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Synthesis and photoreactions of aromatic diols containing bis (azo) and bis (o-nitrobenzyl) chromophores

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ABSTRACT

Aromatic diols containing bis (azo) and bis (o-nitrobenzyl) chromophores viz., (4-hydroxyphenylazo)-2,2/-dinitrodiphenylmethane, 4-hydroxy-3-methylphenylazo-4/-hydroxyphenyl-azo-2,2/-dinitrodiphenyl methane and bis (4-hydroxy-3-methylphenylazo)-2-dinitrodiphenyl methane were synthesized from 4,4-diamino-2,2/-dinitrodiphenylmethane and phenol/0-cresol. As a result of photolysis, the azo group of the diols unergo trans-cis isomerisation and one of the o-nitrobenzyl groups of the diols undergo trans-cis isomerisation and one of the o-nitrobenzyl groups in them undergo redox reaction to nitronitrosocarbinol. There occurred a solubility difference between the irradiated and unirradiated diol. In solution, a photoswtiching behaviour was also observed.

Key words: Aromatic diols, bis(azo), bis(o-nitrobenyl), photoswtiching, nitronitrosocarbinol.

INTRODUCTION

Photoactive multifunctional organic molecules have been investigated for the last few years for requirements in the areas of photolithography[1], printing materials[2], medicinal fields[3] and optical information storage system[4]. The phototransformation of the isomerisable chromophores in organic molecules can also have the potential for use in nanostructuring[5]. By a molecular engineering approach, it is possible to design molecules with such chromophores. When azo chromophore is incorporated in a molecule, it leads to a wide range of unexpected photoisomerisations[6]. The incorporation of o-nitrobenzyl chromophore in a molecule can cause a change in its polarity because of photofragmentation[7] or photorearrangement[8]. However, the photochemical behaviour of the o-nitrobenzyl group in presence of the azo group has not been carried out so far. The present paper describes the synthesis and characterization of a set of aromatic diols containing these two chromophores and their photoreactions in protic and aprotic solvents.

EXPERIMENTAL

IR spectra were recorded on IFS 66U FTIR spectrometer. ^{1}H NMR spectra were recorded on JEOL and GSX 400 MHz spectrometer and ^{13}C NMR spectra were obtained using Bruker 300 MHz spectrometer with TMS as internal standard. UV-vis-spectra were obtained using Schimadzu UV-2100 spectrophotometer. The chromophores were purified by column chromatography using 100-200 mesh silica gel and appropriate mixture of benzene and ethylacetate-benzene midture for elution. The purity of the products was monitored both by UV and TLC measurements. TLC was performed on glass plate coated with silica gel GF254 containing 13% calcium sulphate as binder. Spectroscopic grade solvents were used for all measurements.

The irradiations were carried out with a Philips HPK 125W high pressure mercury lamp in a water-cooled quartz reactor. The rate of converstion of the chromophores was determined by the expression[9], Percentage conversion = $(A_0-A_T) \times 100/A_0$

Where A_0 and A_T are the absorption intensities of the chromophores before and after irradiation at regular intervals respectively.

Synthesis of compounds

4,4′-Diamino-2,2′-dinitrophenylmethane [1b]

4,4′-diaminodiphenylmethane, 1a (m.p. 92°C) was nitrated[10] using a mixture of anhydrous potassium nitrate and 98% sulphuric acid at 0°C. A solution of potassium nitrate (0.05 mol, 5.05g) in conc. sulphuric acid (18 M, 40 mL) at 0°C was added to an ice-cold solution (18 M, 40 mL) dropwise 4,4′ -diaminodiphenylmethane (0.025 mol, 5g) in conc, sulphuric acdi (18 M, 40 mL) dropwide over a period of half an hour, with stirring. The stirring was continued for another 3 h, keeping the reaction mixture at 0°C. The reaction mixture was diluted by pouring it over crushed ice and was then neutralized with ice-cold ammonia solution (1:1). The orange-yellow solid was filtered, washed thoroughly with water and dried. This product was recrystallised from ethylacohol-ethyl acetate mixture (90:10) and that furnished orange-red flakes of 4,4′-diamino 2,2′ -dinitrodiphenylmethan.

