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Photoisomerization of Spironaphthalenones and its Mechanism

Tirumalai R. Kasturi*, Asish B. Mandal,
Ganesha K. B. Prasad and Gonibella J. Raju.

Department of Organic Chemistry
Indian Institute of Science
Bangalore 560 012, India.

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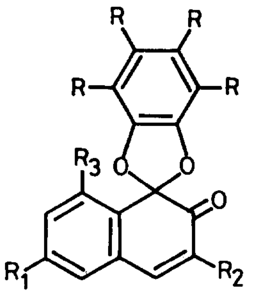
Abstract: Spironaphthalenones **1a-g** & **1j-m** on irradiation, with UV light gives the isomeric spironaphthalenones **2a-g** & **2j-m** in almost quantitative yield. On the other hand, spironaphthalenones **1h**, **1i**, **1n** & **1o** photoisomerized to the isomeric spironaphthalenones in reduced yields. Similar irradiation of **2a-g** & **2j-m** did not bring any change whereas **2h**, **2i**, **2n** & **2o** rearranged to isomeric spironaphthalenones. A probable mechanism has been proposed for this isomerization.

Introduction

The photochemistry of linearly conjugated cyclohexadienones has been studied by different workers. 2,4-Cyclohexadienones have been shown to undergo 1,6-bond cleavage(α - bond) upon photolysis[1,2]. On the other hand, 6,6-spiroepoxy-2,4-cyclohexadienone has been reported[3] to undergo epoxy C—O (β -bond) bond cleavage resulting in the aromatization of the cyclohexadienone system to give salicylaldehyde. A novel photoisomerization of spironaphthalenones 1 and 2 involving a β C—O bond cleavage, has been reported by us in a preliminary communication[4]. In an effort to understand the electronic and steric effects operating in these rearrangement, we have carried out the photoisomerization of several spironaphthalenones **1a-o** & **2a-o** and the results obtained in this study are discussed in this paper.

Results and discussion

The spironaphthalenones **1a-i** (β-dienones) and **2a-i** (α-dienones) were prepared by the oxidation of the corresponding 2-naphthols with o-chloranil in benzene[5a-c]. We have also prepared similar type of spironaphthalenones 1j–o and 2j–o by the oxidation of the corresponding 2-naphthols using *o*-bromanil as oxidizing agent. Structure of the isomeric spironaphthalenones 1j–o and 2j–o was evident from their spectral data[5b].



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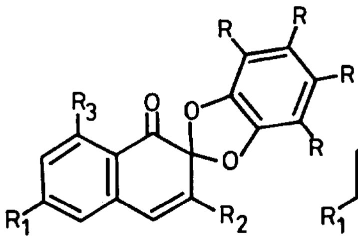

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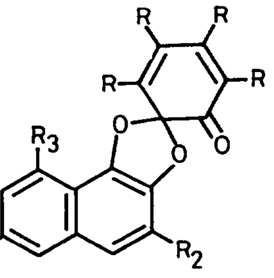

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The β-dienones 1 show two UV absorption bands between 300 and 330 nm, the latter band having a greater ϵ-value while the α-dienones 2 show two bands around 300 and 350 nm with the latter having a lesser ϵ-value. Photolysis of a benzene solution (0.002 – 0.004 M) of spironaphthalenones was carried out in pyrex tubes under deareated conditions using a 450 W medium pressure mercury lamp, which transmits light of wave length >300 nm. After the irradiation, the solution was concentrated and the product / products obtained were characterised by comparison with authentic samples. Results obtained in this study are given in the Table-I.

Inspection of the data reveals that all the β-dienones except the 6-bromo (1i & 1o) and 6-methoxy (1h & 1n) isomerized to the corresponding α-dienones in almost quantitative yield. On the other hand, none of the α-dienones except 6-bromo and 6-methoxy dienones 2i & 2o and 2h & 2n respectively, underwent isomerization on irradiation. While irradiation of 6-bromo α-dienones 2i & 2o resulted in 25 % isomerization to 1i & 1o, the extent of isomerization was as high as 75 % with 6-methoxy α-dienones 2h & 2n. It is apparent that the isomerization of α-dienones to the corresponding β-isomer is more facile in the case of 6-methoxy dienones (2h & 2n) unlike in other cases.

