

The effects of substituents on the photochemistry of β -methyl- β -nitrostyrene

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Abstract

β -Methyl- β -nitrostyrene, (G-phenyl)HC=CRNO₂, **1_a** (R=CH₃, G=H) and five of its derivatives: **1_b** (R=CH₃-, G=*p*-CH₃-); **1_c** (R=CH₃, G=*p*-CH₃O-); **1_d** (R=CH₃-, G=*p*-(CH₃)₂N-); **1_e** (R=CH₃-, G=*m*-CH₃O-); and **1_f** (R=CH₃-, G=*p*-F₃C-) are synthesized and irradiated in the UV region (Scheme 1). The photochemical half-lives of substituted styrenes, **1_a**–**1_f**, are in the order of **1_d** (43.3 min) > **1_c** (15.8 min) > **1_b** (13.3 min) > **1_a** (9.6 min) > **1_f** (6.4 min) > **1_e** (4.4 min). The GPC yields of the corresponding oxime products, (G-phenyl)HC=NOH-R-C=O, **2_a**–**2_f**, in aqueous ethanol are in the order of **2_d**=**2_c** (99.5%) > **2_b** (99.0%) > **2_a** (90.2%) > **2_e** (88.1%) > **2_f** (86.8%). The variations in the yields of oximes, are justified and attributed to the electronic effects of the substituents, G, on the phenyl rings of the styrenes. A Hammett ρ value of 0.7 is obtained for the nitro-nitrite photorearrangement of nitro-olefins. A mechanism is proposed for this reaction. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: β -Nitrostyrene derivatives; Nitroolefins; Substituent effects; Nitro-nitrite; Photorearrangement

1. Introduction

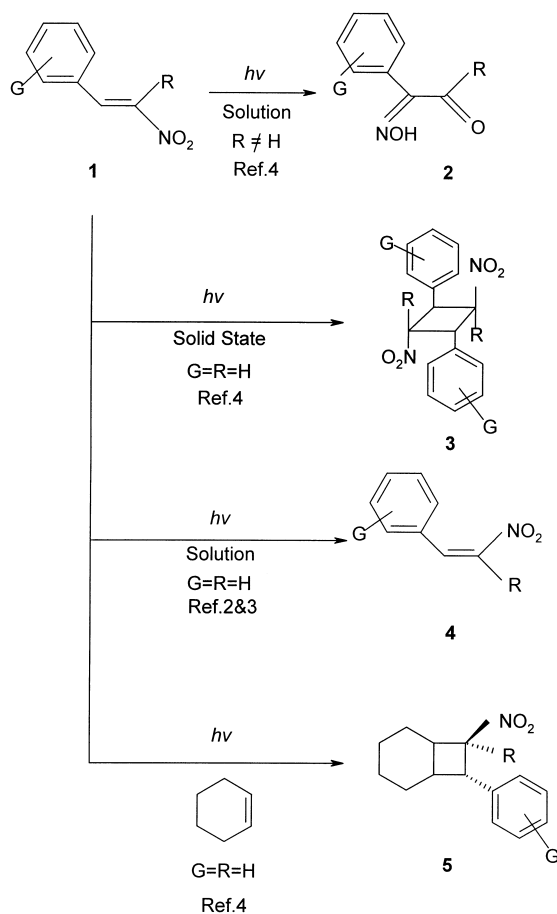
Some derivatives of β -nitrostyrene show antimicrobial and antifungal activities [1]. β -methyl- β -nitrostyrene, **1_a**, and its derivatives are among the organic compounds that may release nitric oxide (NO) [2–4] upon nitro-nitrite photorearrangement.

The photochemistry of β -nitrostyrene, **1_g** (R=H, G=H), has been of interest to photochemists for over a century (Scheme 1). In 1884, Prieb [5] and in 1989 Desiraju and Pedireddi [6] observed the photodimerization of **1_g** to **3** in solid state. Miller [10] in 1957, and Bluhm and Weinstein [9] in 1965, observed the photoisomerization of **1_g** to **4** in solution. The irradiation of **1_g** in cyclohexene gave photoaddition product **5** [7,8]. While photorearrangement of **1_g** to **2_g** has not been reported, analogous photorearrangement of **1_a** (R=CH₃, G=H) to **2_a** has been shown to occur in quantitative yield by Chapman and Reasoner [10]. Chapman rationalized the photorearrangement of **1_a** to **2_a** by means of a mechanistic sequence given in Scheme 2 [11]. In **1_a** the nitro group was believed to be forced out of the plane of the ring or the double bond by the methyl group. This would permit the overlap of the half vacant nonbonding or-

