (Found: C, 52.2; H, 4.4; N, 12.6. $C_{19}H_{20}N_4O_8$ requires C, 52.7; H, 4.6; N, 12.9%); $\nu_{max}(CCl_4)$/cm^{-1} 3010m, 2976m, 1580s, 1550m (NO_2), 1510w, 1410m, 1350s (NO_2), 1300m, 1230m, 1017m, 887s, 800s, 755m and 725m; $\delta_H(CDCl_3)$ 7.2 (8 H, m, Ar), 5.74 (2 H, m, methine), 5.1 (1 H, dd, *J* 13.5, 7.3, $C\mathit{H}^aH^bNO_2$), 4.52 (1 H, dd, *J* 13.5, 5.86, $CH^a\mathit{H}^bNO_2$), 4.10 (1 H, dd, *J* 15.6, 7.81, 4-H^a), 3.0 (1 H, dd, *J* 15.6, 7.3, 4-H^b), 2.36 (3 H, s, CH_3) and 2.34 (3 H, s, CH_3); proton decoupling double irradiation experiments and COSY spectrum clearly established the coupling partners and coupling pattern; $\delta_C(CDCl_3)$ 139.7 (s), 139.5 (s), 130.9 (s), 130.8 (s), 129.6 (d), 129.5 (d), 127.4 (d), 126.5 (d), 83.6 (d, $\mathit{C}HCH_2NO_2$), 80.7 (d, C-5), 76.5 (t, CH_2NO_2), 41.2 (t, C-4), 21.2 (q, CH_3) and 21.1 (q, CH_3); *m/z* (EI, 70 eV) 386 (5%, $M^+ - NO_2$), 251 (11), 223 (5), 164 (71), 119 (64), 118 (100), 115 (22), 105 (15), 91 (39), 77 (12) and 65 (20).

Styrene (**1a**). Photolysis of a mixture of **1a** (0.45 g, 4.36 mmol) and TNM (1.7 g, 8.72 mmol) in CH_3CN (10 cm^3) for 4 h resulted in the complete disappearance of styrene. Work-up of the photolysate afforded an orange slurry. From the high resolution ^{1}H NMR spectral peak integration of the crude product we inferred that **2a** was formed as a mixture of diastereoisomers in the ratio 6:1. The major diastereoisomer of **2a** was purified as described for **2b** (0.6 g, 80%); m.p. 104 °C (lit.,[8] 104–105 °C); ν_{max}(KBr)/cm^{-1} 3037w, 2984w, 1588vs, 1558s (NO_2), 1436s, 1418s, 1383s, 1365s (NO_2), 1313s, 1271m, 1238m, 1203m, 1186m, 1176m, 1026m, 948m, 929m, 866m and 830m; $\delta_H(CDCl_3)$ 7.4 (10 H, m, Ar), 5.82 (2 H, m, methine), 5.1 (1 H, dd, *J* 14.7, 7.37, $C\mathit{H}^aH^bNO_2$), 4.56 (1 H, dd, *J* 14.7, 4.9, $CH^a\mathit{H}^bNO_2$), 4.15 (1 H, dd, *J* 15.2, 7.37, 4-H^a) and 3.05 (1 H, dd, *J* 15.2, 7.40, 4-H^b); $\delta_C(CDCl_3)$ 133.9 (s), 133.5 (s), 130.1 (s), 129.9 (s), 129.2 (d), 129.1 (d), 127.5 (d), 126.7 (d), 83.9 (d, $\mathit{C}HCH_2NO_2$), 81.4 (d, C-5), 77.0 (t, CH_2NO_2, overlaps with $CDCl_3$ signal) and 41.3 (t, C-4); *m/z* (EI, 70 eV) 358 ($M^+ - NO_2$), 209 (15%), 150 (46), 149 (40), 105 (97), 104 (92), 91 (32), 77 (100) and 65 (13).