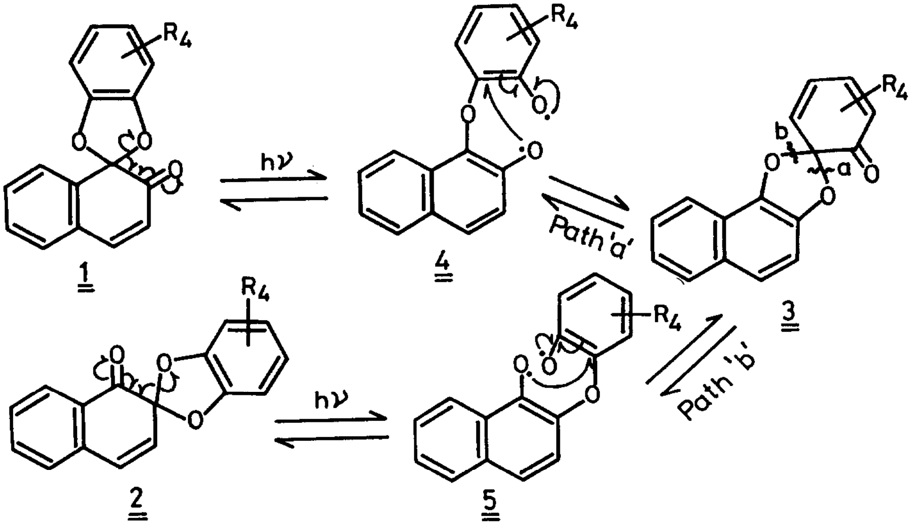
TABLE-I

Isomeric Spironaphthalenones	**Extent of isomerization(%)**	
	1→ 2	2→ 1
1a and **2a**: $R_1=R_2=R_3=R=H$	100	0
1b and **2b**: $R_1=R_2=R_3=H$; R=Cl	100	0
1c and **2c**: $R_1=R_2=H$; $R_3=CH_3$; R=Cl	100	0
1d and **2d**: $R_1=R_2=H$; $R_3=Pr^i$; R=Cl	90	0
1e and **2e**: $R_1=R_2=Bu^t$; $R_3=H$; R=Cl	100	0
1f and **2f**: $R_1=R_3=H$; $R_2=Bu^t$; R=Cl	90	0
1g and **2g**: R_1=CN; $R_2=R_3=H$; R=Cl	95	0
1h and **2h**: R_1=OMe; $R_2=R_3=H$; R=Cl	25	75
1i and **2i**: R_1=Br; $R_2=R_3=H$; R=Cl	75	25
1j and **2j**: $R_1=R_2=R_3=H$; R=Br	100	0
1k and **2k**: $R_1=Bu^t$; $R_2=R_3=H$; R=Br	90	0
1l and **2l**: $R_1=R_3=H$; $R_2=CH_3$; R=Br	100	0
1m and **2m**: R_1=CN; $R_2=R_3=H$; R=Br	90	0
1n and **2n**: $R_1=OCH_3$; $R_2=R_3=H$; R=Br	27	72
1o and **2o**: R_1=R=Br; $R_2=R_3=H$	76	26