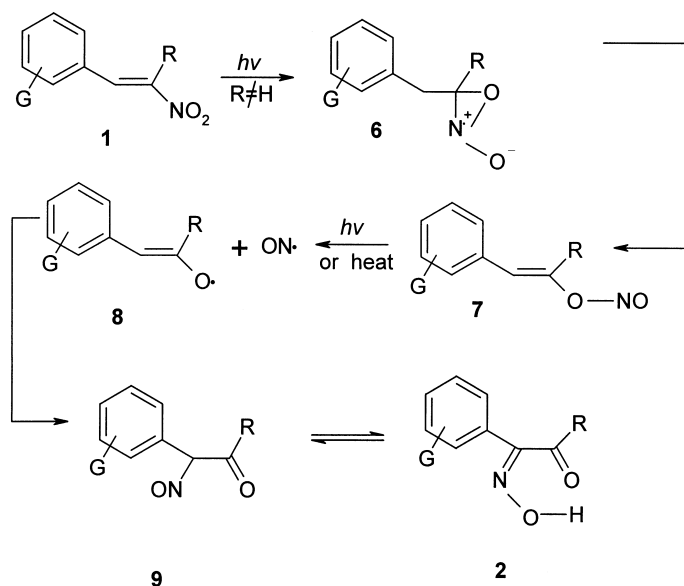
bital with the adjacent orbital of the ring or double bond (in the n, π^* excited state). This overlap leads to the formation of an oxaziridine ring **6** [12], which collapses to nitrite **7** [10,13]. Thermal or photochemical cleavage of **7** gives oxy radical **8**. Readdition of NO at α -carbon gives nitrosoketone **9** which can tautomerize to ketooxime **2_a**. An alternate pathway for rearrangement of **1_a** to **2_a** was suggested by Kan [14], via an intramolecular rearrangement, where dissociation of **7** and its recombination with NO was not considered. The mechanistic reaction schemes proposed by Chapman [10,11] and Kan [14] were both almost completely hypothetical since no studies of the nature of the intermediates were undertaken. In irradiation of **1_a**, Ioki [15] reported the esr of oxyl radical **8**. This observation is a strong evidence to support the formation of nitrite **7**, through the photochemical rearrangement of **1_a**, as suggested by Chapman. Reports on the ‘formation and decay of anthryloxy radicals produced via higher excited triplet n, π^* states of nitroanthracenes’ [16]; and ‘laser desorption/ionization time-of-flight mass spectroscopy of nitrite polycyclic aromatic hydrocarbons’ [17], and laser-induced decomposition of 3-nitro-1,2,4-triazol-5-one (NTO) [18] provide further evidence for nitro-nitrite rearrangement, followed by loss of NO (Scheme 2).

The effects of substituents (G) on the photorearrangement of **1** to **2** (Scheme 1) have been investigated by

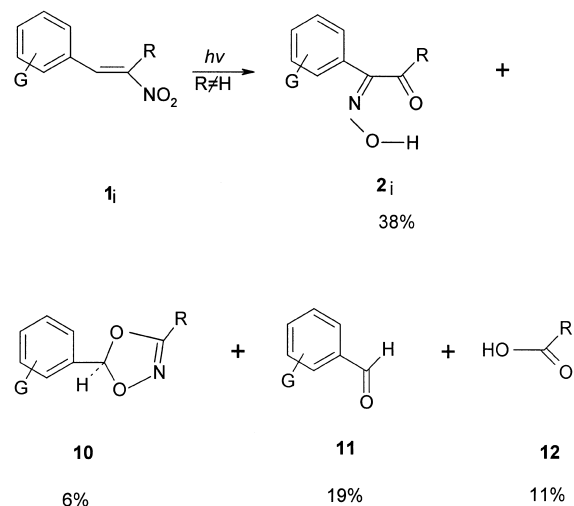
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Scheme 1. Photochemistry of β -R- β -nitrostyrene and its G-phenyl derivatives, **1**: **a**(R=CH₃, G=H); **b**(R=CH₃, G=4-H₃C-); **c**(R=H₃C-, G=4-H₃CO-); **d**(R=H₃C-, G=4-(CH₃)₂N); **e**(R=H₃C-, G=3-H₃CO-); **f**(R=H₃C-, G=4-F₃C-); **g**(R=H, G=H); **h**(R=Ph, G=H); **i**(R=4-O₂N-Ph, G=H); **j**(R=H₃C-, G=4-O₂N-); **k**(R=H₃C, G=3-O₂N-).



Scheme 2. Mechanism of photochemical rearrangement of β -methyl- β -nitrostyrene, **1_a**(R=CH₂, G=H), proposed by Chapman [11].

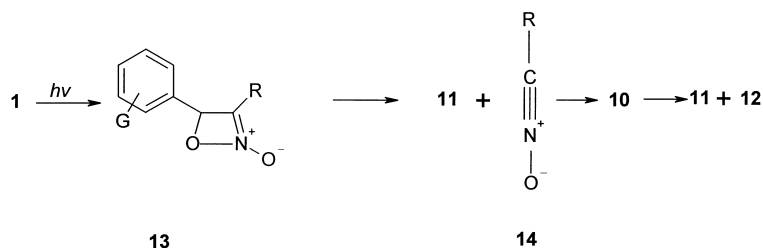


Scheme 3. Product distribution of irradiation of *cis*- α ,4-dinitrostilbene, **1_i** (R=4-O₂N-Ph, G=H) [19].

