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Reaction of Spironaphthalenones with Hydroxylamine: Part I. A Reinvestigation of the Mechanism

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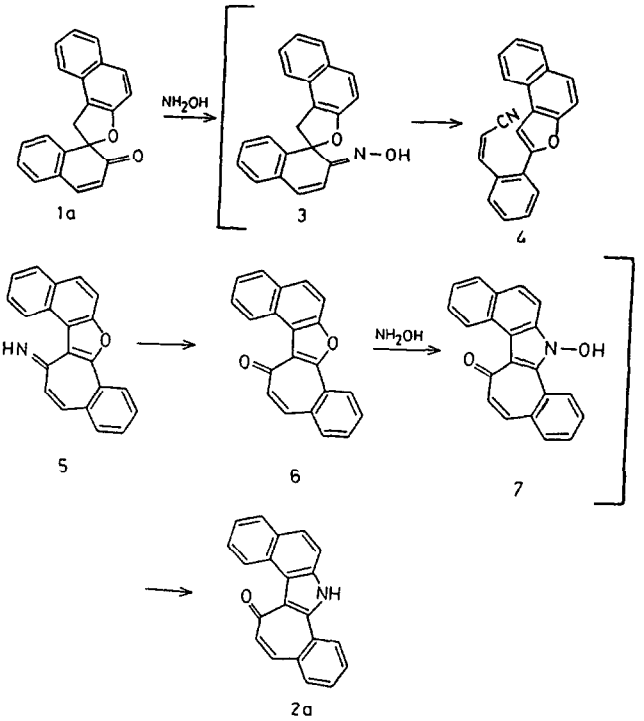
Abstract: Spironaphthalenones **1b-g** on reaction with hydroxylamine hydrochloride gave the expected pyrrolotropones **2b-g**. Furanotropone **6**, postulated as an intermediate in the formation of pyrrolotropones, remained unchanged on reaction with hydroxylamine hydrochloride in ethanol. Reaction of unsymmetrical spironaphthalenones **1h-o** with $NH_2OH.HCl$ gave the rearranged pyrrolotropones **2h-o**.

Abel[1] has reported the formation of an anomalous compound designated the 'anhydro-oxime' in the reaction of spironaphthalenone **1a** with hydroxylamine hydrochloride. Structure of this compound has been investigated[2] and based on a few classical transformations, Dean *et al*[3] have suggested the cycloheptaindole (**pyrrolotropone**) structure **2a** for this compound. They have also suggested a mechanism for the formation of **2a** (Scheme 1), through the intermediacy of furanotropone **6** which was not isolated by them.

One of the compounds isolated in the 2,3-dichloro-5,6-dicyano-1,4-benzoquinone oxidation of the spironaphthalenone **1a** by Kasturi *et al*[4]. is the furanotropone **6** and its structure was unambiguously confirmed by X-ray crystal structure analysis. If the mechanism proposed by Dean *et al.*[3] were to be correct, reaction of **6** with NH_2OH under similar reaction conditions should give the pyrrolotropone **2a**. However, no reaction occurred when **6** was treated with NH_2OH, the starting material being recovered quantitatively[5]. It is obvious that the mechanism does not involve the intermediacy of furanotropone **6**. The mechanism (Scheme 1) also requires two moles of NH_2OH for the conversion of **1a** to **2a**, but we, have found[6] that one mole of NH_2OH is enough for the formation of pyrrolotropone **2a** from **1a** in almost the same yield; however, the reaction takes a longer time. In view of these

findings, an alternative mechanism had to be visualised for this reaction and work was initiated in this direction.



Scheme 1

As a first step in our investigation, it was necessary to confirm the structure of 2a. The only information that could be obtained from its ^{1}H NMR, which exhibited signals in the aromatic region, was the presence of a vinylic ∝-proton of an enone system [δ 6.97 (d, J = 12.3 Hz)] and a NH

