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DDQ Oxidation Of Bisnaphthols - Structures Of Novel Products

Tirumalai R. Kasturi*[†], Srirangam K. Jayaram[†], Jitendra A. Sattigeri[†], Palle V.P.Pragnacharyulu[†], Tayur N.Guru Row[$], Renuka K[$], Kailasam Venkatesan[†], Noor Shahina Begum[‡], Netaji Munirathinam[‡]

Departments of Organic Chemistry[†], Inorganic and Physical Chemistry[‡], Solid State and Structural Chemistry Unit[$], Indian Institute of Science, Bangalore - 560 012, INDIA

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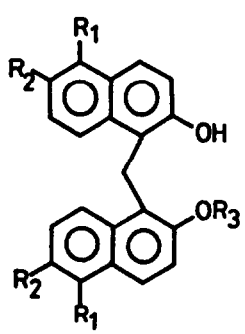
Abstract

Oxidation of bisnaphthols (1a-c) with DDQ resulted in the formation of 10a-a", 10b-b",14a-c and 19a-c in addition to earlier reported products. Structures were assigned on the basis of detailed spectral analyses(^{1}H, ^{13}C, ^{1}H-^{1}H HOMOCOSY and FUCOUP). Structures 10b, 14c and 19a were further confirmed by single crystal X-ray analyses. The formation of these compounds has been explained by a suitable mechanism.

INTRODUCTION

Oxidation of bis(2-hydroxy-1-naphthyl)methane (1a) with 2,3-dichloro-5,6-dicyanoquinone (DDQ) has been reported[1] to give the spironaphthalenone (3a), the isomeric dispironaphthalenones (4a) and the dimer (5a) of 1,2-naphthoquinone-1-methide. Formation of these products has been visualised[1]



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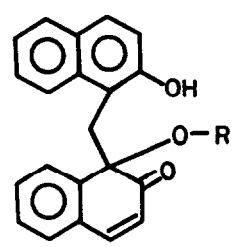
a: $R_1 = R_2 = R_3 = H$
b: $R_1 = Me$; $R_2 = R_3 = H$
c: $R_1 = R_3 = H$; $R_2 = Br$
d: $R_1 = R_3 = H$; $R_2 = Bu^t$
e: $R_1 = R_3 = H$; $R_2 = OMe$
f: $R_1 = R_2 = H$; $R_3 = Me$



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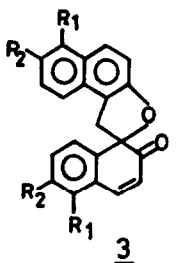
a: R = 2,3,4,5-tetrachlorophenol
b: R = 2,3-dichloro-5,6-dicyanophenol



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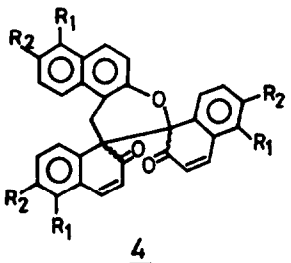

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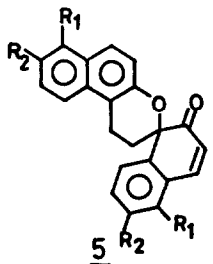

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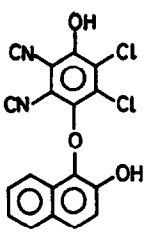
a: $R_1 = R_2 = H$ b: $R_1 = Me$; $R_2 = H$

c: $R_1 = H$; $R_2 = Br$ d: $R_1 = H$; $R_2 = Bu^t$ e: $R_1 = H$; $R_2 = OMe$

through the intermediacy of the initially formed quinol ether **2b**. The quinol ether **2b** could undergo disproportionation[1] to give the 1,2-naphthoquinone-1-methide and the oxydiphenol **6**, which could intramolecularly couple to give the *p*-dienone **7**. Intramolecular coupling of similar diphenols are reported in literature[2,3]. Isolation of the *p*-dienone **7** and the dimer **5a** could thus support the postulated mechanism for the formation of **4**. Even though the formation of 1,2-naphthoquinone-1-methide, as the dimer **5a**, is reported[1] in this reaction, the *p*-dienone **7** has not so far been isolated. With a view to isolating



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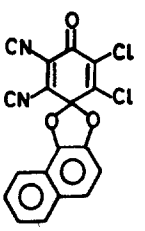

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this compound from the less polar fraction obtained in small amounts from this oxidation and not investigated thoroughly[1,4], a reinvestigation of this oxidation reaction on a fairly large scale was undertaken. The results obtained are discussed further.

RESULTS AND DISCUSSION

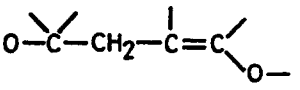
Oxidation of bisnaphthol **1a** (10 g) with DDQ (1.1 eq) was carried out in dry benzene following the reported[1,4] procedure. The precipitated DDHQ was filtered off and the residue obtained, after concentration *in vacuo*, was chromatographed over neutral alumina. Benzene-hexane (1:1) elution gave a white solid (1.0 gm). Further elution with benzene, followed by 10% EtOAc-$CHCl_3$ furnished the reported compounds **3a**, **4a**, & **5a**. The benzene-hexane fraction was rechromatographed and purified further by preparative TLC when four new compounds designated as **A**(50 mg), **B**(250 mg), **C**(360 mg) and **D**(100 mg) in the order of increasing polarity were obtained. Structures of these compounds were determined on the basis of detailed spectral analyses.

Structure of Compounds A and B

Both compounds were isomeric as seen from their mass spectra [M^+ m/z 440; identical fragments at

m/z 282 and 281(100 %)]. NMR spectrum of the minor compound **A** exhibited doublets of one proton intensity at δ 3.77(J=15.8 Hz), 4.56(J=15.8 Hz), 6.29(J=9.8Hz), 6.84(J=9.8Hz), 6.90(J=8.7 Hz), and 6.96(J=8.8 Hz), while that of the major compound **B** showed the same at δ 3.41(J=15.8 Hz), 4.64(J=15.8 Hz), 6.32(J=9.9 Hz), 6.84(J=9.9 Hz) and 6.92(J=8.8 Hz). The rest of the signals appeared in the aromatic region. It is evident from the above spectral data that the upfield doublets around δ 3.5 and 4.5 (J=15.8 Hz) are mutually coupled and must arise from the non-equivalent benzylic methylene protons appearing as an AB quartet. The ^{1}H-^{1}H 2D HOMOCOSY of **A** and **B** showed that the doublets at δ 6.29 & 6.32 are mutually coupled to those at 6.84 in both the compounds, indicating the presence of a styrene system. The ^{13}C nmr spectra of both the compounds were almost similar and exhibited positive signals [SEFT] around δ 37 & 91 characteristic of benzylic CH_2 and quaternary carbon attached to oxygen respectively. It is evident from the above data that the two compounds are isomeric.