Pinhey and Rizzardo [19], Tang and Reasoner [20], Matsuura and coworkers [21], and by the present authors [22–25]. Pinhey and Rizzardo found that on irradiation in acetone, *cis*- α -nitrostilbene, **1_h**(R=Ph,G=H), converts in high yield into a mixture of isomers of benzilmonooxime, **2_h**(R=Ph,G=H); whereas **1_i**(R=4-ON₂-Ph-, G=H), under similar conditions gives **2_i**, in only 38% yield. The product distribution is shown in Scheme 3.

The mechanism for formation of products other than the oxime **2_i** suggested by Pinhey and Rizzardo, is shown in Scheme 4.

Tang and Reasoner developed a new technique for the synthesis of **2** and its derivatives by irradiation of the substituted styrenes **1** in 95% ethanol [20]. The yield of the correspon-



Scheme 4. The mechanism of formation of products other than **2** in irradiation of *cis*- α , 4-dinitrostilbene, **1**_i (R=4-O₂N-Ph, G=H) [19].

ding oximes were almost quantitative (90–100%) except for **2**_j (R=CH₃, G=4-O₂N-, 15%) and **2**_k (R=CH₃, G=3-O₂N-, 19%). It was suggested that electron-withdrawing groups at the *para*- or *meta*-positions of the phenyl ring inhibit the nitro-nitrite rearrangement and give some fragmentation products. The possibility of a competition between aromatic nitro group attached at *p*- or *m*-position and unsaturated β -nitro group during the irradiation was also suggested. Matsuura and coworkers investigated the photochemical reactions of a series of substituted (E)-**1** and proposed that the nitro-nitrite rearrangement, leading to the oximes **2**, and the intermolecular cycloaddition, leading to the aldehydes **11**, are competitively taking place through different excited states [21]. In order to gain more insight into the multiplicity of the reaction, the quenching effect of piperylene on the formation of **2**_a and **11**_a was examined in the photoreaction of **1**_b. Addition of piperylene inhibited the formation of **11** with no effect on the formation of **2**_a, indicating two different excited states are involved. Thus, it was proposed that the excited state responsible for the formation of **11** is the lowest triplet state, whereas the unquenchable state responsible for the formation of **2**_a is either a singlet or a higher triplet state [21].

The purpose of the present study was to investigate the effects of various phenyl substituents (G), on the kinetics, and the product distribution of, photochemical rearrangement of **1**. The CF₃ group, with the Hammett substituent σ (sigma) of 0.54 at the *para*-position in **1**_a (R=CH₃, G=CF₃), was chosen for this study since it exerts an electron withdrawing effect almost as great as the NO₂ group, with the σ of 0.78 at the *para*-position, but is not capable of absorbing light at the wave length employed. *m*-CH₃O group (σ =0.12) in **1**_c (R=CH₃, G=3-CH₃O-) is another electron withdrawing substituent. *p*-CH₃O (σ =-0.27) in **1**_c (R=CH₃, G=4-CH₃O-); *p*-CH₃ (σ =-0.17) in **1**_b (R=CH₃-, G=4-H₃C-) and *p*-(CH₃)₂N (σ =-0.83) in **1**_d (R=H₃C, G=4-(CH₃)₂N-) are electron donating substituents with various Hammett substituent σ values.

2. Experimental details

A Hanovia type 400-W low-pressure mercury arc lamp was used as UV-irradiation source. The lamp was inserted into the immersion well of a jacketed pyrex tube. The tube

was fitted into a 550 ml. capacity reaction vessel equipped with a thermometer, gas dispersion tube, and a condenser. Ultraviolet spectra were recorded on a Shimadzu model UV-200. IR spectra were determined on a Shimadzu model IR-460. IR of solid samples were run in KBr pellets. NMR spectra were performed on a Jeol FT-NMR, JNM-EX-90A. with NMR field strength of 90 MHz. GC/MS spectra were recorded on a Perkin-Elmer 8420 capillary gas chromatograph with ITD Finnigan-Mat Perkin-Elmer ion trap detector. Vapor phase chromatography was carried out on a Varian model 1720 with disc integrator and temperature programming capability. Analysis were performed on a Heraeus CHN-O-Rapid instrument. Melting points were taken on simple oil-bath melting point apparatus and are uncorrected.

2.1. Synthesis

2.1.1. β -Methyl- β -nitrostyrene derivatives, **1**

Two different pathways were used for the synthesis of the derivatives of **1**. The method of Gaired and Lappin [26] was used for synthesis of **1**_a, **1**_b, **1**_c and **1**_d; whereas the procedure of Robertson [27] was used for **1**_e and **1**_f. The results are as follows.

1_a [10]: Light yellow crystals, m.p. 63–64°C (from EtOH) *m/z* 163 (M⁺• 41.7%), 162(1.8), 146(13.3), 135(10), 117(25.9), 116(45), 115(100), 106(38.3), 91(55), 77(16.7), 63(20).