Quenching experiments were carried out to get an idea of the excited state involved in the photoisomerization under study. The dienones **1b** and **1g** were chosen for this study, the results of which could be extrapolated to the other cases also. The two bands in the UV spectrum of the dienones could have arisen due to $\pi\pi^*$ and $n\pi^*$ absorptions. Probably, the excited state involved in the isomerization process could be $n\pi^*$ state since $\pi\pi^*$ absorption is cut off by the pyrex filter. An idea of the triplet energy of the dienone **1b** was obtained by approximate calculations. The lowest singlet energy (Es_o) is calculated as 75.3 KCals/ mole using the equation[6] $Es_o = h/\lambda o$. The lower range for the singlet energy of the dienone is 75.3 KCals/mole and hence, the triplet energy of the dienone must lie slightly below the value of 75.3 KCals/mole. Hence, triplet quenchers like naphthalene (E_T= 61 KCals/mole) and 1,3 -cyclohexadiene (E_T= 52.4 KCal/mole), with low triplet energies and having UV absorptions[7] at 275 and 223.5 nm respectively were chosen for this study. The effect of adding quencher on the irradiation process was determined by comparing the yield of the products obtained by irradiation of a solution of the dienone containing quencher with that obtained by a control (without quencher) irradiation carried out simultaniously under identical conditions. The non-occurance of quenching (vide experimental) of the photoisomerization of dienones **1b** and **1g** with triplet quenchers such as naphthalene and 1,3-cyclohexadiene suggests that the isomerization is originating from the lowest excited singlet state. The photoisomerization of all other dienones could be considered as proceeding similarly.

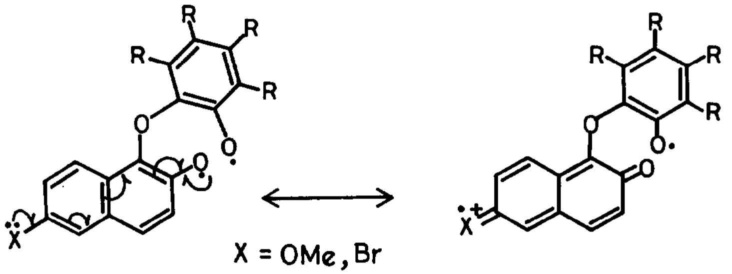
Mechanism of Photoisomerization

The photochemical isomerization involving singlet state perhaps follows a radical pathway[8]. Homolytic cleavage of the β C—O bond[9] of the dienone 1 could give the diradical intermediate **4** which could result in the formation of the cyclohexadienone intermediate 3. Similarly, the same intermediate 3 could also be formed via the diradical intermediate 5 resulting from initial β C—O bond cleavage of the dienones 2. A proposed mechanism of the photoisomerization could be visualised as in the scheme-I.



Scheme-I

Cleavage of β C—O bond by path 'a' followed by reorganisation leads to the formation of dienone 1. Similarly, cleavage of βC—O bond by path 'b' followed by reorganisation results in formation of dienone 2. Due to the greater resonance stabilization of the diradical intermediate 5 compared to **4**, the opening of the intermediate cyclohexadienone 3 perhaps occurs preferentially[10,12] in such a way as to give the α-dienone 2. This explains the absence of isomerization of α-dienones **2**, since the cyclohexadienone **3** which could be formed due to the β C—O bond cleavage of the dienones **2** should revert back to the starting α-dienones. In case of 6-methoxy (**2h** & **2n**) and 6- bromo (**2i** & **2o**) dienones, the diradical intermediate **4** is more resonance stabilized due to the electron releasing methoxy & bromo groups and hence, the opening of the cyclohexadienone 3 could occur via the path 'a' to give the dienone 1. The greater extent of isomerization in the case of 6-methoxy α-dienones **2h** & **2n** relative to that of 6-bromo α-dienones **2i** & **2o** is perhaps due to the greater electron releasing ability of the methoxy group.



The role of steric factor in the above photochemical isomerization seems to be negligible as is evident from the quantitative isomerization of **1e**, **1f** & **1l** to the corresponding isomeric dienones **2e**, **2f** & **2l** and also from the absence of any such isomerization of the dienones **2e**, **2f** & **2l** back to the dienones **1e**, **1f** & **1l** respectively, inspite of irradiation for longer time.

EXPERIMENTAL SECTION

All melting points reported herein are uncorrected. UV (nm) and IR (cm^{-1}) spectra were recorded on a HITACHI Model 557 Double wave length/ Double beam and HITACHI 270-50 Infrared spectrophotometers respectively. NMR spectra were recorded on a Jeol FX-90 Q spectrometer with Me_4Si as internal standard (δ =0 ppm). MS (70 eV) were recorded on a Jeol MS-DX 303 spectrometer fitted with a built-in direct inlet system. Analytical and preparative TLC were carried out using silica gel. All organic extracts were dried over anhydrous Na_2SO_4. Column chromatography was carried out using neutral alumina.