In order to get more insight into the nature of the compounds, the long-range heteronuclear chemical shift correlation with full coupling [FUCOUP[5]] of compound **B** was studied. The carbon signal at δ 37.64 is correlated to the AB quartet centered at δ 4.02. The quaternary carbon at δ 91.93 showed a long range ($^3J_{CH}$) correlation to the proton signal at δ6.32 (δ^{13}C 126.68). The downfield signal at δ 157.54 showed a $^3J_{CH}$ coupling to the 'AB' quartet. The presence of the moiety **8** was evident from the above data. The relatively upfield signal at δ 117.76 which showed long-range correlation to the 'AB' quartet as well as to the doublets at δ 6.84(^{13}C 133.21) suggested the presence of system **9**. The formation of dihydro compounds(m/z 442, exhibiting proton multiplets at δ2.6 and 3.2) on catalytic hydrogenation(10% Pd-C)



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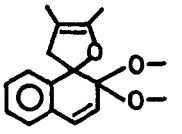

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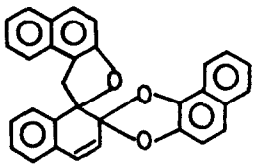
further corroborated the presence of a styrene system in **A** and **B**.

On the basis of the above data, and a comparison of ^{13}C chemical shifts for the characteristic carbons of compounds **A** & **B** with those of the known spiroketones having either a dihydronaphthofuran or a dihydronaphthopyran (QMD/DSN)[6] skeleton, [Table I], structure **10** could be assigned to these compounds.

Table I : Chemical Shifts Values (δ ppm) of Characteristic Carbons in Compounds[6].

Carbon	spironaphthofuran	QMD	DSN	A	B	C	
Spiro(C-1)	88-92	81-83	82.42	91.93	91.88	90.28	83.03
Methylene	41-43	32-33(C-1')	26.25	37.98	37.84	39.50	32.44
Aromatic carbon carrying oxygen	157-158	152-153	152.02	157.54	157.63	157.96	149.76



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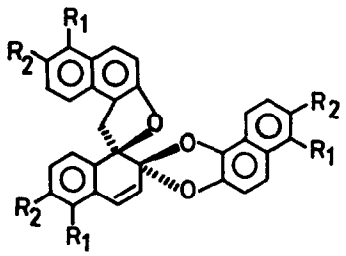
The isomeric compounds **A** & **B** could therefore be represented by either **10a** or **10b**. NOE studies of compounds **A** & **B** [Table II] indicated that the 3-H in the compound **A** is closer to the methylene protons than in the compound **B**.

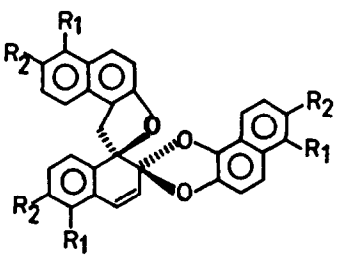
Table II: NOE studies of compounds **A** and **B**.

Compound	$-CH_2$ doublets irradiated	enhancement in the intensities of the styrene protons	
		3-H	4-H
A	3.37	3.3	2.3
	4.56	3.1	-
B	3.40	1.7	1.0
	4.64	2.0	-

An inspection of Dreiding models of **10a** and **10b** revealed that the methylene protons in **10a** are closer to the 3-H. Also the C-8 proton and the 3′ oxygen come closer, perhaps resulting in the shielding of this proton. Thus, compound **A** which showed four doublets in the δ 6-7 region and also exhibited larger NOE for 3-H was assigned the structure **10a** and compound **B**, the isomeric structure **10b**.



10a: $R_1 = R_2 = H$
a′: $R_1 = Me$; $R_2 = H$
a″: $R_1 = H$; $R_2 = Br$



10b: $R_1 = R_2 = H$
b′: $R_1 = Me$; $R_2 = H$
b″: $R_1 = H$; $R_2 = Br$

The assigned structure **10b** was further confirmed by X-ray crystal structure analysis of **B**(fig. 1). The dihydro compounds obtained on hydrogenation of compounds **A** and **B** could, respectively, be assigned

structures **11** and **12**.

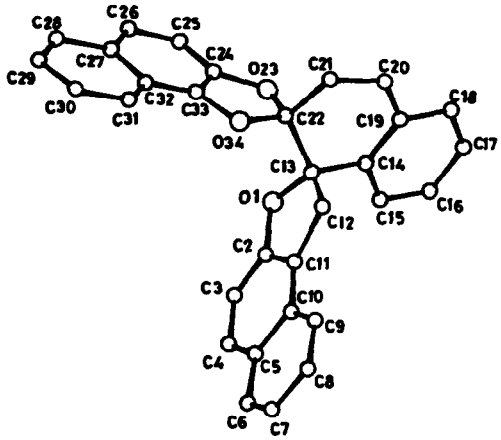
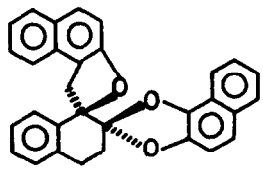


FIG.1 PLUTO diagram of 10b.



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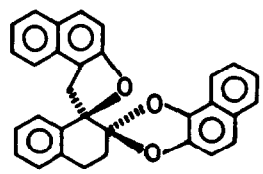

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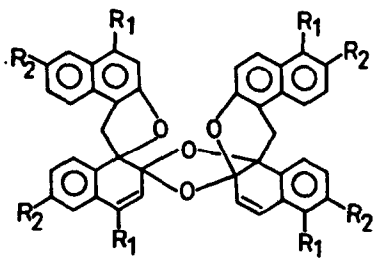
Structure of compound C

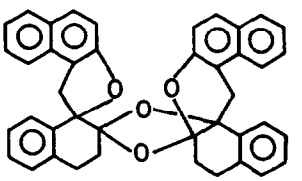
Compound C showed a molecular ion at m/z 596 analysing for $C_{42}H_{28}O_4$. This compound exhibited two pairs of doublets at δ 2.94 (J=17.3Hz,1H) and 3.80 (J=17.3Hz,1H), and 3.06(J=15.6Hz,1H) and 4.40 (J=15.6Hz,1H). In addition, it showed doublets of one proton intensity at δ 5.30(J=9.9 Hz), 6.17(J=9.8 Hz), 6.30(J=9.9 Hz) and 6.60(J=9.8 Hz). It is clear from the spectral data that the two doublets at δ 2.94 and 3.06 are mutually coupled to those at δ 3.80 and 4.40 (J=17.3 Hz and J=15.6Hz) respectively, suggesting the presence of two sets of non-equivalent benzylic methylene protons, constituting the 'AB'quartets. The ^{1}H-^{1}H 2D HOMOCOSY of this compound revealed that the doublets at δ 5.30 and 6.17 are mutually coupled to those at δ 6.30 and 6.60 respectively indicating the presence of two styrene moieties. The presence of benzylic methylene was confirmed from its ^{13}C nmr spectrum (SEFT) which exhibited positive signals at 32.44 and 39.50. Further, the presence of quaternary carbon carrying oxygen was seen from positive signals at δ 83.0 and 90.28. The presence of unsaturated carbons carrying oxygen was evident from positive signals at δ 149.76 and 157.96. The much upfield positive signals (quaternary) in the aromatic-region at δ 101.72 and 109.22 must arise from carbons carrying two oxygens. A FUCOUP spectrum of this compound revealed that these two carbons show long-range coupling to the styrene hydrogens indicating the presence of two such systems in the molecule. Further, the quaternary carbon

at δ90.28 showed a long-range coupling to the methylene protons at 3.80 indicating the presence of Ar-CH_2-C-O- system. Catalytic hydrogenation of compound C resulted in a tetrahydro derivative (m/z 600) showing in its ^1H nmr spectrum multiplets in the upfield region(between 1.5-3.0) integrating for eight protons. The presence of two styrene units in C was thus evident.