Bis(4-hydroxyphenylazo)2,2′-dinitrophenyl methane [1c]

To an ice-cold solution of 4,4′-diamino 2,2′ -dinitrodiphenylmethan (6.25 mmol, 1.8g) in sulphuric acid (6 M, 15 mL), was added an aqueous of sodium nitrite (1.1g, 5mL) dropwide over a period of 10 minutes, with continuous stirring. The excess of nitrous acid formed was neutralised with urea (0.75g). The diazonium salt solution was diluted with ice-cold water and the pH of the solution was maintained at 7-7.5 by adding sodium acetate. The resulting solution was added dropwise to ice-cold alkaline solution of phenol (12.5 mmol, 0.8 mL). The reaction mixture was cooled and kept for 2 hrs. A solid was separated, washed well with water, and dried. The crude product was recrystallised from ethyalcohol-ethyl acetate mixture.

4,4′-hydroxy-3-methylphenylazo-4′-hydroxyphenylazo-2′-dinitrodiphenylmethane [1d]

4,4′-diamino 2,2′-dinitrodiphenylmethane was diazotized and coupled with 1:1 mixture of phenol and o-cresol: To an ice-cold solution of 4,4′-diamino 2,2′-dinitrodiphenylmethan. (0.025 mol, 7.2 g) in sulphuric acid (6M, 50 mL), aws added an aqueous solution of sodium nitrite (4.4g, 20 mL) over a period of 20 minutes with continuous stirring. The excess of nitrous acid formed was destroyed with urea (3g). The diazotized solution was coupled with an alkaline solution of a mixture of phenol (0.25 mol, 1.6 mL) and o-cresol (0.025 mol) 2.6 mL), by maintaining the pH of the solution at 7-7.5. A brown solid was separated, Washed with water and dried. The crude product was purified by column chromatography using ethylalcohol-ethyl acetate as eluting mixture.

Bis (4-hydroxy-3-methylphenylazo)-2′-dinitrodiphenylmethane [1e]

The diazonium chloride prepared by reacting an ice-cold solution of 4,4′-Diamino-2,2′-dinitrophenylmethane (0.0218 mol, 6.3g) in sulpuric acid (6M , 45 mL) with aqueous solution of sodium nitrite (4.4g, 70 mL) was coupled with an alkaline solution of o-cresol (0.044 mol, 4.55 mL) at 0-5°C and the pH of the solution ws maintained at 7-7.5 by adding sodium acetate before the addition of o-cresol. The brown solid was collected, washed with water, dried and recrystallized from ethylalcohol-ethyl acetate mixture.

Photolysis of 1c/1d/1e in 2-propanol

A solution of 1c/1d/1e (250mg) in dry 2-propanol (500 mL) was deoxygenated by bubbling nitrogen gas for 20 minutes. The stirred solution was irradiated for 32 hrs. After the irradiation, TLC examination of the solution showed the complete conversion of the starting material. The solvent was then removed by distillation under reduced pressure. The photolysate was purified by recrysallisation from ethyl acetate to give cis-bis(4-hydroxyphenylazo)-2-nitro-2′-nitroso-diphenylcarbinol(5c), cis-4-hydroxy-3-methylphenylazo-4′-hydroxyphenylazo-2-nitro-2′-nitroso dipheynlcarbinol (5d) and cis-bis (4-hydroxy-3-methylphenylazo)-2-nitro-2′- nitrosodiphenyl-carbinol(5e,) corresponding to 1c, 1d and 1e respectively.