¹HNMR (CDCl₃) Δ : 2.5(3H,s,Me), 7.2–7.7(5H,m,ArH), 8.0(1H,s). UV λ_{\max} (EtOH), 305 nm, ϵ_{\max} , 115. Yield 52%.

1_b [23]: yellow needles 54.5–55.5°C (from EtOH) *m/z* 177(M⁺• 38%), 162 (40), 149(18), 130(47), 129(100), 119(41), 105(55), 91(9) and 77(19).

¹HNMR (CDCl₃) Δ : 2.3(3H,s,Me), 2.5(3H,s,Me); 7.1–7.5(4H,m,ArH), 8.0(1H,s). UV λ_{\max} (EtOH), 305 nm, ϵ_{\max} , 123.

IR (KBr) cm⁻¹: 3030, 2980, 1644, 1600, 1516, 1430, 1380, 1318, 1210, 1190, 980, 920, 870, 810, 810. Yield 52%.

1_c [21]: Yellow needles, m.p. 45–46°C (from EtOH) *m/z* 193(M⁺• 35%), 178(9), 162(33), 165(10), 147(23), 146(44), 145(100), 134(37), 121(51), 105(15), 93(18).

¹HNMR (CDCl₃) Δ : 2.5(3H,s,Me), 3.8(3H,s,CH₃O), 6.9–7.6(4H,d,ArH), 8.0(1H,s). UV λ_{\max} (EtOH), 343 nm, ϵ_{\max} , 133.

IR (KBr) cm^{-1} : 3030, 2950, 1640, 1599, 1514, 1500, 1380, 1297, 1256, 1180, 1030, 980, 868, 830, 520. *Yield* 52%.

1d: Red crystals, m.p. 62–63°C (from EtOH) m/z 206(M^+ 29%), 191(15%), 160(13%), 162(14%), 159(43%), 158(100%), 147(37%), 134(56%), 118(14%), 106(21%).

¹HNMR (CDCl_3) Δ : 2.5(3H,s,Me), 3.0(6H,s,(CH₃)₂N), 6.6–7.6(4H,d,ArH), 7.9(1H,s). **UV** λ_{max} (EtOH), 421 nm, ϵ_{max} , 112.

IR (KBr) cm^{-1} : 2970, 1630, 1597, 1523, 1484, 1372, 1342, 1280, 1193, 940, 870, 813. *Yield* 47.8%.

Analysis: Calculated for C₁₁H₁₄N₂O₂: C, 64.08; H, 6.80; N, 13.59; found: C, 64.03; H, 6.15; N, 13.52.

1e [22]: Yellow needles, m.p. 46–47°C (from EtOH) m/z 193(M^+ 31%), 178(11), 162(31), 165(12), 147(25), 146(44), 145(100), 134(36), 121(53), 105(15), 93(21).

¹HNMR (CDCl_3) Δ : 2.5(3H,s,Me), 3.7(3H,s,CH₃O), 6.7–7.4(4H,m,ArH), 8.1(1H,s). *Yield* 23%.

1f [22]: Deep yellow plates, m.p. 40–41°C (from EtOH) m/z 231(M^+ 38%), 203(7), 185(23), 184(44), 183(100), 172(38), 162(39), 143(15), 131(17).

¹HNMR (CDCl_3) Δ : 2.5(3H,s,Me), 7.5–7.7(4H,m,ArH), 8.1(1H,s). *Yield* 19%.

2.1.2. 1-Phenyl-1,2-propanedione-1-oxime derivatives, 2

A solution was prepared by dissolving 2 g of the desired β -methyl- β -nitrostyrene derivative in 550 ml of 95% undenatured ethanol. The solution was degassed for one-half an hour with N₂ prior to irradiation. The ultraviolet irradiation was stopped after 3 h and the solvent removed under reduced pressure. The concentrate was decolorized with norite A in hot ethanol and recrystallized from a 50:50 solution of benzene and ethanol, then recrystallized several times from 95% ethanol. The results were as follows.

2a [10]: White crystals, m.p. 171–172°C (from EtOH) m/z 163(M^+ 30%), 158(31), 146(13), 135(7), 117(23), 116(91), 115(100), 106(33), 91(45), 77(19), 63(17).

¹HNMR (CDCl_3) Δ : 2.5(3H,s,Me), 7.1–7.5(5H,m,ArH). *Yield* 49%, *GPC Yield* 90.2%.

2b [23]: White crystals, m.p. 169–170°C (from EtOH) m/z 177(M^+ 33%), 162(53), 149(11), 134(100), 121(10), 91(25), 86(23), 77(17). **UV** λ_{max} (EtOH), 421 nm, ϵ_{max} , 214.

¹HNMR (CDCl_3) Δ : 2–3(3H,s,CH₃), 2.5(3H,s,CH₃), 7.1–7.4(4H,d,ArH). *Yield* 48%, *GPC* 99.0%.

2c [21]: White crystals, m.p. 155–156°C (from EtOH) m/z 193(M^+ 31%), 178(17), 162(30), 150(100), 107(14). **UV** λ_{max} (EtOH), 421 nm, ϵ_{max} , 218.