Based on the above spectral data and on comparison of the ^{13}C values of the characteristic carbons with those of compounds containing the dihydronaphthofuran and dihydronaphthopyran skeletons(Table II), structure **14a** was tentatively assigned to this compound. Consequently, the tetrahydro derivative could be represented by structure **15**. The mass spectral fragmentation of compound **14a** leading to an



14 a: $R_1 = R_2 = H$
b: $R_1 = Me$; $R_2 = H$
c: $R_1 = H$; $R_2 = Br$



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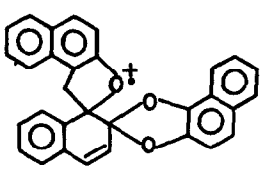
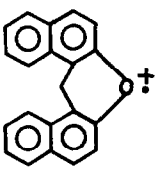
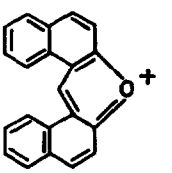
intense ion at m/z 440 (**16**) could arise by retro Diels-Alder cleavage of the molecular ion resulting in the loss of naphthoquinone methide moiety. Further loss of naphthoquinone unit leads to the fragment **17** at m/z 282. Facile loss of a hydrogen from **17** results in the formation of the highly stable fragment ion **18** at m/z 281[7,8]



16 m/z 440



17 m/z 282



18 m/z 281

Compound C did not give single crystal suitable for X-ray crystal structure analysis. However, X-ray crystal analysis of its bromo analogue **14c**, obtained in the same way from bisnaphthol **1c**, could be

carried out and this confirmed the structure. The PLUTO diagram of this is given below(Fig. 2).

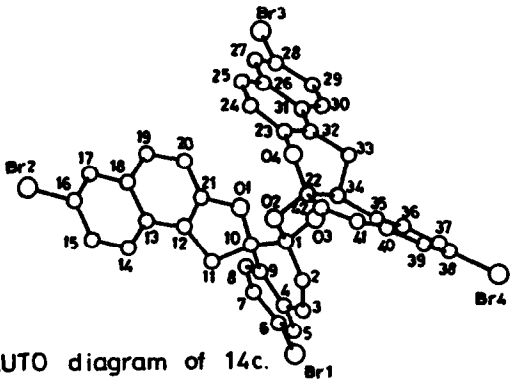


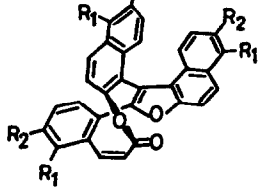
FIG. 2 PLUTO diagram of 14c.

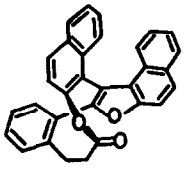
Structure of Compound D

It showed a molecular ion at m/z 438 analysing for $C_{31}H_{18}O_3$. The presence of a carbonyl function was evident from the IR spectrum (1735 cm^{-1}). The ^1H nmr spectrum exhibited only a doublet at 5.77 (J=12.3 Hz). All other signals appeared in the aromatic region. The doublet at δ5.77 was coupled to the doublet at δ 7.33 (J=12.2 Hz)(double irradiation). The presence of an ester or a lactone was evident from the much upfield carbonyl signal at δ 164.59 [^{13}C nmr]. The downfield signals at δ149.42, 152.54 and 152.82 are indicative of unsaturated carbons carrying oxygen function. The mass spectrum exhibiting intense fragments at m/z 410 (M-28) and 394 (M-44) corresponding to a CO & CO_2 loss indicated the presence of a lactone moiety. Hence, the system Ar-O-CO-CH=CH-Ar must be present in the molecule.

Compound **D**, on catalytic hydrogenation (Pd-C 10%), gave a dihydro compound (m/z 440) exhibiting ν_{CO} at 1760 cm^{-1} suggesting loss of conjugation. Appearance of multiplets between δ2.56-2.68 (1H) and 2.76 - 2.83 (1H)(keto methylene) and δ3.00-3.05 (2H) (benzylic) in its ^1H nmr spectrum, suggested saturation of the double bond. LAH reduction of compound **D** resulted in the formation of an allylic alcohol (m/z 444) exhibiting important ^1H nmr signals at 3.44 (t,D_2O exchangeable), 3.9 (d,J=7 Hz), 5.48(td) and 6.60(br d,J=11.4 Hz), characteristic of the system Ar-CH=CH-CH_2OH.

The observed spectral and chemical data led to tentative assignment of the macrocyclic lactone structure **19a** for this compound. On the basis of the J values (12 Hz) for the doublet of the α-enone proton (δ 5.77), the enone system was tentatively assigned *cis*-geometry. The dihydro and the allylic alcohol derivatives could be represented by structures **20** and **21** respectively. The tentative stucture





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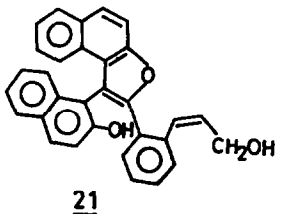

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19a: $R_1 = R_2 = H$ b: R_1=Me, R_2=H

c: R_1=H; R_2=Br d: R_1 = H; R_2=

e: R_1 = H; R_2=-Bu^t

19a assigned was confirmed by the X-ray crystal structure analysis of D(Fig. 3).

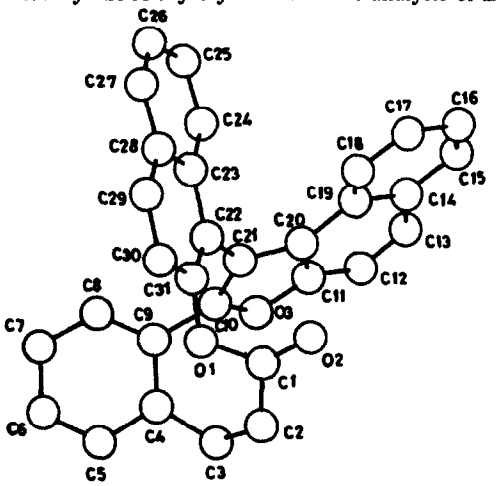
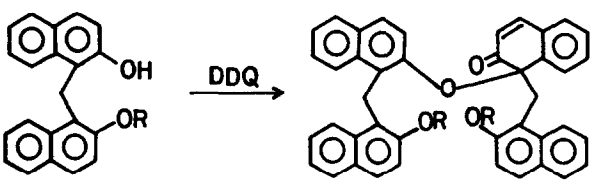


FIG.3 PLUTO diagram of 19a.