Photolysis of 1c/1d/1e in acdified 2-propanol

A solutino 1c/1d/1e (250 mg) in dry 2-propanol (500 mL) containing conc. sulphuric acid

(1 mL) was irrdiated for 16 hr. The TLC examination of the solution was carried out to ascertain the completion of the reaction. The solution was neutralized with anhydrous sodium carbonate. The precipitated sodium was filtered off. The solvent was distilled under reduced pressure. The resulting phogolysate was recrystallised from ethyl acetate to give cis-bis(4-hydroxyphenylazo)-2-nitro-2′-nitroso-diphenylcarbinol(5c), cis-4-hydroxy-3-methylphenylazo-4′-hydroxyphenylazo-2-nitro-2′-nitroso dipheynlcarbinol (5d) and cis-bis (4-hydroxy-3-methylphenylazo)-2-nitro-2′-nitrosodiphenyl-carbinol(5e,) corresponding to 1c, 1d and 1e respectively.

Photolysis of 1c/1d/1e in ethyl acetate

A solutino 1c/1d/1e (250 mg) in dry 2-propanol (500 mL) containing conc. sulphuric acid (1 mL) was irrdiated for 38 hr. Then the same procedure for the photolysis in 2-propanol was carried our to give cis-bis(4-hydroxyphenylazo)-2-nitro-2′-nitroso-diphenylcarbinol(5c), cis-4-hydroxy-3-methylphenylazo-4′-hydroxyphenylazo-2-nitro-2′ -nitroso dipheynlcarbinol (5d) and cis-bis (4-hydroxy-3-methylphenylazo)-2-nitro-2′-nitrosodiphenyl-carbinol(5e,) corresponding to 1c, 1d and 1e respectively.

Photolysis of 1c/ 1d/ 1e in acidified ethyl acetate

The irrdiation of 1c / 1d / 1e (250 mg) dissolved in dry ethyl acetate (500 mL) containing 1 mL of conc. sulphuric acid, for 20 hrs, followed by the work up the solution as before, yielded cis-bis(4-hydroxyphenylazo)-2-nitro-2′-nitroso-diphenylcarbinol(5c), cis-4-hydroxy-3-methyl phenylazo-4′-hydroxyphenylazo-2-nitro-2′-nitroso dipheynlcarbinol (5d) and cis-bis (4-hydroxy-3-methylphenylazo)-2-nitro-2′- nitrosodiphenyl-carbinol(5e,) corresponding to 1c, 1d and 1e respectively.

The physical and analytical data of the synthesized titled compounds are given as follows:

4,4′-Diamino-2,2′-dinitrophenylmethane [1b]

Yield: 70.20 %; m.p. 204-206 °C; IR (KBr υ_{max} in cm^{-1}); 1329, 1520, 3447, 3366, ^{1}H NMR ($CDCl_3$, δppm): 3.0 (s, 2H, Ph-CH_2-Ph), 4.8 (s, 4H, NH_2), 7.8 (d, 2H, Ph), 7.4 (d, 2H, pH), 8 (s, 2H, Ph); ^{13}C NMR ($CDCl_3$, δ ppm): 32 (CH_2), 124, 130, 135, 157, 159, 170 (Ph); EI ms: m/z: 288.02: Anal. Cald. for $C_{13}H_{12}N_4O_4$ (288.27) Cal. C:54.16; N:19.44. Found C:54.0; H4:17, N: 19.34.

Bis(4-hydroxyphenylazo)2,2′-dinitrophenyl methane [1c]

Yield: 62%; m.p. 372°C; IR (KBr υ_{max} in cm^{-1}); 1274, 1531, 1350, 1603, 2925, 2856, 3421; UV (2-propanol λ_{max} in nm): 248, 378; ^{1}H NMR (CD_3COCD_3, δppm): 3.2 (s, 2H, Ph-CH_2-Ph), 9.10 (s, 4H, NH_2), 7.8-8 (m, 8H, Ph), 8.77-8.1 (m, 6H, pH), ^{13}C NMR ($CDCl_3$, δ ppm): 32 (CH_2), 116, 120, 127, 135, 137, 139, 144, 153, 155, 170 (Ph); EI ms: m/z: 498.20: Anal. Cald. for $C_{25}H_{18}N_6O_6$ (498.47) Cal. C:60.24; H3.61; N:16.86. Found C:60.20; H:3.58, N: 16.78.