¹HNMR (CDCl_3) Δ : 2.5(3H,s,CH₃), 3.8(3H,s,CH₃-O), 6.8–7.3(4H,d,ArH). *Yield* 48%, *GPC* 99.5%.

2d: White crystals, m.p. 174–175°C (from EtOH) m/z 206(M^+ 29%), 191(19), 189(17), 178(11), 163(42), 162(43), 148(37), 134(100), 118(14).

¹HNMR (CDCl_3) Δ : 2.5(3H,s,CH₃), 3.0(CH,s,2CH₃), 6.6–7.3(4H,dd,ArH). *Yield* 52%, *GPC* 99–5%.

Analysis: Calculated for C₁₁H₁₄N₂O₂: C, 64.08; H, 6.80; N, 13.59; found: C, 63.89; H, 6.52; N, 13.14.

2e [22]: White crystals, m.p. 115–116°C (from EtOH) m/z 193(M^+ 25%), 178(9), 162(30), 165(13), 163(42), 150(31), 147(45), 146(43), 145(100), 134(30), 121(51), 105(11).

¹HNMR (CDCl_3) Δ : 2.5(3H,s,CH₃), 3.7(3H,s,OCH₃), 7.2–7.4(4H,m,ArH). *Yield* 62%, *GPC* 88.1%.

2f [22]: White crystals, m.p. 189–190°C (from EtOH) m/z 231(M^+ 33%), 216(29), 188(23), 162(39), 145(100), 143(15).

¹HNMR (CDCl_3) Δ : 2.5(3H,s,CH₃), 7.6–7.8(4H,s,ArH). *Yield* 39%, *GPC* 86.8%.

2.2. Photoproducts

The photoproduct yields were determined by gas chromatography using the method of Rosie and Grob [28]. Retention times for three different internal standards: biphenyl, benzophenone and fluoren-9-one as well as styrenes, **1a–f** and oximes, **2a–f**, were obtained using 20% SE-30 column at 175°C and average helium flow rate of 140 ml/min. Response factors for proper molar ratios of pure styrenes and oximes over the corresponding suitable internal standard were determined. Using the disc integrator data, the calculated yields of various oximes were: **1a** 90.2%; **1b**, 99.0%; **1c**, 99.5%; **1d**, 99.5%; **1e**, 88.1; **1f**, 86.8%.

2.3. Preliminary kinetic studies

A solution of 0.0035 mol of each derivatives in 550 ml of 95% undenatured ethanol was irradiated for 2 h. The progress of the reaction was followed by the ultraviolet/visible spectroscopy in 200–400 nm region. An example of the absorbance spectra is shown in Fig. 1. Vibrational fine structures were absent in all UV spectra. The results indicated that the unsaturated nitro group gradually disappears. This disappearance is initially first order for less than 30% conversions for all cases studied. First order plots of log (Absorbance) vs. time is shown in Fig. 2. In this figure the absorbances are corrected for extinction at the monitoring wavelength. The 'rate constants' for **1a** to **1f** are 0.073, 0.052, 0.039, 0.016, 0.158 and 0.109, respectively. Considering the method employed, these 'rate constants', are of qualitative value. The half-lives for **1a** through **1f** are 9.6, 13.3, 17.7, 43.3, 4.4 and 6.4 min, respectively. The relative rates for **1a** through **1f** are 1.0, 0.7, 0.5, 0.2, 2.2 and 1.5, respectively.

A straight line with slope of 0.7 is obtained when log k (specific rate constant of **1a** to **1f**) over k_0 (specific rate constant of **1a**) is plotted against the corresponding σ as shown in Fig. 3.

3. Results and discussion

Six nitroolefins, **1a** through **1f** were synthesized and irradiated in the UV region. The GPC yield of the corresponding