In order to establish the generality of this reaction, bisnaphthols **1b-c** were similarly oxidized with DDQ, when the corresponding sets of compounds (in addition to the already reported compounds) were obtained. Structures of all these compounds were evident from their spectral data.

Mechanism of Formation of the Compounds

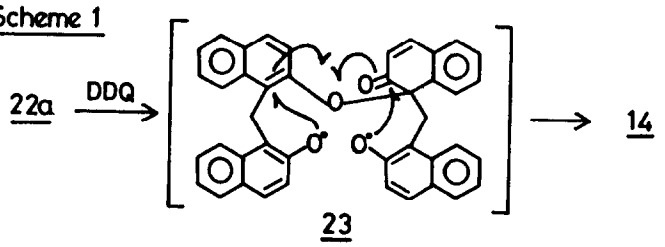
A tentative mechanism involving the intermediacy of dimeric species **22a** & **23** could explain the formation of the compounds in the oxidation of **1** with DDQ. Barton[9] and Hewitt[10] have in fact isolated such dimeric compounds **22b** in the DDQ oxidation of bisnaphthol monoether **1f**. The intermediate **23** may undergo three C-O couplings resulting in the compound **14** (Scheme 1) or two C-O couplings to give isomeric ketals **10** with the elimination of 1,2-naphthoquinone-1-methide which dimerises to give **5**(Scheme 2). Loss of quinonemethide moiety from the intermediate **23** results in a diradical intermediate **24** which can undergo a C-C coupling leading to formation of the isomeric dispironaphthalenones **4**. The diradical **24** could undergo further oxidation with DDQ, followed by a C-O coupling and further transformations to give the macrocyclic lactone **19** (Scheme 3). Thus, the intermediate **22a** satisfactorily explains the formation of the compounds in the DDQ oxidation of bisnaphthols. The formation of the isomeric dispironaphtholenones **4** has earlier[1] been explained through the intermediacy of oxydiphenol **6**. The failure to isolate the expected *p*-dienone **7** does not, however, rule out this possibility.



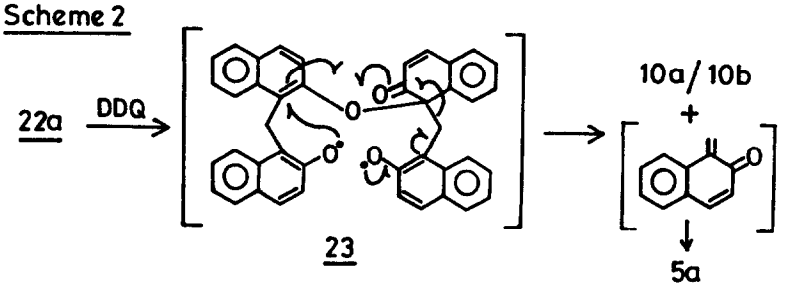
1a: R = H
f: R = Me

22a: R = H
b: R = Me

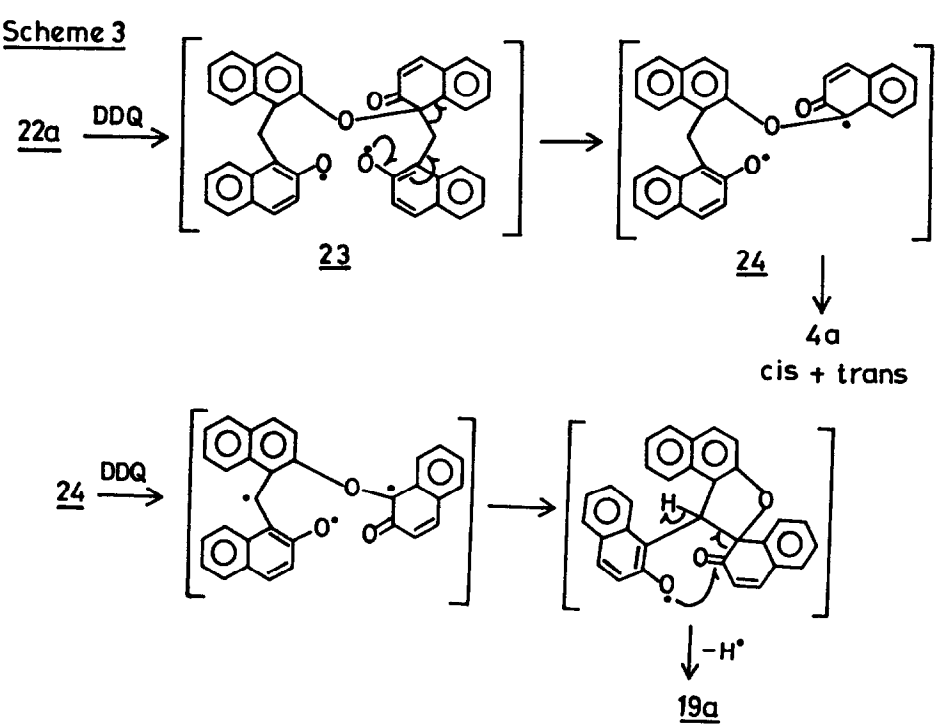
Scheme 1



Scheme 2



Scheme 3



As seen from the above mechanism (Scheme 3), the dispironaphthalenone **4** should undergo further DDQ oxidation to give the lactone **19**. Accordingly, an oxidation of **4a** was carried out with DDQ in dry benzene. After 10 hr of refluxing, the lactone was obtained in 17% yield along with the starting dispiro-

naphthalenone. Similar oxidation of *cis*-dispironaphthalenones **4b-d** gave the corresponding lactones **19b-d**, characterised by spectral data. The *J* value (12 Hz) of the α-enone proton in these compounds is in conformity with the assigned *cis* geometry.

EXPERIMENTAL

All melting points are uncorrected. IR(cm^{-1}) were recorded on Perkin-Elmer model 781 spectrophotometer. PMR spectra were recorded on a Bruker-WH-270 MHz or Bruker-ACF-200 MHz. FT NMR spectrometers and the CMR were recorded on a Bruker-WH-270 spectrometer with an operating frequency of 67.89 MHz. 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.

General procedure for oxidation of bisnaphthols: A solution of bisnaphthol (1 eq) in benzene was refluxed with DDQ (1.1 eq.) for 12 hr. The precipitated DDHQ was filtered off after cooling . The filtrate was concentrated and chromatographed over neutral alumina. Elution with benzene : hexane(1:1) gave a solid which was further separated into four components by preparative TLC(chromatotron).