p-*Methoxystyrene* (**1c**). Photolysis of a solution containing **1c** (0.5 g, 3.7 mmol) and TNM (1.15 g, 0.56 mmol) in CH_3CN (10 cm^3) for 2 h resulted in the complete disappearance of the starting material. Usual work-up followed by column chromatography yielded *p*-methoxy-β-nitrostyrene (0.59 g, 90%) as a yellow crystalline solid: m.p. 86 °C (lit.,[24] 86–87 °C).

p-*Chlorostyrene* (**1d**). A solution containing **1d** (0.5 g, 3.6 mmol) and TNM (1.1 g, 5.4 mmol) in CH_3CN was photolysed for 4 h. After work-up the crude product was recrystallised from ethanol. *p*-Chloro-α-nitroacetophenone (**4**) was obtained as a yellow solid (0.64 g, 90%), m.p. 152 °C (lit.,[25] 167 °C). As the literature reported m.p. was different, we resorted to complete characterization (Found: C, 48.1; H, 3.0; N, 6.9. $C_8H_6NO_3Cl$ requires C, 48.1; H, 3.0; N, 7.0%); ν_{max}(KBr)/cm^{-1} 1702s (C=O), 1619m, 1592s, 1562s (NO_2), 1457s, 1402s, 1326m (NO_2), 1286m, 1193s, 1093m, 841s, 777s, 793s and 576s; δ_H([$^2H_6$]DMSO) 7.94 (2 H, d, *J* 8.78), 7.67 (2 H, d, *J* 8.78) and 6.52 (2 H, s, CH_2); δ_C([$^2H_6$]DMSO) 187.55 (s), 142 (s), 132 (s), 129.7 (d), 129.6 (d) and 81 (t).

β-*Bromostyrene and* para-*substituted derivatives* (**5a–d**). Photolysis of a mixture of **5** (4 mmol) and TNM (8 mmol) in CH_3CN (10 cm^3) for 4–8 h yielded the corresponding β-nitrostyrene (**3**) as the only product in 90–95% yield. The β-nitrostyrenes were isolated by column chromatography as yellow crystalline solids and identified by comparison with the corresponding authentic samples; **3a**, m.p. 57–59 °C (lit.,[26] 57–59 °C); **b**, m.p. 101 °C (lit.,[27] 101 °C); **c**, m.p. 86 °C (lit.,[24] 86–87 °C); **d**, 113 °C (lit.,[28] 113–114 °C).

trans-*Stilbene* (**9**). A solution of stilbene (0.54 g, 3 mmol) and TNM (1.8 g, 9 mmol) in CH_2Cl_2 (20 cm^3) was red in colour. Photolysis of the mixture led to the bleaching of the colour and within 5 h the colour bleached to a very pale yellow. After work-up of the reaction mixture the crude product was chromatographed over silica gel. Elution with hexane yielded a colourless crystalline solid which was identified as *threo*-2,3-diphenyl-1,1,1,3-tetranitropropane (**10a**): m.p. 147 °C (Found: C, 47.4; H, 3.2; N, 14.6. $C_{15}H_{12}N_4O_8$ requires C, 47.8; H, 3.2; N, 14.9%); ν_{max}(KBr)/cm^{-1} 1624vs, 1603vs, 1557vs, 1497m, 1456m, 1357s, 1295s, 858m, 820m, 789m, 776m, 724s, 700m and 579m; $\delta_H(CDCl_3)$ 7.5 (10 H, m), 6.53 (1 H, d, *J* 11.4) and 5.65 (1 H, d, *J* 11.4); $\delta_C(CDCl_3)$ 131.9 (d), 130.2 (d), 129.8 (d), 129.3 (d), 129.2 (d), 128.5 (s), 127.6 (s), 92.5 (d) and 52.3 (d); *m/z* (EI, 70 eV) 331 10%), 330 (33, $M^+ - 46$), 285 (5), 284 (7), 238 (7), 191 (25), 179 (22), 178 (23), 165 (18), 132 (100), 105 (62), 102 (31), 91 (13) and 77 (30). Elution with a mixture of hexane and ethyl acetate (5%, v/v) yielded another colourless crystalline solid which was identified as the *erythro*-isomer **10a**: m.p. 96 °C; ν_{max}(KBr)/cm^{-1} 2831w, 1636vs, 1499vs, 1458s, 1360s, 1333s, 1292s, 1204m, 1178m, 1077m, 1052m, 1029m, 926m, 886m, 816s, 761s, 748s, 698s, 637m, 624m, 616m and 524m; $\delta_H(CDCl_3)$ 7.4 (10 H, m), 5.61 (1 H, d, *J* 5.86), 5.0 (1 H, d, *J* 5.86 Hz); $\delta_C(CDCl_3)$ 135.9 (s), 135.6 (s), 129.9 (d), 129.7 (d), 129.4 (d), 129.2 (d), 127.2 (d), 125.5 (d), 84.9 (d) and 55.3 (d); *m/z* (EI, 70 eV) 235 (5), 221 (5), 204 (5), 178 (7), 165 (7), 133 (12), 132 (100), 116 (10), 106 (14), 105 (47), 102 (45), 89 (10) and 77 (40).