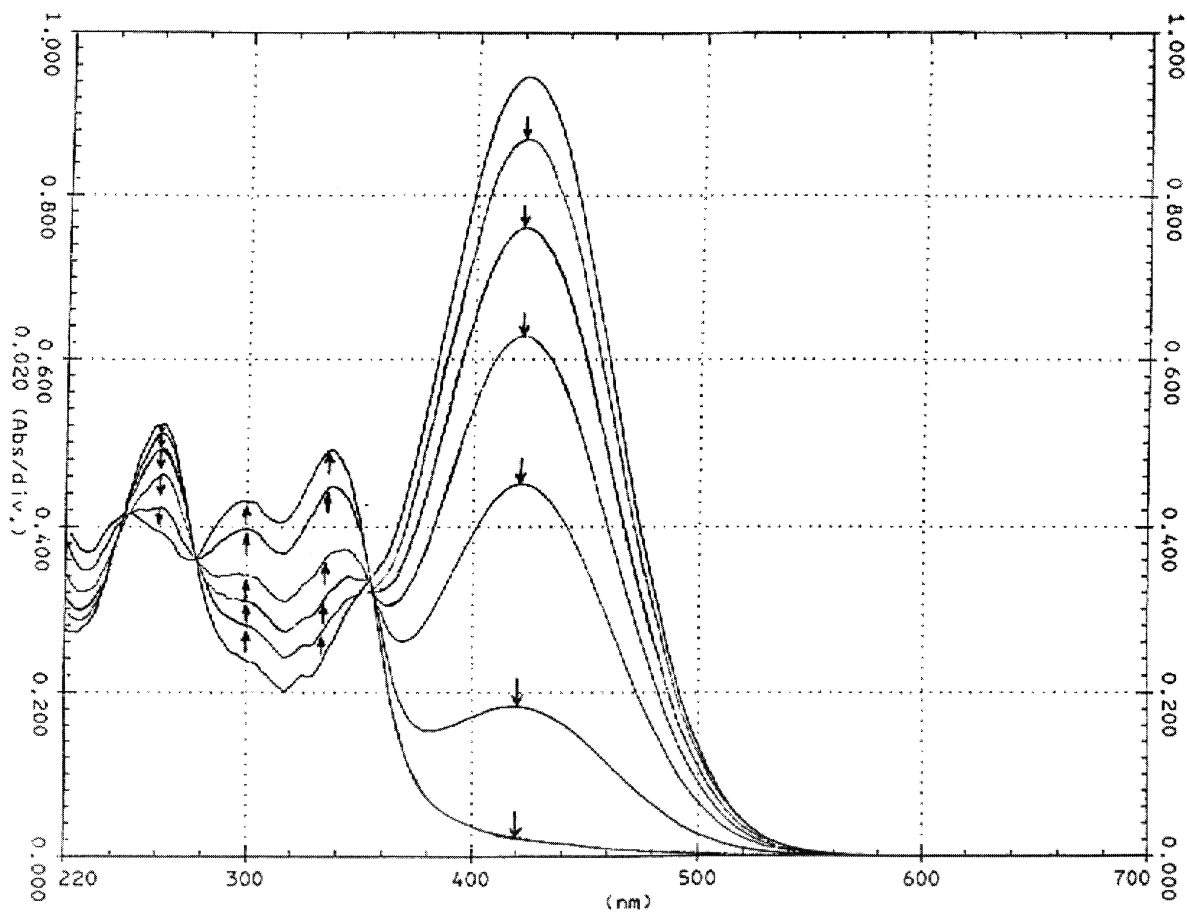


Fig. 1. The progress of UV-Vis photolysis of *p*-N,N-dimethylamino- β -methyl- β nitrostyrene, **1a** in 95% undenatured ethanol via Hanovia type 400-W low-pressure mercury arc lamp under N_2 .

oxime products **2a–2f** in aqueous ethanol varied between 87 and 100%: **2d**=**2c**(99.5%)>**2b**(99.0%)>**2a**(90.2%)>**2e**(88.1%)>**2f**(86.8%). Electron donating groups attached at *para*-position of the phenyl ring promoted the nitro-nitrite rearrangement (Scheme 1). Electron withdrawing groups attached to the *para*-or *meta*-positions of the phenyl ring

partially inhibited this photorearrangement and gave some fragmentation products, **10–12** (Scheme 3). Since the GPC photochemical yield of **2f** ($G=CF_3$, $R=CH_3$) is 86.8% and the value of the σ for trifluoromethyl group at the *para*-position is 0.54 and that of the nitro group at the *para*-position is in the same order of 0.78, hence

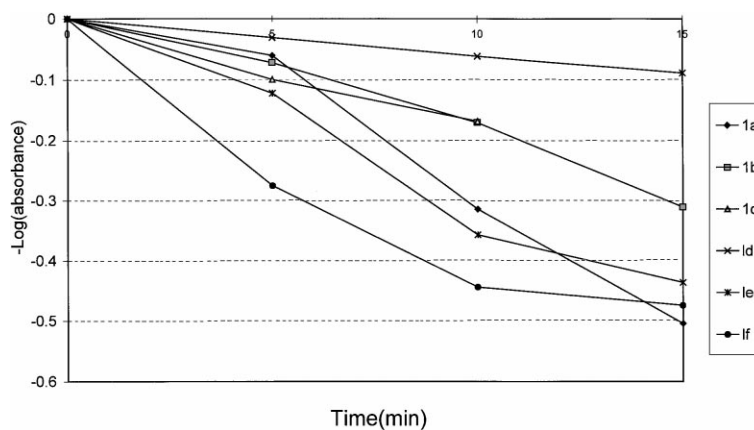


Fig. 2. Substituent effects on the kinetics of photochemistry of β -Methyl- β -Nitrostyrene derivatives, **1**. $-\log A$ (of **1**) vs. time (minutes). The absorbances are corrected for extinction at the monitoring wavelength.