4,4′-hydroxy-3-methylphenylazo-4′-hydroxyphenylazo-2′-dinitrodiphenylmethane [1d]

Yield: 60%; m.p. 368°C; IR (KBr υ_{max} in cm^{-1}); 1274, 1352, 1530, 1594, 2924, 2853, 3412; UV (2-propanol λ_{max} in nm): 250, 379; ^{1}H NMR (CD_3COCD_3, δppm): 2.29 (s, 3H, CH_3), 3.25 (s, 2H, Ph-CH_2-Ph), 9.12 (s, 1H, OH_2), 9.2 (s, 1H, OH), 7.77-7.72 (m, 3H, Ph), 8-7.8 (m, 4H, pH), 8.77-8.1 (m, 6H, Ph); ^{13}C NMR ($CDCl_3$, δ ppm): 20 (CH_3), 32(CH_2) 117, 120, 121, 123, 126, 128, 132, 135, 146, 148, 157, 170, (Ph); EI ms: m/z: 512.24; Anal. Cald. for $C_{26}H_{20}N_6O_6$ (512.50) Cal. C:60.93; H: 3.90; N:16.40. Found C:60.92; H:3.88, N: 16.38.

Photolysis of 1c/1d/1e in 2-propanol

Yield: 58%; m.p. 365°C; IR (KBr υ_{max} in cm^{-1}); 1275, 1349, 1530, 1595, 1530, 2928, 2852, 3411; UV (2-propanol λ_{max} in nm): 255.5, 380; ^{1}H NMR (CD_3COCD_3, δppm): 2.29 (s, 6H, two CH_3), 3.3 (s, 2H, Ph-CH_2-Ph), 9.2 (s, 2H, OH),7.77-7.72 (m, 6H, Ph), 8.77-8.1 (m, 6H, pH), ^{13}C NMR ($CDCl_3$, δ ppm): 20 (CH_3), 32(CH_2) 116, 120, 124, 128, 128, 131, 135, 137, 139, 146, 154, 157, 170(Ph); EI ms: m/z: 526.27; Anal. Cald. for $C_{27}H_{22}N_6O_6$ (526.53) Cal. C:61.6; H: 4.18; N:15.97. Found C:61.12; H:4.15, N: 15.94.

Photoproduct of 1c (5c): Cis-bis(4-hydroxy phenylazo)-2-nitro-2′-nitroso-diphenylcarbinol

Yield: 72%; m.p. 380°C; IR (KBr υ_{max} in cm^{-1}); 3414, 2928, 1588, 1349, 1530, 1503, UV (dioxane, λ_{max} in nm): 364.252, ^{1}H NMR

(CD_3COCD_3, δppm): 3.1-3.2 (d, 1H, OH), 4-4.1 (s, 1H-CH-), 9.12 (s, 2H, OH), 7.8-8 (m, 8H, Ph), 8.77-8.1 (m, 6H, pH), ^{13}C NMR (TFA-D, δ ppm): 60 (-CHOH-) 117, 121, 124, 128, 130, 133, 156 (Ph); EI ms: m/z: 498.20; Anal. Cald. for $C_{25}H_{18}N_6O_6$ (498.47) Cal. C:60.24; H: 3.61; N:16.81. Found C:60.15; H:3.56, N: 16.74.