Oxidation of 2-naphthols with o-bromanil.

General Procedure: The oxidation reactions of 2-naphthols were carried out in refluxing dry benzene for 6 hrs using the reactants in 2:1 molar ratio(o-bromanil : 2-naphthol). After the removal of solvent in vacuo, the residue was chromatogrphed over neutral alumina using benzene as eluent.

a) with 2-naphthol: Reaction of 2-naphthol (0.5 gm) and o-bromanil (2.92 gm) in benzene (50 ml) gave a yellow solid which was chromatographed over neutral alumina using benzene as eluent to get a yellow crystalline solid (698 mg, 35.8%). This was purified by **PTLC** (hexane-chloroform 4:1) to give two compounds. These were characterised as i) 2,2-(tetrabromo-*o*-phenelenedioxy) naphthalene-1(2*H*)-one (2j ,328 mg): m.p. 206°C (chloroform-hexane); IR (nujol) 1599 and 1698 ; UV ($CHCl_3$) 246.5 (19,780) and 296 (6,850); ^{1}H NMR ($CDCl_3$) 6.30(1H,d, *J*=10.0 Hz), 6.92(1H,d, *J*=10.0 Hz), 7.23-7.77(3H,m) and 8.05(1H,dd, *J*=1.8 & 7.2 Hz); MS: m/e 562(M^+); Anal. calcd. for $C_{16}H_6O_3Br_4$: C, 34.16; H, 1.06. Found: C, 34.11; H, 1.08%. and ii)1,1-(tetrabromo-*o*-phenelenedioxy) naphthalene-2(1*H*)-one (1j, 370 mg): m.p. 236°C(chloroform-hexane); IR(nujol) 1597 and 1689 ; UV($CHCl_3$) 246(19.230) and 330(9,350); ^{1}H NMR ($CDCl_3$) 6.18(1H,d, *J*=10.0 Hz) and 7.28-7.74(5H,m); MS: m/e 562(m^+); Anal. calcd. for $C_{16}H_6O_3Br_4$: C, 34.16; H, 1.06. Found: C, 33.93; H, 1.02%.

b) with 6-*tert*-butyl-2-naphthol: Reaction of 6-*tert*-butyl-2-naphthol[13](0.5 gm) and *o*-bromanil (2.1 gm) in benzene (50 ml) gave a yellow solid which was chromatographed over neutral alumina using benzene as eluent to get a yellow solid (506 mg: 32.6%). This was purified by **PTLC** (hexane-chloroform 4:1) to give two dienones. The less polar compound was identified as the β-dienone (**1k**, 280 mg): m.p. 203°C(chloroform-hexane); IR (nujol) 1587 and 1686 ; UV ($CHCl_3$) 249.6(22,000) and 329.2(7,360); ^{1}H NMR($CDCl_3$) 1.35(9H,s), 6.18(1H,d, *J*=9.9 Hz) and 7.23-7.69(4H,m); MS: m/e 618(M^+); Anal. calcd. for $C_{20}H_{14}O_3Br_4$: C, 38.83; H, 2.26. Found: C, 38.57; H, 2.24%. The more polar compound was characterised as the α-dienone (**2k**, 226 mg): m.p. 198°C (chloroform- hexane); IR (nujol) 1599 and 1695 ; UV ($CHCl_3$) 250.2 (22,800) and 319 (7,350); ^{1}H NMR ($CDCl_3$) 1.34(9H,s), 6.25 (1H,d, *J*=9.9 Hz), 6.88 (1H, d, *J*=9.9 Hz), 7.25 (1H,d, *J*=1.8 Hz), 7.45(1H, dd, *J*= 1.8 & 8.1 Hz) and 7.95 (1H,d, *J*=8.2 Hz); MS: m/e 618 (M^+); Anal. calcd. for $C_{20}H_{14}O_3Br_4$: C, 38.83; H, 2.26. Found: C, 38.74; H, 2.26%.