(I): A solution of the bisnaphthol **1a** (10 g) in benzene (500 ml) on oxidation with DDQ (8.5 g) for 12 hr gave: (i)**(±)-(1S*,2R*)-Dispironaphthalene-1,2′(1′*H*)-naphtho[2,1-b]furan-2,2″-naphtho[1,2-d]-1,3-dioxole, 10a** (50 mg) m.p. 252°(d) ($CHCl_3$-hexane); IR (nujol): 1650, 1630 and 1605 cm^{-1}; ^1H NMR(270 MHz, $CDCl_3$): 3.97('AB quartet' centre, J_{AB}=15.8 and $\Delta\nu_{AB}$ = 321.7Hz, 2H, CH_2), 6.29(d, *J*= 9.7 Hz,1H, C-3H), 6.84(d, *J*=9.7Hz, 1H, C4-H), 6.90(d, *J*=8.7Hz,1H), 6.96(d, *J*=8.8 Hz, 1H) and 7.24-7.81(m, 14H);^{13}C NMR(SEFT, $CDCl_3$): positive signals at 37.98(C-1′), 91.88(C-1), 117.32(C-2), 117.32 (C-9′a), 119.41, 129.64, 129.91, 130.13, 130.84, 139.92, 142.23, 142.38, and 157.63 (C-3′a) and negative signals at 109.16, 119.92, 120.39, 120.75, 122.74, 123.07, 123.67, 124.17, 125.62, 126.7(x2), 128.01, 128.17, 128.47, 128.79, 129.08, 129.34, and 133.22; M.S m/z 440(M^+,48), 423(4), & 281(100%); Analysis calcd. for $C_{31}H_{20}O_3$ C, 84.55; H, 4.55. Found C,84.73; H,4.69 %. (ii) **(±)-(1R*,2R*)-Dispironaphthalene-1,2′ (1′*H*)-naphtho[2,1-b]furan-2,2″-naphtho[1,2- d]-1,3-dioxole 10b**, (250 mg), m.p. 218°C ($CHCl_3$-hexane); IR(nujol): 1655,1635 and 1610 cm^{-1}; ^1H NMR(270 MHz, $CDCl_3$) : 4.02('AB quartet centre', J_{AB}=15.8Hz, $\Delta\nu_{AB}$=332.1Hz, 2H), 6.32(d, *J*=9.6 Hz, 1H), 6.84 (d, *J*=9.6 Hz, 1H), 6.92(d,*J*=8.8 Hz, 1H), 7.15-7.78(m, 15H); ^{13}C NMR(SEFT, $CDCl_3$): positive signals at 37.84, 91.93, 117.36(x2), 119.64, 129.77, 130.14, 130.76, 139.63, 141.05, 144.19 and 157.54 and negative signals at 110.17, 111.78, 119.45, 121.27, 122.72, 123.06, 123.38, 124.25, 125.65, 126.68(x2), 128.05, 128.15, 128.59, 128.81, 129.08, 129.42, and 133.21; MS m/z: 440(M^+,57), 423(4), 297(5),and 281(100%); Analysis calcd. for $C_{31}H_{20}O_3$ C,84.55; H,4.55. Found C,84.75; H,4.62%. (iii) **Dispironaphthalene- 1,2′(1H′)-naphtho [2,1-b]furan-2(4″*H*), 2″(5″*H*) {dibenzo[a,h]xanthenyl}[6a,13a-d]-1,3-dioxole 14a**, (360 mg), m.p. 248- 249°C (d) ($CHCl_3$-hexane); IR(nujol): 1630, 1610 and 1580 cm^{-1}; ^1H NMR(270 MHz, $CDCl_3$): 3.37('AB quartet' centre, J_{AB}=17.3 and $\Delta\nu_{AB}$ = 233Hz, 2H, C-1′H), 3.73('AB quartet' centre, J_{AB}= 15.6 Hz and $\Delta\nu_{AB}$ = 363.3Hz, 2H, C-13‴H), 5.30(d, *J*=9.9Hz, 1H, C-3H), 6.17(d, *J*=9.7 Hz, 1H, C-6″H), 6.30 (d, *J*=10 Hz, 1H, C-4H), 6.60(d, *J*=9.8Hz, C-5‴H), 6.96-7.39(m,14 H) and 7.69-7.84(m, 6H); ^{13}C NMR(SEFT, $CDCl_3$): positive signals at 32.44(C-1′), 39.50(C-13‴), 83.03(C- 1), 90.02, 101.72, 109.22(C-2), 110.74, 117.36, 129.39, 129.58, 129.92, 130.31, 132.32, 140.03, 140.96, 149.76, and 157.96 and negative signals at 113.30, 119.35, 122.05, 122.83(x 2), 123.45 (x 2), 126.28, 126.49, 126.66, 127.23, 127.49(x 2), 127.82 (x 2), 128.62 (x 4), 128.86(x 2), 130.16(C-4) and 132.22 ; MS m/z 596 (M^+, 1), 440 (36), 423 (3), 312 (8) and 281 (100 %). Analysis calcd. for $C_{42}H_{28}O_4$ C, 84.56; H, 4.70. Found: C, 84.61; H, 4.89 %. (iv) **Lactone of *cis*-2-{1′-(2″ -hydroxy-1″-naphthyl)naphtho[2,1-b]furan-2′-yl}cinnamic acid 19a** (100 mg), m.p. 294-295°C ($CHCl_3$-hexane): IR(nujol); 1735 and 1615 cm^{-1}; ^1H NMR(270 MHz, $CDCl_3$): 5.77(d, *J*=12.3Hz, 1H, C-3H), 7.01-7.49(m, 9H), 7.33(d, *J*=12.2 Hz, 1H, C-4H), 7.67(d, *J*=8.8Hz, 1H) and 7.79-7.92(m, 6H); ^{13}C NMR(SEFT, $CDCl_3$):positive signals at 116.54, 119.86, 122.12, 130.72(x2), 131.56, 133.42, 137.15(x2), 149.42, 152.24, 152.89, and 164.56(C=O) and negative signals at 112.06, 120.83, 121.36, 121.66, 124.36(x2), 125.38, 125.67, 125.99, 126.65(x2), 127.19, 128.15, 128.45, 128.57(x2), 129.65, 130.20, 131.25 and 143.06; MS m/z : 438(M^+, 77), 410(M-CO, 54) and 394(M-CO_2,100). Analysis calcd. for $C_{31}H_{18}O_3$ C,84.93; H,4.11% Found C,84.50; H,4.02 % . Further elution with benzene followed by 10% EtOAc-$CHCl_3$ gave the spironaphthalenone **3a** (1.2 g), quinone methide dimer **5a**, (1.1g), *cis*-dispironaphthalenone **4a**, (1.75 g) and *trans*-dispironaphthalenone **4a**, (100 mg).