1-*Phenylcyclohexene* (**11**). Photolysis of a mixture of **11** (0.5 g, 3.16 mmol) and TNM (0.93 g, 4.75 mmol) in CH_3CN (10 cm^3 for 3 h resulted in the complete disappearance of the starting material. Work-up of the photolysate yielded a viscous oil from which a colourless crystalline solid was obtained by dissolving the crude product in CH_2Cl_2 containing 10% (v/v) ethyl acetate and cooling the solution in the freezer. The product was further purified by recrystallization from a mixture of CH_2Cl_2 and hexane (0.9 g, 85%). The product was identified as 2-nitro-1-phenyl-1-trinitromethylcyclohexane (**12**): m.p. 115 °C (Found: C, 43.6; H, 3.6; N, 15.6. $C_{13}H_{14}N_4O_8$ requires C, 44.1; H, 3.9; N, 15.8%); $\nu_{max}(CCl_4)/cm^{-1}$ 1677w, 1603s, 1585, 1555s, 1446m, 1360m and 1290m; $\delta_H(CDCl_3)$ 7.6 (2 H, m), 7.42 (3 H, m), 5.6 (1 H, dd, *J* 11.2, 3.9), 2.9 (1 H, m), 2.6 (1 H, m), 2.2 (2 H, m), 1.75 (2 H, m) and 1.52 (2 H, m); $\delta_C(CDCl_3)$ 132.1 (d), 130.2 (d), 128.8 (d), 128.5 (s), 88.8 (d, C-2), 58.1 (s, C-1), 34.9 (t, C-3), 27.6 (t, C-6), 24.5 (t) and 21.0 (t); *m/z* (EI, 70 eV) 354 (5%, M^+), 173 (20), 158 (64), 157 (94), 143 (25), 130 (33), 115 (54), 105 (95), 91 (100), 77 (54) and 55 (22).

X-Ray Crystallographic Determination.—Crystal data for compound **2b**.* $C_{19}H_{20}N_4O_8$, *M* 432.4, triclinic, space group $P\bar{1}$, *a* 9.020(6), *b* 10.486(5), *c* 12.804(2) Å, α 104.777(3), β 98.213(5), γ 111.531(3)°, *V* 1051.0(9) Å^3, D_c 1.37 g cm^{-3}, *Z* 2, μ 0.69 cm^{-1}, (Mo-Kα) 0.710 69 Å, colourless, needle, crystal size 0.3 × 0.3 × 0.4 mm, *T* 296 K, 25 reflections with $\theta \approx 15°$ from different zones of reciprocal lattice were used to determine the cell parameters using the method of short vectors, followed by least squares refinement, range of 2θ $4 < 2\theta < 50°$, range of *hkl* 0,10; −12, +12; −15, +15; reflections measured 2356, unique reflections with $I > 3\sigma(I)$ 2038, number of variables 356, *R*(*F*) defined as $\Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.0413$, R_w defined as $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.0427$, $w = 2.5257/[\sigma 2(F) + 0.00032F^2]$, reflection data were measured with an Enraf–Nonius CAD-4 diffractometer in θ/2θ scan mode, reflections with $I > 3\sigma(I)$ were considered observed, structure was solved by SHELXS-86 program and refined by SHELXS-76 program.[29]