c) with 3-methyl-2-naphthol: Reaction of 3-methyl-2-naphthol[14] (0.5 gm) and *o*-bromanil(2.66 gm) in benzene (50 ml) gave a yellow solid which was chromatographed over neutral alumina using benzene as eluent to get a yellow solid (406 mg, 27.8 %). This was purified by **PTLC** (hexane-chloroform 4:1) to give two dienones. These were characteriscd as i) the α-dienone(**2l**, 342 mg), m.p. 205°C (chloroform-hexane); IR(nujol) 1592 and 1689 ; UV($CHCl_3$) 248.6 (21,120) and 295.4(6,000); ^{1}H NMR($CDCl_3$) 2.06(3H,d, *J*=1.4 Hz), 6.63(1H,d, *J*=1.4 Hz), 7.14-7.46(2H,m), 7.58(1H, ddd) and 7.99(1H,dd, *J*=1.2 & 7.2 Hz); MS: m/e 576(M^+); Anal. calcd. for $C_{17}H_8O_3Br_4$: C, 35.41; H, 1.38. Found: C, 35.22; H, 1.38%. and ii) the β-dienone(**1l**, 164 mg), m.p.211°C (chloroform-hexane); IR(nujol) 1597 and 1680 ; UV($CHCl_3$) 247.4(21,200) and 334(5,660); ^{1}H NMR($CDCl_3$) 2.03(3H,d, *J*=1.4 Hz) and 7.25-7.74(5H,m); MS: m/e 576(M^+); Anal. calcd. for $C_{17}H_8O_3Br_4$: C, 35.41; H, 1.38. Found: C, 35.17; H, 1.32%.

d) with 6-cyano-2-naphthol: Reaction of 6-cyano-2-naphthol[15](0.5 gm) and *o*-bromanil(2.48 gm) in benzene(50 ml) gave a yellow solid which was chromatographed over neutral alumina using ethylacetate as eluent to get a yellow crystalline solid (383 mg, 22%). This was purified and characterised as the β-dienone (**1m**), m.p. 222°C (chloroform); IR(nujol) 1593, 1695 and 2230 ; UV($CHCl_3$) 249(17,125), 308(4,280) and 328(4,500); ^{1}H NMR($CDCl_3$): 6.35(1H,d, *J*=10.0 Hz), 7.47(1H,d, *J*=10.0 Hz), 7.67-7.87(3H, m); MS: m/e 587(M^+); Anal. calcd. for $C_{17}H_5O_3NBr_4$: C, 34.75; H, 0.85; N, 2.25. Found: C, 34.87; H, 0.82; N, 2.25%.

e) with 6-methoxy-2-naphthol: Reaction of 6-methoxy-2-naphthol[16] (0.5 gm) and *o*-bromanil(2.24 gm) in benzene (50 ml) gave a yellow solid which was chromatographed over neutral alumina using benzene as eluent to get a yellow crystalline solid (549 mg, 33.3%). This was purified by **PTLC** (chloroform-hexane 1:4) to give two dienones. These were characterised as

i) the α-dienone (**2n**, 471 mg), m.p. 187°C (chloroform-hexane); IR(nujol) 1597 and 1689 ; UV(CHCl$_3$) 258(30,520) and 330(9,610); ^{1}H NMR (CDCl$_3$) 3.86(3H,s), 6.23(1H,d, *J*=10.0 Hz),6.64-6.90(3H,m) and 7.95(1H,d, *J*=8.6 Hz); MS: m/e 592(M$^+$); Anal. calcd. for $C_{17}H_8O_4Br_4$: C, 34.45; H, 1.35. Found: C, 33.99; H, 1.29%. and ii) the β-dienone (**1n**, 78 mg), m.p. 199°C(chloroform-hexane); IR(nujol) 1593 and 1692 ; UV(CHCl$_3$) 258.2(22,940) and 324(6,800); ^{1}H NMR(CDCl$_3$) 3.91(3H,s), 6.20(1H,d, *J*=9.9 Hz), 6.87-7.03(2H,m), 7.39 (1H, d, *J*=9.9 Hz) and 7.67(1H,d, *J*= 8.1 Hz); MS: m/e 592(M$^+$); Anal. calcd. for $C_{17}H_8O_4Br_4$: C, 34.45; H, 1.35. Found: C, 34.57; H, 1.40%.