(II) A similar oxidation of bisnaphthol (1b, 8 g) with DDQ (6.1 g) followed by workup gave: (i)(±)(**1S*, 2R***)-**5,6′,5‴- Trimethyldispironaphthalene-1, 2′ (1′*H*)-naphtho[2,1-b]furan-2,2′- naphtho[1,2-d]-1,3-dioxole 10a′**,(35 mg), m.p. 231° C. IR(nujol): 1650, 1630 and 1610 cm^{-1}; ^1H NMR(200 MHz, $CDCl_3$): 2.45(s, 3H), 2.60(s, 6H), 4.01('AB quartet'centre, J_{AB}=15.7Hz and $\Delta\nu_{AB}$=249.5Hz, 2H, CH_2), 6.3(d, *J*=10.1 Hz, 1H), 6.96(d, *J*=9.05 Hz, 1H), 7.1-7.40(m, 11H), 7.49(d, *J*=8.9Hz, 1H), 7.70(d, *J*=9.0Hz, 1H). Analysis calcd. for $C_{34}H_{26}O_3$ C,84.26 H,5.37. Found C,84.60; H, 5.39%. MS m/z: 482(M^+,46), 309(100%).(ii)(±) (**1R*,2R***)-**5,6′,5‴-Trimethyldispironaphthalene- 1,2′(1′*H*)-naphtho[2,1-b]furan 2,2″-naphtho[1,2-d]-1,3-dioxole 10b′**, (155 mg), m.p. 251°(d)C; IR(nujol): 1650, 1630 and 1610 cm^{-1}; ^1H NMR(200 MHz, $CDCl_3$): 2.47(s,3H), 2.61(s, 3H), 2.67(s, 3H), 3.92('AB quartet' centre, J_{AB}=15.8Hz, $\Delta\nu_{AB}$=240.3Hz, 2H, CH_2), 6.30 (d, *J*=10.1Hz, 1H), 6.9-7.89(m, 14H). Analysis calcd. for $C_{34}H_{26}O_3$ C,84.26; H,5.37%. Found C,84.64; H,5.39%; MS m/z: 482(M^+,39), 309(100%) (iii)**5,6′,2‴,9‴-Tetramethyldispironaphthalene-1,2′(1′*H*)- naphtho[2,1-b]furan-2(4″*H*),2″ (5″*H*){dibenzo[a,h] xanthenyl}[6a,13a-d]-1,3-dioxole 14b**, (125 mg). m.p. 230°C. IR(nujol): 1630, 1610 and 1580 cm^{-1}; ^1H NMR(200 MHz, $CDCl_3$) 2.23(s,3H), 2.36(s,3H), 2.64(s, 3H), 2.68(s, 3H), 3.24('AB quartet' centre, J_{AB}=17.5Hz & $\Delta\nu_{AB}$=171.53Hz), 3.62('AB quartet' centre, J_{AB}=15.7Hz & $\Delta\nu_{AB}$=271.54Hz), 5.26(d, *J*=10.2Hz, 1H), 6.09(d, *J*= 10.1Hz, 1H), 6.45 (d, *J* =10.2Hz, 1H), 6.76 (m, 13H), 7.48 (d, *J* = 8.35 Hz, 1H), 7.87 (d, *J* = 9.0 Hz, 1H), 7.90 (d, *J*= 9.11 Hz, 1H). Analysis calcd. for $C_{45}H_{36}O_4$ C,84.66; H,5.52%. Found C,84.32; H,5.48%. MS m/z: 482(M^+-170,11), 309(100%) (iv) **Lactone of *cis*-5″,6,6′-trimethyl-2-{1′- (2″-hydroxy-1″-naphthyl)naphtho[2,1-b]furan-2′-yl}cinnamic acid 19b**,(90 mg) IR(nujol): 1731 cm^{-1}; ^1H NMR(270 MHz, $CDCl_3$): 2.41(s, 3H), 2.72(s, 3H), 2.75(s, 3H), 5.77(d, *J*=11.9Hz, 1H), 6.92(d, *J*=7.2Hz, 2H), 7.02-7.36(m, 8H), 7.69(d, *J*=9.0Hz, 1H), 7.98(d, *J*=9.3Hz, 1H), 8.07(d, *J*=9.1Hz, 1H). MS m/z: 480(M^+,70), 436(M^+-44,100%). Analysis Calcd. for $C_{34}H_{24}O_3$ C,85.0;H,5.0%. Found C,85.34; H,5.1%.

Further elution with benzene followed by 10% EtOAc-$CHCl_3$ gave the spironaphthalenone **3b**, quinone methide dimer **5b**, *cis*- & *trans*-dispironaphthalenone **4b**.

(III): Similar oxidation of bisnaphthol(**1c**, 6.0 g) with DDQ(3.2 g) gave on usual workup: (i)(±) (**1S*, 2R***)-**6,7′,6″- Tribromodispironaphthalene-1,2′(1′*H*)-naphtho[2,1-b]-furan-2,2″- naphtho[1,2-d]-1,3-dioxole 10a″**,(35 mg). m.p.178-80°C. IR(nujol) : 1650, 1630 and 1610 cm^{-1}; ^1H NMR(200 MHz, $CDCl_3$): 3.92('AB quartet' centre, J_{AB}=15.8Hz, $\Delta\nu_{AB}$=245.05 Hz, CH_2, 2H), 6.33(d, *J*=9.8Hz, 1H), 6.80(d, *J*=9.9Hz, 1H), 6.82 (d, *J*= 8.8 Hz, 1H), 7.14-7.58 (m, 10H), 7.90(d, *J* = 8.6 Hz, 1H), 7.91(d, *J* = 8.7 Hz, 1H); MS m/z: 437, 439, 441(M^+- 237). Analysis calcd. for $C_{31}H_{17}Br_3O_3$ C,55.19; H,2.52%. Found C,55.18; H,2.64%. (ii)(±)(**1R*,2R***)-**6,7′,6″- Tribromodispironaphthalene-1,2′(1′*H*)-naphtho [2,1-b]furan-2,2″-naphtho[1,2-d]-1,3-dioxole 10b″**, (144 mg). m.p. 190-1°C;IR(nujol): 1650, 1630 and 1610 cm^{-1}; ^1H NMR(200 MHz, $CDCl_3$): 3.93 ('AB quartet' centre , *J*=15.8 Hz and $\Delta\nu_{AB}$=244.9 Hz, CH_2, 2H), 6.27(d, *J*=9.8 Hz, 1H), 6.82 (d, *J*=8.8 Hz,1H), 6.86(d,*J*=9.8 Hz,1H),7.13-7.56(m,11H); MS m/z: 437,439, 441(M^+-237). Analysis calcd. for $C_{31}H_{17}Br_3O_3$ C,55.19, H,2.52%. Found C,55.34; H,2.76%. (iii)**6,7′,3″,10″- Tetrabromodispironaphthalene-1,2′(1′*H*)-naphtho[2,1-b]furan-2(4″*H*) ,2(5″*H*)-{dibenzo[a,h]xanthenyl}-[6a,13a-d]-1,3-dioxole 14c**,(210mg). m.p. 219-220°C. IR(nujol):1630, 1610 and 1580 cm^{-1}; ^1H NMR(200 MHz, $CDCl_3$): 3.22('AB quartet'centre, *J*=17.2Hz and $\Delta\nu_{AB}$=161.9Hz, CH_2,2H), 4.11('AB quartet'centre, J_{AB}=15.7Hz and $\Delta\nu_{AB}$=260.41Hz, CH_2, 2H), 5.29(d, *J*=9.9Hz, 1H), 6.13(d, *J*= 9.81Hz, 1H), 6.19(d, *J*=10 Hz, 1H), 6.45 (d, *J*= 9.8 Hz, 1H), 6.78- 7.9(m,16H); MS m/z; 674, 676, 678, 680 (M^+-234), 437, 439, 441(M^+- 471). Analysis calcd. for $C_{42}H_{24}Br_4O_4$ C,55.1; H,2.64%. Found C,55.85; H,3.01%. (iv) **Lactone of *cis*-5,6″,7′-tribromo-2-{1′-(2″-hydroxyl-1″-naphthyl)naphtho[2,1-b]furan-2′-yl}cinnamic acid 19c**, (70 mg). m.p.203- 205°C ; IR(nujol): 1730 and 1590 cm^{-1}; ^1H NMR(270 MHz, $CDCl_3$): 5.79(d, *J*=12 Hz, 1H, C-3H) and 6.90-8.13(m, 14 H); MS(chemical ionisation, NH_3) m/z: 679(MH+6,55), 677(MH+4, 80), 675(MH+2,80), 673(MH+, 40), 632(35), 377(15) and 350(20 %). HRMS calcd for $C_{31}H_{15}Br_3O_3$ 671.8571. Found 671.8381