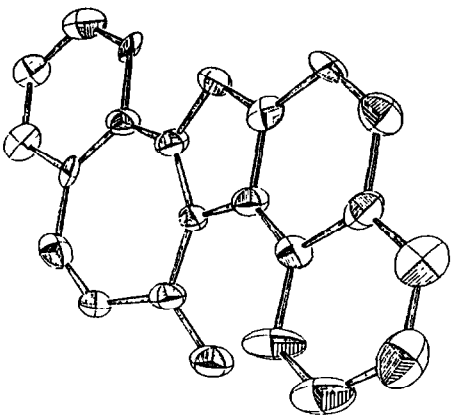
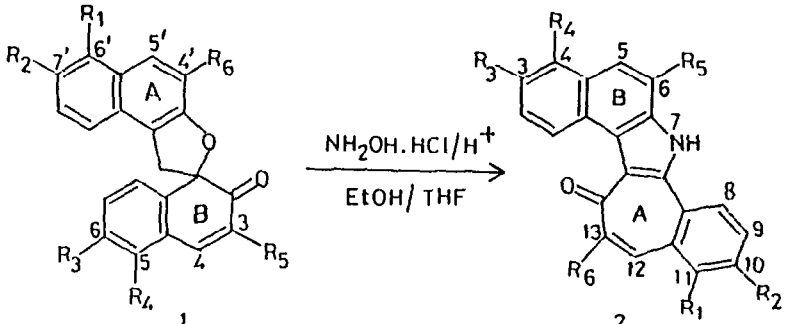


Fig 1 A Perspective view of molecule 2a

group [δ 12.97 (s, D_2O exchangeable)]. A reasonably good ^{13}C NMR could not be obtained due to its high insolubility. However, X-ray crystal structure analysis (Fig.1) confirmed beyond doubt the structure proposed by Dean et al[3].

In order to establish the generality, it was necessary to study this reaction using a variety of substrates 1b-g. These were synthesised in a two step process involving preparation of bisnaphthols adopting the Shearing and Smiles procedure[7] and their subsequent oxidation with $K_3Fe(CN)_6$. When the NH_2OH reaction was carried out with substrates 1b-g, the corresponding pyrrolotropones 2b-g, were formed. All these compounds