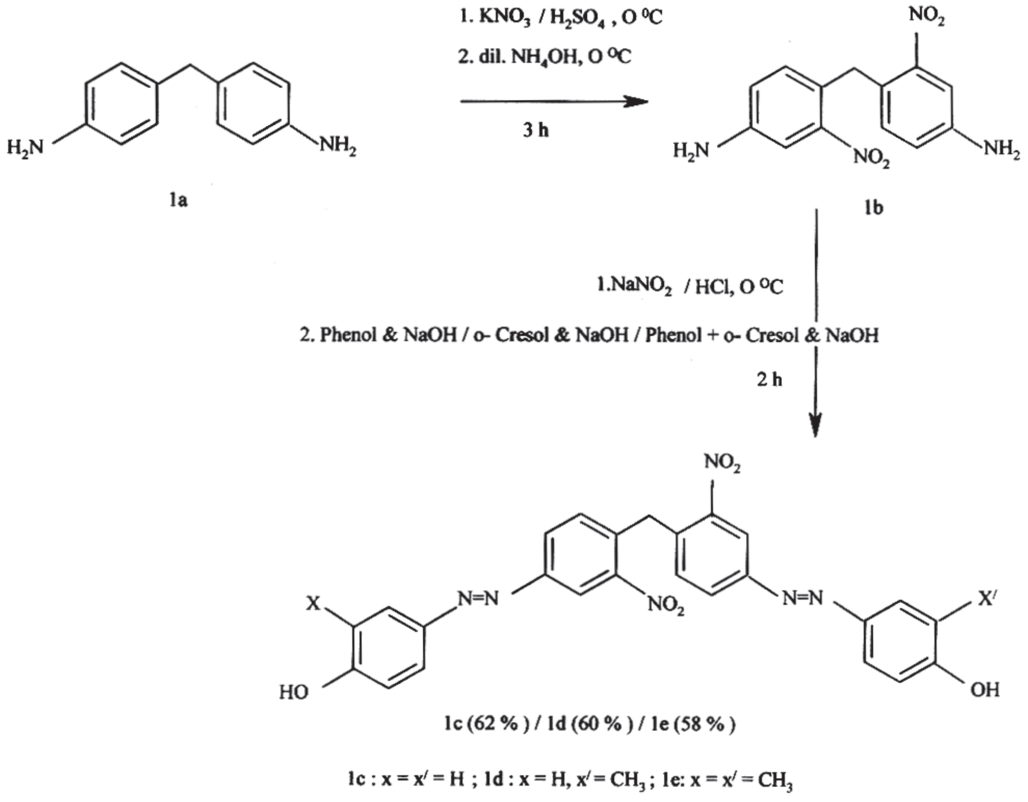
Photoproduct of 1e (5e): Cis-bis(4-hydroxy-3-methylphenylazo)-2-nitro-2/-nitroso-diphenylcarbinol

Yield: 68%; m.p. 370°C; IR (KBr υ_{max} in cm^{-1}); 3400, 2930, 1590, 1349, 1530, UV (dioxane, λ_{max} in nm): 366.253, ^{1}H NMR (CD_3COCD_3, δppm): 2.29 (s, 6H, two CH_3) 3.1-3.2 (d, 1H, OH), 4-4.1 (d, 1H, -CH-), 9.2 (s, 2H, OH), 7.77-7.72 (m, 6H, Ph), 8.77-8.1 (m, 6H, pH), ^{13}C NMR (TFA-D, δ ppm): 21 (CH_3), 60 (-CHOH-) 116, 122, 124, 125, 126, 128, 130, 132, 134, 147, 157 (Ph); EI ms: m/z: 526.27; Anal. Cald. for $C_{27}H_{22}N_6O_6$ (526.53) Cal. C:61.60; H: 4.18; N:15.97. Found C:61.54; H:4.13, N: 15.89.