Further elution with benzene followed by 10% EtOAc-$CHCl_3$ gave the spironaphthalenone **3c**, quinone methide dimer **5c**, *cis*- & *trans*- dispironaphthalenones **4c**.

General procedure for the oxidation of dispironaphthalenones with DDQ A solution of dispironaphthalenone(1 eq.) in dry benzene was refluxed with DDQ (1.1 eq) for 12 hr. The precipitated hydroquinone was filtered off after cooling the reaction mixture. The filtrate was concentrated and chromatographed over neutral alumina. Elution with benzene gave the lactone (**19**) which was purified by recrystallisation ($CHCl_3$-Hexane). Further elution with 10% EtOAc- $CHCl_3$ gave the starting material.

(I) *cis*-Dispironaphthalenone **4a** (440 mg) in dry benzene (30 ml) and DDQ (250 mg) gave the lactone **19a** (75 mg) and the starting material (140 mg).

(II) *cis*-Tribromodispironaphthalenone **4c**,(170 mg) in dry benzene (15 ml) and DDQ (65 mg) gave the lactone **19c**(20 mg).

(III) *cis*-Tri(1-methylcyclohexyl)dispironaphthalenone **4d**, (364mg) in dry benzene (15 ml) with DDQ (125 mg) gave the lactone **19d**, (65 mg). m.p. 206°C; IR(nujol): 1735 and 1595 cm^{-1}; ^1H NMR(270 MHz, $CDCl_3$) : 1.14(s,3H,CH_3),1.18(s,3H, CH_3), 1.25(s, 3H, CH_3), 1.31-2.25(m, 30H, cyclohexyl H), 5.75(d, J=12.2Hz, 1H, C-3H) and 7.03-7.87(m, 14H, ArH). Analysis calcd. for $C_{52}H_{54}O_3$ C,85.95; H,7.44. Found C,85.57; H,7.25 %.

(IV) *cis*-Tri-*tert*-butyldispironaphthalenone **4e** (150 mg) in dry benzene on reaction with DDQ (65 mg) for 12 hr gave after chromatography (neutral alumina ,benzene eluent) the lactone **19e** (25 mg) m.p. 210-211°C ($CHCl_3$-hexane); IR(nujol): 1731 cm^{-1} ^1H NMR (90 MHz,$CDCl_3$):1.25(s, 18H, 2xBu^t), 1.32(s, 9H, Bu^t), 5.65(d, J=10Hz, 1H), 6.9-7.2(m, 6H), 7.2-7.45(m, 2H), 7.5-7.8(m, 6H); MS:m/z 606(M^+,50), 562 (100), 505(15), 57(70,C_4H_9).Analysis calcd. for $C_{43}H_{42}O_3$ C,85.1; H,6.9. Found C,84.8; H,6.9%.

Catalytic hydrogenation - General procedure : A solution of the compound (50 mg) in dry EtOAc(20 ml) was stirred with 10% Pd-C catalyst (10 mg) in an atmosphere of hydrogen until hydrogen uptake ceased (12 hr). After the removal of catalyst, the solvent was removed *in vacuo* and the residue crystallised from $CHCl_3$-Hexane.

(I) Hydrogenation of compound **10a** gave the dihydro derivative **11** (40 mg), m.p. 262-263°C; IR(nujol): 1640,1605 cm^{-1}; ^1H NMR(270 MHz, $CDCl_3$): 2.22-2.46(m, 2H, C-3H), 2.91-3.30 (m, 2H, C-4H), 3.79 ('AB quartet' centre, J_{AB}= 15.8 Hz, and $\Delta\nu_{AB}$= 63.28 Hz,2H, CH_2) and 6.73-7.64(m, 16H); MS: m/z 442 (M^+,94), 285(19), 284(68), 283(100), 282 (12) and 281(23%); HRMS cald. for $C_{31}H_{22}O_3$ 442.1569. Found 442.1540.

(II) Hydrogenation of **10b** gave the dihydro derivative(**12**, 40 mg) m.p. 256°C IR(nujol): 1655, 1640 and 1605 cm^{-1}; ^1H NMR(270 MHz, $CDCl_3$): 2.57-2.73(m,2H,C-3H),3.30-3.35 (m,2H,C-4H),3.97('AB quartet'centre,J_{AB}=16.2 and $\Delta\nu_{AB}$= 113.3Hz, 2H, CH_2), 7.0(d, J=8.8Hz, 1H), 7.12(d, J=8.7Hz, 1H) and 7.19-7.82(m, 14H); MS m/z 442(M^+,74), 285(18), 284(66), 283(100), 281(13%). HRMS calcd for $C_{31}H_{22}O_3$ 442.1569. Found 442.1575.