a) $\underline{1}$ $R_1 = R_2 = R_3 = R_4 = R_5 = R_6 = H$ $\underline{2}$

b) $R_2 = R_3 = Br$; $R_1 = R_4 = R_5 = R_6 = H$

c) $R_2 = R_3 = OMe$; $R_1 = R_4 = R_5 = R_6 = H$

d) $R_2 = R_3 =$  ; $R_1 = R_4 = R_5 = R_6 = H$

e) $R_2 = R_3 =$ t-bu ; $R_1 = R_4 = R_5 = R_6 = H$

f) $R_1 = R_4 = CH_3$; $R_2 = R_3 = R_5 = R_6 = H$

g) $R_5 = R_6 = CH_3$; $R_1 = R_2 = R_3 = R_4 = H$

h) $R_5 = CH_3$; $R_1 = R_2 = R_3 = R_4 = R_6 = H$

i) $R_6 = CH_3$; $R_1 = R_2 = R_3 = R_4 = R_5 = H$

j) $R_2 = R_6 =$ t-Bu ; $R_1 = R_3 = R_4 = R_5 = H$

k) $R_1 = CH_3$; $R_2 = R_3 = R_4 = R_5 = R_6 = H$

l) $R_5 = Br$; $R_1 = R_2 = R_3 = R_4 = R_6 = H$

m) $R_2 = R_3 = R_5 = Br$; $R_1 = R_4 = R_6 = H$

n) $R_2 = Br$; $R_1 = R_3 = R_4 = R_5 = R_6 = H$

o) $R_3 = Br$; $R_1 = R_2 = R_4 = R_5 = R_6 = H$

Scheme 2

Table I. UV, IR and ^{1}H NMR spectral data of pyrrolotropones 2b-o

Compd. No.	UV $\lambda_{max}(\epsilon)$	IR cm^{-1}	^{1}H NMR data	
			Cl3	Rest of the signals
2b		3250-3150 1620	6.9 (d,J=12.4)	7.59-9.40(m,9H,ArH) 13.15(NH)
2c		3250-3150 1620 1595	6.92 (d,J=12.8)	3.90(s,OCH_3) 3.95(s,OCH_3) 7.21-9.46(m,9H,ArH) 12.75(NH)
2d		3300-3150 1620	6.92 (d,J=12.7)	1.26(s,6H,2$C^{CH_3}_{CH_3}$) 1.4-1.7(m,16H) 2.14(m,4H) 7.6-9.41(m,9H,ArH) 12.84(NH)
2e	224(12,006) 250(9,523) 282(14,965) 309(9047) 366(5476)	3300-3200 1620	7.09 (d,J=12.4)	1.44(s,t-Bu) 1.45(s,t-Bu) 7.28-8.06(m,8H,ArH) 9.30(NH) 9.38(d,J=9.0,1H,ArH)
2f		3300-3300 1620	6.93 (d,J=12.0)	2.73(s,$ArCH_3$) 2.89(s,$ArCH_3$) 7.66-9.4(m,9H,ArH) 12.86(NH)
2g		3300-3200 1625	—	2.59*(d,J=0.8,Cl3-CH_3) 2.70(s,$ArCH_3$) 7.43-8.02(m,9H,ArH) 9.04(NH) 9.12(d,J=8.4,1H,ArH)
2h	220(14,126) 248(13,446) 283(15,610) 309(12,225) 362(5,456)	3250-3150 1620	7.08 (d,J=12.7)	2.75(s,$ArCH_3$) 7.4-8.12(m,10H,ArH) 9.18(NH) 9.38(d,J=8.6,1H,ArH)
2i	220(16,752) 246(16,069) 281(15.889) 308(11,533) 363(5605)	3200-3100 1615	—	2.6*(d,J=0.8,Cl3-CH_3) 7.46-9.20(m,11H,ArH) 9.26(NH)
2j	226(24,056) 282(18,239) 299(19,081) 308(17,984) 358(9,974)	3300-3200 1620	—	1.4(s,9H,t-Bu) 1.53(s,9H,t-bu) 7.45-8.84(m,11H,ArH) 12.68(NH)
2k		3300-3200 1620	6.9 (d,J=13.1)	2.79(s,$ArCH_3$) 7.49-9.04(m,12H,ArH) 12.9(NH)
2l		3250-3150 1630	6.99 (d,J=12.5)	7.52-9.48(m,10H,ArH) 12.25(NH)
2m		3250-3150 1630	6.94 (d,J=12.5)	7.47-9.19(m,10H,ArH) 12.50(NH)
2n		3250-3150 1620	7.1 (d,J=12.8)	7.65-9.62(m,9H,ArH) 13.20(NH)
2o		3250-3150 1615	7.0 (d,J=13.1)	7.5-9.4(m,12H,ArH) 13.05(NH)

UV spectra were recorded in EtOH; ^{1}H NMR of 2e and 2g-i were recorded in $CDCl_3$ and the others in DMSO-d_6; chemical shifts are in δ values; J values are in Hz; NH signals are D_2O exchangeable; *Signal of methyl α to the ketone in furanotropones appears around δ 2.6 (see ref.18)