f) with 6-bromo-2-naphthol: Reaction of 6-bromo-2-naphthol[17] (0.5 gm) and o-bromanil (1.90 gm) in benzene(50 ml) gave a yellow solid which was chromatographed over neutral alumina using benzene as eluent to get a yellow crystalline solid (454 mg; 31.5%). This was purified by **PTLC** (hexane- chloform 4:1) to give two compounds. The less polar compound was characterised as the α-dienone (**2o**, 216 mg): m.p. 197°C (chloroform-hexane); IR (Nujol) 1584 and 1695 ; UV (CHCl$_3$) 252.6(32,570) and 309.5(9,930); ^{1}H NMR (CDCl$_3$) 6.36(1H,d, *J*=9.9 Hz), 6.87(1H,d, *J*=9.9 Hz), 7.47(1H,d, *J*=1.8 Hz), 7.60(1H,dd, *J*=1.8 & 8.1 Hz) and 7.90 (1H,d, *J*=8.20 Hz); MS: m/e 640(M$^+$); Anal. calcd. for $C_{16}H_{15}O_3Br_5$: C, 30.00; H, 0.78. Found: C,29.99; H, 0.75%. and the more polar compound was identified as the β-dienone(**1o**, 238 mg): m.p. 232°C(chloroform-hexane); IR(nujol) 1590 and 1690 ; UV (CHCl$_3$) 252.2(27,520) and 319 (6,880); ^{1}H NMR(CDCl$_3$) 6.25 (1H,d, *J*=9.8 Hz), 7.40(1H,d, *J*=9.8 Hz) and 7.54-7.64 (3H,m); MS: m/e 640(M$^+$); Anal. calcd. for $C_{16}H_{15}O_3Br_5$: C, 30.00; H, 0.78. Found: C, 29.87; H, 0.76%.

General procedure for photoirradiation

All irraditions were carried out in dry benzene solution of the compounds (0.002-0.004 moles) in pyrex tubes under deareated conditions using a 450 W medium pressure mercury lamp for 36 hrs. The progress of irradiation was followed by **TLC**. After the irradiation, the solution was concentrated and the products separated by **PTLC** and identified by spectral data. Photoisomerization data is given in the Table-I.

The dienone (**1m**), on irradiation for 36 hrs and purification by **PTLC** yielded the dienone (**2m**) m.p. 217°C (CHCl$_3$); IR(nujol) 1595, 1695 and 2280; UV(CHCl$_3$) 274.5(16,900), 309(4,100) and 333(4,400); ^{1}H NMR (CDCl$_3$) 6.38 (1H,d, *J*=10.0 Hz), 6.89(1H, d, *J*=10.0 Hz) and 7.35-8.14 (3H,m) ; MS: m/e 587(M$^+$); Anal. calcd. for $C_{17}H_5O_3NBr_4$: C, 34.75; H, 0.85; N, 2.38. Found: C, 34.83; H, 0.83; N, 2.29%.

Quenching Experiments

a) A 0.005 M solution of the dienone **1b** was irradiated with 0.01 M solution of naphthalene and 1,3-cyclohexadiene in two different irradiations. A control irradiation was carried out with 0.005 M solution of the dienone in benzene. After 36 hrs of irradiation, the UV measurements showed that the optical density of the absorption at 350 nm was more or less the same in all the three cases, indicating that no quenching had taken place.

b) A similar experiment was carried out with dienone **1g**. The UV measurements showed that the optical densities of the absorption of the band at 300 nm were almost the same in all the three cases indicating that no quenching had taken place.

ACKNOWLEDGMENT

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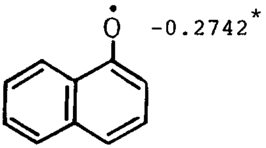

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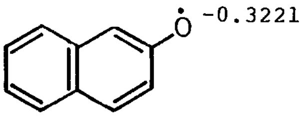

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* atomic orbital spin population.

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