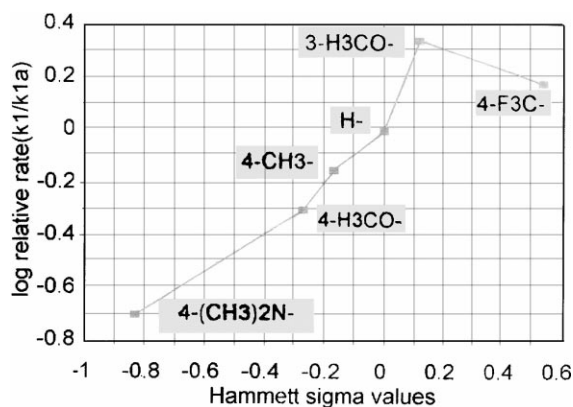


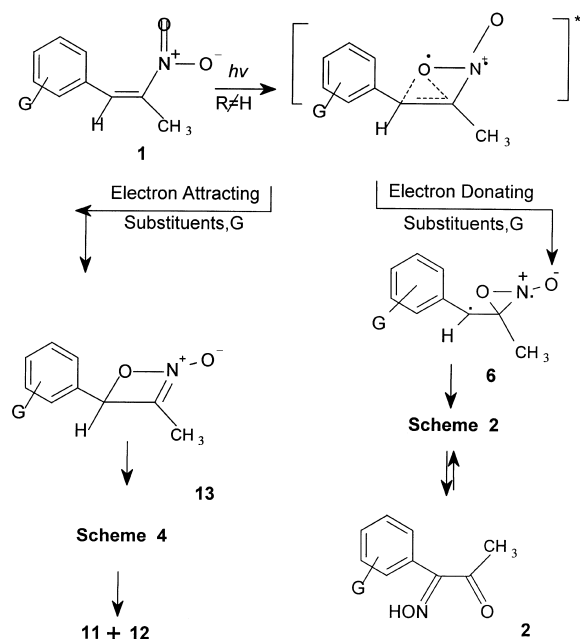
Fig. 3. Correlation of the relative rate coefficients ($\log k/k_0$) for the unimolecular photochemical rearrangement of **1** as a function of Hammett constants σ .

the low (38%) yield of **2_i** ($R=4-O_2N-Ph$, $G=H$) from *cis*- α ,4-dinitrostilbene (**1_i**) as reported by Pinhey and Rizzardo [19] or the low yields of **2_j** (15%) and **2_k** (19%) as reported by Tang [20] can not merely be attributed to the electron withdrawing effect of nitro group. We may conclude that there is a competition between aromatic nitro group attached at *para*- or *meta*-positions and the unsaturated β -nitro group during irradiation. This competition which is in favour of the former may well be the major cause for the lowering of the yield of the oximes with $-NO_2$ group attached at the phenyl ring.

The photochemical half-lives of nitroolefins, **1_a**–**1_f** were in the order of **1_d** (43.3 min) > **1_c** (15.8 min) > **1_b** (13.3 min) > **1_a** (9.6 min) > **1_f** (6.4 min) > **1_e** (4.4 min). Therefore, electron donating groups attached to the *para*- or *meta*-positions of the phenyl ring could decrease the disappearance rate of nitroolefins **1**, while increase the yield of the corresponding oxime **2**.

Also, electron withdrawing groups attached to the *para*- or *meta*-positions of the phenyl ring could enhance the rate of photochemical decomposition of **1**, while decrease the yield of the corresponding oxime **2**. The mechanism shown in Scheme 5 is consistent with our results. This mechanism unifies and includes ideas proposed by Chapman [10,11], Pinhey [19], Matsuura [21], Reasoner and Kassaee [22–25]. Certain features of these reactions deserve some comments. It is clear that the initial reaction is stereoelectronically controlled. In other words, for nitro-nitrite photorearrangement to be initiated by n to π^* overlap, NO_2 group must be out of conjugation with the double bond [11]. The importance of the ability of the substituents to alter the resonance of the system is pointed up by the fact that photoconversion of **1_g** ($R=G=H$) to **2_g** has not been observed (0% yield), while photorearrangement of **1_a**–**1_f** to **2_a**–**2_f**, (Scheme 1) was shown to occur in almost quantitative yields.

The observed λ_{max} is: **1_d** ($G=p-(CH_3)_2N-$, 421 nm) > **1_c** ($G=p-HC_3O-$, 343 nm) > **1_b** ($G=p-CH_3$, 320 nm) > **1_a** ($G=H$, 305 nm) > **1_e** ($G=m-H_3CO-$, 300 nm) > **1_f** ($G=p-F_3C-$, 299 nm).



Scheme 5. Provisional mechanism for photochemistry of β -methyl- β -nitrostyrene and its derivatives, which unifies and includes ideas previously reported [10,11,16,19–25], and is consistent with our results.

The ϵ_{max} order for **1_a** through **1_f** are 115, 123, 133, 112, 103, and 96, respectively.

The Hammett σ values for **1_a** through **1_f** are 0, -0.17 , -0.83 , 0.12 and 0.54, respectively. These results indicate that electron withdrawing groups attached to *para*, **1_f** or *meta*, **1_e** positions could cause the hypochromic effects and hypsochromic shifts in ϵ_{max} and λ_{max} in the opposite order as that of the corresponding Hammett σ substituent values.