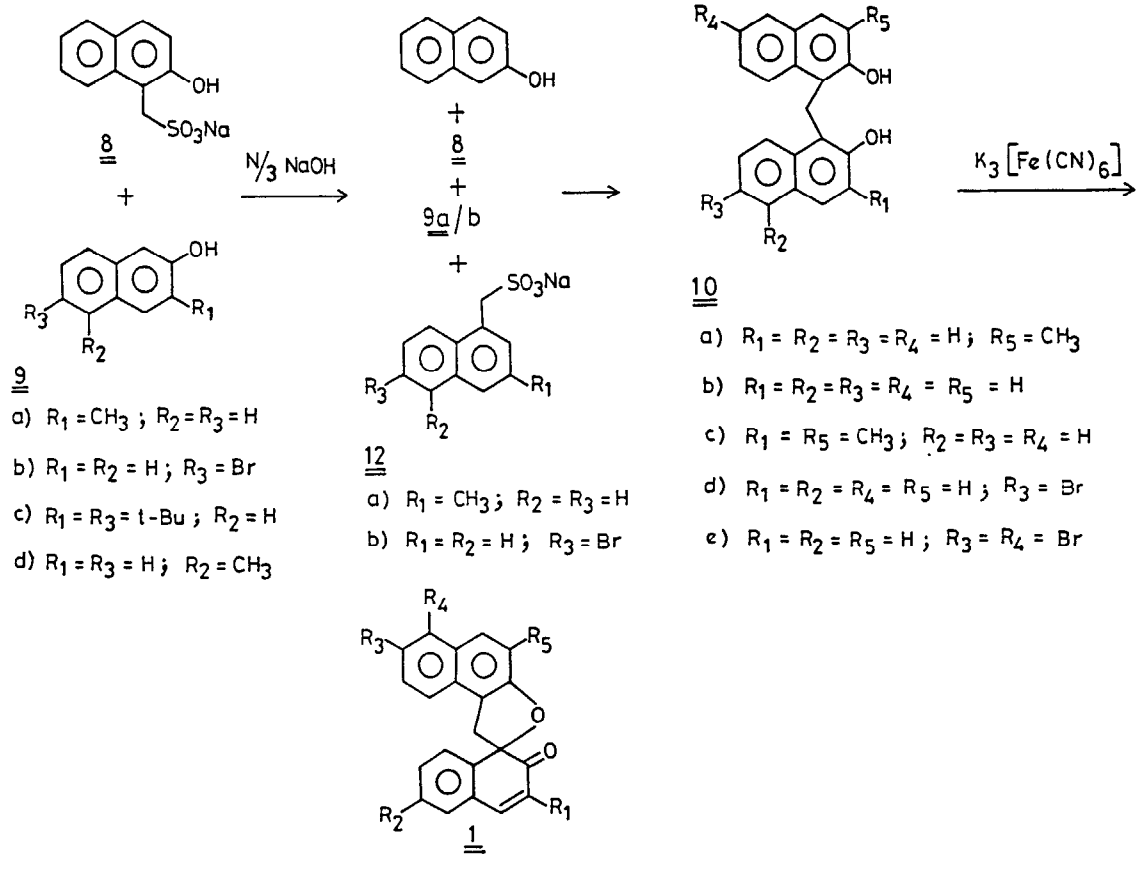
exhibited the characteristic doublet signal[8] for the ∝-proton of the enone system in the tropone ring around δ 6.9 in addition to the aromatic and the NH protons [vide Table I].

In order to find out which of the rings (A or B) in the spironaphthalenone is responsible for the formation of the tropone, we synthesised unsymmetrical substrates **1h-m** for reaction with NH_2OH. Reaction of 3-methyl-2-naphthol (**9a**, Scheme 3) with 2-hydroxy-1-naphthylmethane sulphonate (**8**) in N/3 NaOH solution gave a mixture of bisnaphthols **10a-c** which could be separated by rigorous column chromatography. The formation of these bisnaphthols can be explained by the initial base catalysed desulphomethylation of **8** to sulphomethyl anion ($OHCH_2SO_3^-$), which has been previously postulated as the actual reactant in sulphomethylation reaction[9]. Addition of sulphomethyl anion to **9a** would give rise to 2-hydroxy-3-methyl-1-naphthylmethane sulphonate(**12a**). Condensation between **9a** and the methane sulphonate **12a** would result in the formation of 3,3'-

Table II. ^{1}H NMR spectral data for spironaphthalenones

Compound No.	^{1}H NMR data		
	∝-enone	benzylic $C<^{H_a}_{H_b}$	Rest of the signals
1g	—	3.50(d,J=15.6,1H,Ha) 3.97(d,J=15.6,1H,Hb)	2.07(d,J=1.2,3H,C3-CH_3) 2.53(s,3H,C4'-CH_3) 7.24-7.77(m,10H,ArH)
1h	—	3.51(d,J=15.6,1H,Ha) 3.99(d,J=15.6,1H,Hb)	2.07(d,J=1.2,3H,C3-CH_3) 7.24-7.85(m,11H,ArH)
1i	6.25 (d,J=10.1)	3.51(d,J=15.6,1H,Ha) 4.04(d,J=15.6,1H,Hb)	2.53(s,3H,C4'-CH_3) 7.25-7.77(m,10H,ArH)
1j	6.22 (d,J=10.2)	3.60(d,J=15.6,1H,Ha) 4.15(d,J=15.4,1H,Hb)	1.38(s,9H,t-bu) 1.56(s,9H,t-Bu) 7.3-7.9(m,9H,ArH)
1k	6.24 (d,J=10.2)	3.52(d,J=16.7,1H,Ha) 4.08(d,J=16.7,1H,Hb)	2.70(s,3H,C6-CH_3) 7.2-7.97(m,10H,ArH)
1m	—	3.53(d,J=16.0,1H,H_a) 4.03(d,J=16.0,1H,H_b)	7.44-7.99(m,9H,ArH)
1n	6.2 (d,J=10.1)	3.47(d,J=15.4,1H,H_a) 4.05(d,J=15.4,1H,H_b)	7.2-7.95(m,10H,ArH)
1o	6.3 (d,J=10.2)	3.50(d,J=15.6,1H,H_a) 4.06(d,J=15.6,1H,H_b)	7.2-7.9(m,10H,ArH)