Conclusions

Under neutral conditions in acetonitrile the CT complexes of styrene and its derivatives were found to be stable for several days in the dark except in the case of *p*-methoxystyrene which underwent very slow thermal reaction. The photochemistry of the CT complexes led to the formation of a variety of products ranging from simple nitration products to dimeric adducts. The X-ray crystal structure of the isoxazolidine derivative **2b** from *p*-methylstyrene clearly establishes the ambident nature of the trinitromethide anion to react either through oxygen (O-alkylation) in the present case or through carbon (C-alkylation) in the previously reported adducts from aromatic substrates. Formation of the various products from the styrene derivatives can be explained from the benzyl cation **7** which subsequently undergoes reaction in competing pathways of deprotonation, O-alkylation and C-alkylation. A comparison is made on the photoinitiated thermal nitration of olefins with that of the continuous CT excitation in the case of 1-phenylcyclohexene with TNM.

Acknowledgements

We thank Professor K. K. Balasubramanian, Department of Chemistry, IIT, Madras, for generously providing the photochemical equipment, Regional Sophisticated Instrumentation Centre, IIT, Madras, for high resolution NMR and mass spectral data and X-ray crystallographic work and the CSIR, New Delhi for financial support. One of us (L. M.) thanks IIT, Madras for a graduate fellowship.

References

1 K. V. Altukhov and V. V. Perekalin, *Russ. Chem. Rev.*, 1976, **45**, 1052.

2 (*a*) J. K. Kochi, *Acta Chem. Scand.*, 1990, **44**, 409; (*b*) L. Eberson, M. P. Hartshorn and F. Radner, *J. Chem. Soc., Perkin Trans. 2*, 1992, 1799 and related papers.

3 E. A. Rastino, K. V. Altukhov and V. V. Perekalin, *Zh. Org. Khim.*, 1972, **8**, 523; *Chem. Abstr.*, 1972, **77**, 34064d.

4 J. M. Masnovi and J. K. Kochi, *Recl. Trav. Chim. Pays-Bas.*, 1986, **105**, 286.

5 (*a*) R. W. Bradshaw, *Tetrahedron Lett.*, 1966, 5711; (*b*) K. Torssell, *Acta Chem. Scand.*, 1967, **21**, 1392; (*c*) V. A. Buevich, K. V. Altukhov and V. V. Perekalin, *Zh. Org. Khim.*, 1971, **7**, 1380; *Chem. Abstr.*, 1971, **75**, 151712h; (*d*) C. Lagercrantz and M. Yhland, *Acta Chem. Scand.*, 1962, **16**, 1807.

6 P. Balczewski, R. L. Beddoes and J. A. Joule, *J. Chem. Soc., Chem. Commun.*, 1991, 559.

7 (*a*) J. M. Masnovi and J. K. Kochi, *J. Org. Chem.*, 1985, **50**, 5245; (*b*) S. Sankararaman and J. K. Kochi, *J. Chem. Soc., Perkin Trans. 2*, 1991, 1; (*c*) L. Eberson, M. P. Hartshorn, F. Radner and W. T. Robinson, *J. Chem. Soc., Chem. Commun.*, 1992, 566.

8 K. V. Altukhov, V. A. Tartakovskii, V. V. Perekalin and S. S. Novikhov, *Izv. Akad. Nauk. SSSR.*, 1967, 197; *Chem. Abstr.*, 1970, **72**, 66521p.