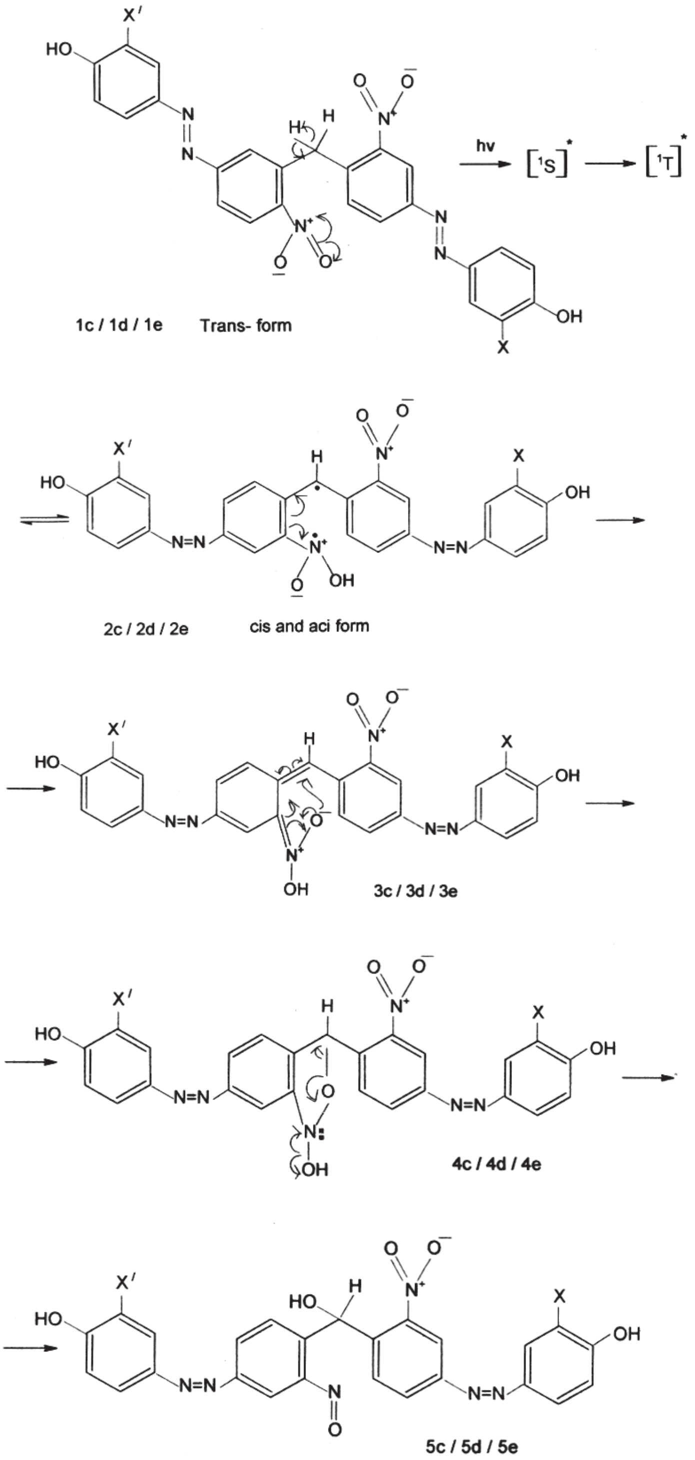
RESULTS AND DISCUSSION

For the dinitro derivative 1b, the IR peaks at 1520 and 1329 cm^{-1} confirmed the nitro substitution. In the ^{13}C NMR spectrum of 1b, there were only six peaks due to aromatic carbons. This indicated that the nitro groups were substituted in a symmetrical fashion in both the phenyl rings. This was further confirmed by ^{1}H NMR signals at δ 7.4 to 8

In the case of the dihydroxy compounds, 1c / 1d / 1e, the IR peaks due to -OH groups were observed at 3421 / 3412 / 3411 cm^{-1} respectively and their C-O stretch were observed at ~1274 cm^{-1}. The peak between 1594 and 1603 cm^{-1} was due to the azo group. In the UV-vis spectra, the peaks observed at 378 / 379 / 380 nm were due to the azo groups (π-π*) and the peaks at 248/ 250 / 255 nm were due to the nitro gropus. In ^{13}C NMR spectra of 1c / 1d / 1e, ten fifteen and twelve signals were observed respectively, due to atomatic carbons, the



Scheme 1:



c : $x = x' = H$; d: $x = H$, $x' = CH_3$; e : $x = x' = CH_3$

Scheme 2:

signals due to methylene carbon was observed at 32 ppm and the signals due to methyl carbon observed at 20 ppm.