^{1}H NMR spectra of **1j**, **1n** and **1o** were recorded at 90 MHz ($CDCl_3$) and others at 270 MHz ($CDCl_3$), chemical shifts are in δ values; J values are in Hz.


OH
SO3Na
8
+
N/3 NaOH
OH
R3
R1
R2
9
a) R1 = CH3 ; R2 = R3 = H
b) R1 = R2 = H ; R3 = Br
c) R1 = R3 = t-Bu ; R2 = H
d) R1 = R3 = H ; R2 = CH3
OH
+
8
+
9a/b
+
SO3Na
R3
R1
R2
12
a) R1 = CH3 ; R2 = R3 = H
b) R1 = R2 = H ; R3 = Br
R4
R5
OH
OH
R3
R1
R2
10
a) R1 = R2 = R3 = R4 = H ; R5 = CH3
b) R1 = R2 = R3 = R4 = R5 = H
c) R1 = R5 = CH3 ; R2 = R3 = R4 = H
d) R1 = R2 = R4 = R5 = H ; R3 = Br
e) R1 = R2 = R5 = H ; R3 = R4 = Br
K3 [Fe(CN)6]
R4
R3
R5
O
O
R2
R1
1
a) R1 = R2 = R3 = R4 = R5 = H
b) R2 = R3 = Br ; R1 = R4 = R5 = H
c) R1 = R5 = CH3 ; R2 = R3 = R4 = H
h) R1 = CH3 ; R2 = R3 = R4 = R5 = H
i) R5 = CH3 ; R1 = R2 = R3 = R4 = H
j) R3 = R5 = t-Bu ; R1 = R2 = R4 = H
k) R4 = CH3 ; R1 = R2 = R3 = R5 = H
n) R3 = Br ; R1 = R2 = R4 = R5 = H
o) R2 = Br ; R1 = R3 = R4 = R5 = H

Scheme 3

disubstituted bisnaphthol 10c, while that between 8 and the generated β-naphthol would give rise to 10b. Bisnaphthol 10a would arise from the expected coupling between 8 and 9a. Similarly, when the condensation of 6-bromo-2-naphthol (9b) with 2-hydroxy-1-naphthylmethane sulphonate(8) was carried out and the resulting bisnaphthols oxidized with $K_3Fe(CN)_6$, spironaphthalenones 1a,b,n & o were isolated after purification by preparative TLC. The formation of spironaphthalenones 1a,b,n & o indicated that the condensation of 8 with 9b has resulted in the formation of bisnaphthols 10b,d & e. This is in conformity with the above mentioned findings and is contrary to the results obtained by Shearing and Smiles[10] who report the isolation of only one bisnaphthol. Spironaphthalenones 1h & i were obtained by the oxidation of the mixture of bisnaphthols 10a-c followed by purification by preparative TLC. Structures of these were evident from ^{1}H NMR . While compound 1i gave a doublet at δ 6.25 for the α-enone proton, it was absent in 1h. Oxidation product of a mixture of bisnaphthols prepared by coupling of 3,6-di-t-butyl-2-naphthol (9c) with 8 was separated by rigorous column chromatography to yield 1j which was characterised by the ^{1}H NMR doublet at δ 6.2. Following similar procedure, spironaphthalenone 1k was prepared by the reaction of 9d with 8. Spironaphthalenone 1m (see Table II for spectral data of spironaphthalenones) was prepared by bromination of dibromoketone 1b followed by dehydrobromination of the resulting bromo adduct, adopting the procedure of Shearing and Smiles[10].