9 K. V. Altukhov, E. V. Rastino and V. V. Perekalin, *Zh. Org. Khim.*, 1969, **5**, 2246.

10 (*a*) E. Schmidt and H. Fischer, *Ber. Dtsch. Chem. Ges.*, 1920, **53**, 1529; (*b*) E. Schmidt, R. Schumacher, W. Bajen and A. Wagner, *Ber. Dtsch. Chem. Ges.*, 1922, **55**, 1751.

11 (*a*) J. M. Masnovi and J. K. Kochi, *J. Am. Chem. Soc.*, 1985, **107**, 7880; (*b*) S. Sankararaman, W. A. Haney and J. K. Kochi, *J. Am. Chem. Soc.*, 1987, **109**, 5235 and 7824; (*c*) S. Sankararaman and J. K. Kochi, *J. Chem. Soc., Perkin Trans. 2*, 1991, 165.

12 (*a*) R. Foster, *Organic Charge Transfer Complexes*, Academic Press, New York, 1969; (*b*) R. S. Mulliken, *J. Am. Chem. Soc.*, 1952, **74**, 811.

13 G. W. Eastland, Y. Kurita and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1843.

14 N. Kornblum, P. Ackermann and R. T. Swiger, *J. Org. Chem.*, 1980, **45**, 5294.

15 L. M. Andreeva, K. V. Altukhov and V. V. Perekalin, *Zh. Org. Khim.*, 1972, **8**, 1419, *Chem. Abstr.*, 1972, **77**, 126479w.

16 I. Fleming, *Frontier Orbitals and Organic Chemical Reactions*, Wiley, New York, 1976, p. 148.

17 D. Kaufman and L. L. Miller, *J. Org. Chem.*, 1969, **34**, 1495.

18 C. L. Perrin, *J. Org. Chem.*, 1971, **36**, 420.

19 R. M. Silverstein, G. C. Bassler and T. C. Morrill, *Spectrometric Identification of Organic Compounds*, Wiley, New York, 1991, 5th edn.

20 C. M. Jackman and S. Sternhill, *Application of NMR Spectroscopy in Organic Chemistry*, Pergamon, New York, 1969, 2nd edn., p. 291.

21 (*a*) S. Penczek, J. Jagur-Grodzinski and M. Szwarc, *J. Am. Chem. Soc.*, 1968, **90**, 2174; (*b*) V. A. Buevich, K. A. Altukhov and V. V. Perekalin, *Zh. Org. Khim.*, 1967, 2248; 1970, **6**, 187.

22 *Vogel's Textbook of Practical Organic Chemistry*, ELBS Longman, Essex, 1989, 5th edn., p. 511.

23 P. Liang, *Org. Synth. Coll. Vol III*, Wiley, New York, 1955, p. 803.

24 E. Knoevenagel and L. Walter, *Ber. Dtsch. Chem. Ges.*, 1904, **37**, 4502.

25 O. Dann, H. Ulrich and E. F. Moller, *Z. Naturforsch.*, 1952, **76**, 344.

26 Ref. 22, p. 1035.

27 O. M. Lerner, *Zh. Prikl. Khim.*, 1958, **31**, 663; *Chem. Abstr.*, 1958, **52**, 18271h.

28 N. Campbell, W. Anderson and J. Gilmore, *J. Chem. Soc.*, 1940, 446.

29 (*a*) G. M. Sheldrick, SHELX-86, Computer Program for the Solution of Crystal Structure from Diffraction Data, University of Göttingen, 1986; (*b*) G. M. Sheldrick, SHELX-76, Computer Program for Crystal Structure Determination, University of Cambridge, 1976.

Paper 3/03080F
Received 2nd *June* 1993
Accepted 16*th August* 1993

---

* Crystallographic data has been deposited at the Cambridge Crystallographic Data Centre. For details of the deposition scheme, see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 2*, 1993, issue 1.