The mass spectrum and elemental analysis of 1c, 1d and 1e also confirmed the proposed structures. This was further confirmed by the ^{1}H NMR spectra. In this spectra, the peaks due to phenolic protons were observed at δ 9.10 / 9.12 / 9.2, the peaks due to methylene protons were observed at δ 3.2 / 3.25 / 3.3 respectively, the peaks due to aromatic protons were observed between δ 7.8-8, 8.77-8.1 and 7.77-7.72 and the peak due to methyl protons were at δ 2.29.

The photoproducts obtained from the photolsyis of 1c, 1d and 1e in 2-protons/acidified 2-propanol / ethyl acetate / acidiffied ethyl acetate, are the same: In the IR spectrum of the photoproducts, intensities of NO_2 peaks ~ 1530 and ~ 1350 cm^{-1} were reduced and a new peak appeared at ~ 1503 cm^{-1} due to the formation of nitroso group and the peak at ~2930 cm^{-1} was retained. The partial oxidation of the $-CH_2$ group to -CHOH at the expense of the reduction of one of the nitro groups in the molecule to nitroso group was confirmed by the increase in intensity of the OH peak at δ 3.1-3.2, and the shifting of the methylene peak to δ 4-4.1 in the ^{1}H NMR spectrum. In the ^{13}C NMR spectrum of the photoproducts, the signal δ 60 and the decrease in the number of signals from 11 to 9, from 17 to 14 and from 14 to 13 respectively and sharp singals δ 128 and 130 further confirmed the proposed structure for the photoproducts.

The isomerisation of the azo chromophore in the molecule was established by the shifting of the IR absorption at 1603 cm^{-1} of 1c, 1594 cm^{-1} of 1d and 1595 cm^{-1} of 1e to 1588, 1584 and 1590 cm^{-1} respectively. The isomerisation was further confirmed by the shifting of UV-absorption at 378-380 nm [trans form, $\pi \rightarrow \pi^*$] of 1c-1e, to 364-366 nm.

Mechanism

To account for the photoproduct of 1c, 1d and 1e during photolysis, the following mehanism is suggested: The spectral details of the photoproducts of 1c, 1d and 1e reveal that as a result of photolysis, the azo group undergoes tran→cis isomerisation and one of the nitro groups undergoes an intramolecular redox reaction. The proximity of methylene group at the o-nitrobenzyl segment causes the electronically excited nitro group at the o-nitrobenzyl segmetn causes the electronicaly excited nitro group to abstract the methylane hydrogen and the nitro group is reduced to nitroso group and the resulting 1,4-biradical (2c-2e) undergo cyclisation to give (4c-4e). The phototransformation[11] proceeds through the nitronic acid, 3c / 3d / 3e, which in turn is formed through their singlet and triplet excited states. The decay of the triplet state to the nitronic acid (aci form) occurs through the biradical intermediate, 2c / 2d / 2e. The nitronic acid further undergoes cyclisation, leading to the benzisoxazoline intermediate 4c / 4d / 4e, which is readily converted to the nitronitroso carbinol, 5c / 5d / 5e (scheme 2).

CONCLUSIONS

The photoproducts, 5c-5e isolated from the photolysis of 1c-1e under various conditions show identical chemical nature, even though the rates of the reactions and the yields are different. The presence of the azo group in the moleculr diminishes the reactivity of the o-nitrobenzyl chromophore as only one of the two nitro groups undergo photoreaction.

Thus, the photolysis of the dils results in an interesting photoredox reaction and isomerisation, in which one of the o-nitrobenzyl groups undergo redox reaction to to nitronitrosocarbinol and the azo group undergo trans-cis isomerisation. In solution, a photo-swtiching behaviour is also observed. The polarity difference due to the redox reaction and isomerisation causes to solubility difference between the irradiated and unirradiated diol. Hence the diols can be used for making positive photoresist materials and also so optical information storage systems by incorporating them as monomers for polymer synthesis.

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