According to the mechanism proposed by Dean et al.,[3] reaction of spironaphthalenone 1h with NH_2OH should result in the formation of pyrrolotropone 2i. When the reaction of 1h was carried out, a single product[11] (M^+, 309) exhibiting a doublet at δ 7.08 (J = 12.7 Hz) corresponding to the α-enone proton was obtained. Further, the characteristic UV absorption pattern of pyrrolotropone was observed (Table I). Based on the spectral data, structure 2h was assigned to this product. The isomeric pyrrolotropone 2i expected from Dean's mechanism should not show a doublet around δ 6.9 . When the reaction was carried out with the spironaphthalenone 1i carrying a methyl group in the naphthalene ring, the resulting pyrrolotropone exhibited no doublet corresponding to the α-proton of the enone system, implying that the methyl group is in the tropone ring α to the keto group as in 2i. Reaction of 1j with NH_2OH gave the pyrrolotropone 2j (no doublet at δ 7.0 region; t-butyl group is α to the keto). Pyrrolotropone 2k results from the reaction of spironaphthalenone 1k. Spironaphthalenones 1l & m carrying bromo substituents at C3 position gave rearranged pyrrolotropones 2l & m showing the characteristic doublet around δ 7.0 region for the α-enone proton (Table I). It is obvious from the

above experiments that it is the ring A,but not the ring B of the spironaphthalenones that is transformed to the tropone ring of the pyrrolotropones.

The present work has clearly demonstrated that: (i) furanotropone **6** is not an intermediate in the formation of pyrrolotropones;(ii) only one mole of NH_2OH is required in the reaction and(iii) ring A and not the ring B of spironaphthalenone is converted to the tropone ring. In view of these findings, which are not in accordance with Dean's mechanism[3], an alternate mechanism has to be visualised and further work is in progress in this direction.

Experimental Section

All m.ps reported herein are uncorrected. UV(nm) spectra were recorded on a Shimadzu spectrophotometer. IR(cm^{-1}) spectra were recorded either on a Hitachi Model 270-50 double wavelength/double beam or Perkin-Elmer Model 781 instruments. ^1H NMR data was recorded on a JEOL FX 90 Q (90 MHz) or a Bruker-WH-270 (270 MHz) instrument using TMS as an internal standard. Mass spectra were recorded on a JEOL MS-DX 303 spectrometer operating at 70 eV and fitted with a built-in inlet system.

Spironaphthalenones 1b-e : These were prepared according to reported procedures[12,13].

3-Methyl-bis(2-hydroxy-1-naphthyl)methane : Sodium salt of 2-naphthol-1-methane sulphonic acid[14] (8 ,1.2 gm) and 3-methyl-2-naphthol (800 mg) were dissolved in N/3 NaOH solution (30 ml) and refluxed for 6 hrs.The solution was cooled and neutralised with dil.HOAc. The white solid which separated out was filtered, washed with water and dried (850 mg). The mixture of bisnaphthols, thus obtained, was separated by column chromatography (silica gel, benzene-$CHCl_3$) to give **(i)** bis(3-methyl-2-hydroxy-1-naphthyl)methane (**10c**, 490 mg); m.p.208°C (d) ($CHCl_3$-hexane) ; IR (nujol) 3300-3350, and 1610 cm^{-1}; ^1H NMR (270 MHz; DMSO-d_6) 2.39 (s,6H,2 $ArCH_3$), 4.83 (s, 2H,benzylic CH_2), 7.30-8.18(m,12H,ArH) ;MS; m/e 328 (M^+, 68) 309 (17), 171 (62) and 158 (100%).Anal.Calcd.for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14.Found C, 83.96; H, 5.90%. **(ii)** 3-methyl-bis(2-hydroxy-1-napthyl)methane (**10a**, 290 mg); m.p.179-180°C($CHCl_3$-hexane) ; IR (nujol) 3300-3400, and 1630 cm^{-1}; ^1H NMR (270 MHz, DMSO-d_6) 2.37 (s,3H,$ArCH_3$), 4.82 (s,2H,benzylic CH_2), 7.07-8.24 (m, 13H, ArH); MS; m/e 314 (M^+, 24) 171(13), 158(73) and 144 (100%). Anal.Calcd.for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77.Found : C, 84.29; H, 5.49%, and **(iii)** bis(2-hydroxy-1-naphthyl)methane(**10b**, 30 mg); m.p. 199°C (lit.[7] 199°C).