(III) Hydrogenation of**14a** furnished the tetrahydro compound **15**,(35 mg) m.p 278-279°C, IR(nujol): 1630 and 1605 cm^{-1}; ^1H NMR(270 MHz, $CDCl_3$): 1.5-1.6(m,1H),2.36-2.38(m,2H), 2.41-3.10(m,5H),3.46 ('AB quartet'centre, J_{AB}=17.3 & $\Delta\nu_{AB}$=273.5Hz, 2H, CH_2), 3.50('AB quartet' centre, J_{AB}=15.7Hz, $\Delta\nu_{AB}$= 156.1 Hz, 2H, CH_2) and 6.85-7.84(m, 20H); MS m/z: 600(M^+,66), 285(7), 284(32), 283(20), 282(2) and 281(4%); HRMS calcd. for $C_{42}H_{32}O_4$ 600.2301. Found 600.2349.

(IV) Hydrogenation of the compound (**19a**) gave the dihydro derivative (**20**, 45 mg) m.p. 230-231°C, IR(nujol):1760 cm^{-1}; ^1H NMR(270 MHz, $CDCl_3$): 2.56-2.68(m,1H, C_3-H), 2.76- 2.83(m, 1H, C-3H), 3.00-3.5(m, 2H, C-4H) and 6.88-7.94 (m, 16H); MS m/z: 400(M^+,90), 412(52),411(36), 270(22),269(100) and 268(20%); HRMS calcd for $C_{31}H_{20}O_3$ 440.1412.Found 440.1434.

LAH reduction of lactone: Solution of compound (**19a**, 200 mg) in dry THF (30 ml) was added slowly to a suspension of $LiAlH_4$ in dry THF (10 ml) in an atmosphere of N_2 and stirred for 2 hr . Saturated NH_4Cl was added and the THF distilled off. The residue after treatment with dil. HCl, was extracted with $CHCl_3$. The organic layer was dried, solvent removed, and residue purified on column (silica gel,benzene) to give the *cis*-2-{1′-(2″-hydroxy-1″- naphthyl)naphtho[2,1-b]furan-2′-yl}cinnamic acid, (**21**, 180 mg), m.p 160° C ($CHCl_3$-Hexane), IR(nujol): 3200-3500(OH), 1625 and 1600cm^{-1}; ^{1}HNMR(90MHz, $CDCl_3$): 3.49(t, 1H, D_2O exchangeable, OH), 3.96(br d, J=7.0Hz, 2H, CH_2),5.54(td, J=7.0 and 11.4 Hz,1H, *CH*-CH_2-OH), 5.5(br s, 1H, D_2O exchangeable, Ar-OH), 6.67(d, J=11.4 Hz, 1H, *CH*=CH-CH_2OH) and 6.94-7.93(m, 16H); MS: m/z 442(M^+, 100), 424(97), 407(47) and 281(87%). HRMS calcd. for $C_{31}H_{24}O_3$ 442.1569. Found 442.1581

Oxidation of oxydiphenol with DDQ: A solution of oxydiphenol (25 mg) was refluxed with DDQ[1] (1.4 g) in dry benzene(250 ml) for 8 hr. The hydroquinone was filtered off and the solvent removed to

obtain a yellow solid which was chromatographed over neutral alumina . Elution with benzene gave a white solid which was further purified by preparative TLC (2:1 hexane benzene) to give a compound (30 mg) identical (TLC, IR and ^{1}H NMR) with compound **10b**. Further elution with 10% EtOAc-$CHCl_3$ gave the *cis*-**4a** (135 mg) and *trans*-**4a**(20 mg) .

Crystal Structure Determination

Crystal structure of 10b

Crystal data: $C_{31}H_{20}O_3$, M=440, Monoclinic, Space group $P2_1/a$, a= 9.47(1)Å, b= 22.659(2)Å, c= 10.861(1)Å, β=109.66°(1), V=2194 Å^3, Z=4, D(calc)=1.33gcm^{-3}, MoK radiation, λ=0.7107Å. 3574 reflections were collected on an Enraf Nonius CAD-4 Diffractometer of which 1788 unique reflections with intensities above 3 (I) level were used in the calculation. The structure was solved by direct methods using SHELXS 86[11] and refined by the full-matrix least square procedure, to afford a final R value of 0.078. A PLUTO[13] diagram of the molecule is given in Fig. 1.

Crystal structure of 14c

Crystal data: $C_{44}H_{24}Br_4O_4$, M=912.26, Monoclinic, Space group $P2_1/n$, a=17.034(3), b=11.328(2), c=17.765(2)Å, β=91.25°(2), V=3427.2Å^3, Z=4. Dm=1.76 g cm^{-3}, Dc=1.77 g cm^{-3}, Mo K radiation, λ=0.7107Å. Three dimensional intensity data were collected on an Enraf-Nonius CAD4 diffractometer. The structure was solved by Patterson technique using SHELXS 86 and refined by the full-matrix least square programme, SHELX 76[12]. The final R and Rw values are 0.068 and 0.071 respectively. The number of significant reflections with $I \geq 3\sigma(I)$ used were 3009. A perspective view of the molecule drawn with PLUTO, is shown in Fig 2.

Crystal structure of 19a

Crystal Data: $C_{31}H_{18}O_3$, M=438, Monoclinic, Space Group P21/c, a=16.683(1)Å, b=7.631(1)Å, c=17.682(1)Å, β=100.01°, λ=1.5418Å, Dc=1.3122 gcm^{-3}, Z=4. Of the total of 2192 reflections collected on a Enraf Nonius CAD4 diffractometer, 1570 reflections of the intensities above 3 (I) level, were used in the calculations. The structure was solved by the direct method using SHELXS-86 and refined by the full-matrix least square procedure with the assumption of positional anisotropic thermal parameters for all non-hydrogen atoms to afford the final R value of 0.050. A PLUTO diagram of the molecule is given in Fig 3. The ten membered lactone ring adopts an unusual *cis-cis* configuration about the double bond [Torsion angles: C(1)-C(2)-C(3)-C(4)= -3.6°; C(9)-C(10)-C(21)-C(22)=1.4°] with the ten-membered ring in boat-boat conformation. The ring therefore displays short distances between C(4)—O(1)=2.89 Å and C(1)—C(21)=2.85Å.

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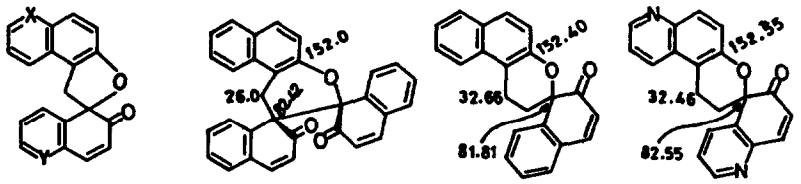

Few ^{13}C values for spironaphthofuran skeleton[1,14]

X	Y	carbon		
		spiro	methylene	aromatic carrying oxygen
CH	CH	89.33	42.88	157.81
CH	N	88.48	42.30	157.71
N	CH	89.72	42	158.02
N	N	88.8	42.2	157.71

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