Electron donating groups attached to *para*-position of the phenyl ring could cause the hyperchromic effects and bathochromic shifts of the β -nitrostyrene in ϵ_{max} [29]¹ and λ_{max} values in the opposite order as that of the corresponding σ values. Comparison of the observed bathochromic or hypsochromic shifts or hyperchromic and the hypochromic effects in substituted β -methyl- β -nitrostyrenes with those of the model compound **1** corroborate the ability of the substituents to offer electronic inhibition to the resonance of the system. In the case of electron donating substituents ‘better resonance’ may make the $-NO_2$ group more planar with the double bond of the styrene, hence a competition for *cis*–*trans* isomerization lowers the rate. We are studying such a possibility at the present time.

A simple Hammett equation technique is applied in order to estimate the sign, the order of magnitude and the charge at the transition state [30]. A ρ value of 0.7 was obtained for the unimolecular photorearrangement of **1** as a function of σ constants (Fig. 3). This rather small ρ value reflects the

¹ λ_{max} value of **1_d** does not follow the opposite order of σ values. This may be due to the ‘inhibition’ of resonance possibly caused by N,N-dimethylamino group which is sterically forced out of the plane.

small sensitivity of the substrate to the electronic effects of the substituents. Therefore, much of the photochemistry is controlled by the nitro group chromophore and not the benzene ring! While the mechanism of the reaction may involve radical like intermediates, electron withdrawing groups predict to increase the rate or equilibrium constant. Such is the case observed in this paper.

The excited $-\text{NO}_2$ might undergo fluorescence, phosphorescence, radiationless decay or energy transfer to the double bond of styrene via exciplexes². In order to form such exciplexes or biradicals during nitro-nitrite rearrangement, an interaction between the half field n orbital of $\beta\text{-NO}_2$ and π^* orbital of the double bond must occur at some stage of the rearrangement. Two possible orientations of n orbital with the C_α and C_β of the π^* are possible which lead to two different products of aldehyde **11** and oxime **2**, respectively. The relative stabilities of these two orientations would then control the relative rates of formation of the different products. When the reactions are irreversible, the relative amount of products may be predicted if the relative stabilities of the orientation complexes are calculated [25,31,32]. The frontier orbitals of **1** are the half-vacant nonbonding HOMO of $-\text{NO}_2$ as the donor or nucleophile, and the empty π^* LUMO of the double bond, as the acceptor. LUMO energy is expected to increase in going to more conjugated derivatives with electron releasing substituents, **1b**, **1c** and **1d** which show higher λ_{max} values; thereby decreasing the energy to be gained on interaction of this orbital with the HOMO of the nucleophile. Hence, lower rates are expected for photoreaction of the derivatives of **1** with electron releasing substituents. The observed rates in this study meet this expectation and suggest the possibility of nucleophile–electrophile combination as the rate determining step. Both the LUMO coefficients and the charge on β -carbon of the double bond are expected to decrease with increasing unsaturation (λ_{max}). Electron releasing substituents are expected to place higher coefficients on C_α which in turn give higher yields of the corresponding oximes. When the substituted aromatic ring is sufficiently electron releasing, as in **1b**, **1c** and **1d**, a relatively more positive charge may be stabilized on the β -carbon of the double bond of styrene and the attack from oxygen of $\beta\text{-NO}_2$ occurs at the β -carbon which results in a relatively higher yield of **6** (Schemes 2 and 5). Also, when the substituted aromatic ring is sufficiently electron attracting, as in **1e** and/or **1f**, a relatively less positive charge may be stabilized on the β -carbon of the double bond of the styrene in a way that the attack from oxygen of $-\text{NO}_2$ occurs at the α carbon and results in a relatively higher yield of **13**. The possibility of concerted formation of oxetane, **13** (Scheme 4), also exists. Geometric requirements for this 2+2 concerted addition of $-\text{N}=\text{O}$ to $\text{C}=\text{C}$ are better provided via **1e**, and **1f** which have electron attracting groups on their phenyl rings with less conjugation and lower λ_{max} values.

Moreover, photorearrangement of **1** under employed conditions is an irreversible process with no secondary reaction processes [32].

4. Conclusions

Four general conclusions can be derived from the investigations presented in this article.

First, it has been shown that electron donating groups attached to *para*-position of the phenyl ring of **1** promote the nitro-nitrite rearrangement, while electron-attracting groups at the *para*- or *meta*-positions of the phenyl ring inhibit this photorearrangement. Second, electron withdrawing groups attached at the *para*- and *meta*-positions of the phenyl ring of **1** enhance the initial rate of photochemical decomposition of β -methyl- β -nitrostyrene and its derivatives. This behaviour is in contrast to the electron donating substituents. Third, electron donating groups attached to *para*-position of the phenyl ring caused hyperchromic effect and bathochromic shifts. This was in contrast to electron attracting groups. Fourth, a rather small Hammett ρ value reflects the small sensitivity of nitro-nitrite photorearrangement to the electronic effects of substituents. This minimal substituent effects suggest that, much of the photochemistry is controlled by the nitro group chromophore rather than the benzene ring.

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² Formation of such exciplex or biradical could be reversible.

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