Oxidation of bisnaphthols 10 with $K_3Fe(CN)_6$: To a mixture of bisnaphthols **10a-c** obtained in the above coupling reaction(8 gm) in 10% KOH solution (300 ml) was added $K_3Fe(CN)_6$ (17 gm) and the mixture was stirred for 3 hrs. Extraction with CH_2Cl_2 followed by removal of solvent left a yellow solid (5 gm) which was separated by careful column chromatography (silica gel, $CHCl_3$-hexane mixtures) to give four compounds identified as : **(i)** 3,4'-dimethyl-spiro(naphthalene-1(2H),2'(1'H)-naphtho[2,1-b]furan}-2-one (**1g**,2.2 gm); m.p.;153°C ($CHCl_3$-hexane);IR (nujol) 1660 and 1630 cm^{-1}; MS; m/e 326 (M^+, 88), and 310 (100%);Anal.Calcd.for $C_{23}H_{18}O_2$: C, 84.66; H, 5.52. Found C, 84.7; H, 5.5%. **(ii)** 3-methyl-spiro[naphthalenone-1(2H), 2'(1'H)-naptho[2,1-b]furan}-2-one (**1h**,1.2 gm); m.p. 133°C (acetone-hexane); IR (nujol) 1670 and 1620 cm^{-1}; MS; m/e 312 (M^+, 7) 295(100), 239 (21), 139(15) and 120(18%).Anal.Calcd.for $C_{22}H_{16}O_2$: C, 84.68; H, 5.25%. Found C,

84.61; H, 5.22%. **(iii)** 4'-methyl-spiro[naphthalene-1(2H),2'(1'H)-napththo [2,1-b]furan]-2-one (**1i**,1.3 gm); m.p.139°C ($CHCl_3$-hexane); IR(nujol) 1670 and 1600 cm^{-1}; MS; m/e 312 (M^+, 70), 295(100) and 239(33%); Anal. Calcd.for $C_{22}H_{16}O_2$: C, 84.43; H, 5.12. Found C, 84.65; H, 5.15%. **(iv)** Spiro[naphthalene-1(2H), 2'(1'H)-naphtho[2,1-b]furan]2-one(**1a**,100 mg), m.p.171°C (lit.[15], 171-172°C).

6,7'-Dibromo-spiro[naphthalene-1(2H),2'(1'H)-naphtho[2,1-b]furan]-2-one(1b) and spironaphthalenones 1n & o:

Sodium salt of 2-naphthol-1-methane sulphonic acid (2.6 gm) and 6-bromonaphthol (3.5 gm) were dissolved in N/3 NaOH solution (97 ml) and refluxed for 6 hrs. The solution was cooled and neutralised with dil.AcOH. The white solid which separated out was filtered , washed with water and dried (2.5 gm).

To the above mixture of bisnaphthols (1 gm) in 10% KOH solution (30 ml) was added $K_3Fe(CN)_6$ (1.6 gm) and the mixture was stirred for 3 hrs. Extraction with CH_2Cl_2 followed by removal of solvent left a yellow solid (600 mg) which was separated by PTLC (Silica gel, benzene:hexane)into four compounds which were identified as:**(i)** 6,7'-Dibromo-spiro[naphthalene-1(2H),2'(1'H)-naphtho[2,1-b]furan]-2-one (**1b**,120 mg); m.p.197°C (lit.[15], 196°C). **(ii)**6-Bromo-spiro[naphthalene-1(2H),2'(1'H)-naphtho[2,1-b]furan]-2-one(**1o** ,110 mg); m.p.182°C;IR(nujol):1665 and 1630 cm^{-1}; MS;m/e 377(M^+,70%) **(iii)** 7'-Bromo-spiro[naphthalene-1(2H),2'(1'H)-naphtho[2,1-b]furan]-2-one (**1n**, 100 mg); m.p.185°C;IR(nujol) 1670 and 1620 cm^{-1}; MS;m/e 377(M^+,67%). **(iv)** Spiro[naphthalene-1(2H),2'(1'H)-naphtho[2,1-b]furan]-2-one (**1a**,120 mg) m.p.171°C (lit[15],171-172°C).

6'-Methyl-spiro[naphthalene-1(2H),2'(1'H)-naphtho[2,1-b]furan]-2-one (1k): A mixture of sulphonate **8** (7.72 gm), 5-methyl-2-naphthol[16] (5 gm) and N/3 NaOH (190 ml) was refluxed for 6 hrs. The reaction mixture was cooled, neutralised with dil.AcOH and the resulting solid was filtered, washed with water and dried (5 gm). A solution of this solid (5 gm) in 10% KOH (187 ml) containing $K_3Fe(CN)_6$ (10.62 gm) was stirred for 3 hrs. The reaction mixture was extracted with CH_2Cl_2, washed with 5% NaOH, water and dried. The residue obtained after removal of solvent was purified by column chromatography (silica gel, benzene) followed by repeated fractional crystallisation to give **1k** (140 mg); m.p. 173-174°C ($CHCl_3$-hexane);IR 1670 and 1630 cm^{-1}. Anal.Calcd.for $C_{22}H_{16}O_2$: C, 84.63; H,5.12%. Found C,84.49; H, 5.13%.

3,6,7'-Tribromo-spiro[naphthalene-1(2H), 2'(1'H) naphtho[2,1-b]furan]-2-one (1m): A solution of spironaphthalenone **1b** (500 mg) in glacial HOAc (5 ml) containing bromine (280 mg) was stirred for 2 hrs.at 0°C followed by 6 hrs. at room temperature (25°C). The solid obtained after dilution with water (50 ml) was filtered and dried to give 3,4,6',7'-tetrabromo-spiro [3,4-dihydro-naphthalene-1 (2 H),2'(1'H)naphtho[2,1-b]furan]-2-one(800 mg); m.p (crude) 140-142°C (d); IR(nujol) 1730 cm^{-1}; ^1H NMR (90 MHz,$CDCl_3$) 3.53(d, J= 16.0 Hz, 1H,benzylic CH), 4.26(d,J=16.0 Hz, 1H,benzylic CH), 4.96(d, J= 3.0 Hz, 1H, C3-H), 5.42(d,J=3.0 Hz,1H, C4-H), 7.22-8.0(m,8H, ArH) an analytically pure sample could not, however, be obtained.

A solution of the above crude bromo compound (800 mg) in pyridine (10 ml) was stirred at 60°c for 8 hrs., neutralized with dilute HCl (50 ml) and extracted with $CHCl_3$ (3x25 ml). The chloroform extract was washed with water and dried. The product obtained after removal of $CHCl_3$ was purified by column chromatography (neutral alumina) using $CHCl_3$ as eluent. Crystallisation gave yellow needles of **1m**(420 mg); m.p 198-199°C ($CHCl_3$-hexane) ; IR (nujol) 1695 and 1635cm^{-1}; MS; m/e 532(M^+,10%).Anal.Calcd.for $C_{21}H_{11}Br_3O_2$: C, 47.16; H, 2.05. Found: C, 47.14; H, 2.08%.

4',7'-Di-t-butylspiro[naphthalene-1(2H), 2'(1'H)-naphtho[2,1-b]furan]-2-one (1j) : To a mixture of sodium salt of 2-naphthol-1-methanesulphonic acid[14] 8 (3.24 gm) and 3,6-di-t-butyl-2-naphthol[17] (9c ,3.4 gm), N/3 NaOH (80 ml) was added and refluxed for 6 hrs. The solution was cooled, neutralised with dil.AcOH and the resulting white solid was filtered, washed with water and dried (3.54 gms). A mixture of this solid (3.54 g) and $K_3Fe(CN)_6$ (4.68g) in 10% KOH (98 ml) was stirred for 3 hrs. The reaction mixture was extracted with CH_2Cl_2, washed with 5% NaOH, water and dried. The residue obtained on removal of solvent gave on column chromatography (silica gel, benzene-hexane) the title compound 1j (150 mg); m.p.168-169°C ($CHCl_3$-hexane); IR (nujol) 1665 and 1625 cm^{-1}. Anal.Calcd.for $C_{29}H_{30}O_2$: C, 84.81; H, 7.35 Found C, 85.19; H, 7.13%.

General procedure for the reaction of spironaphthalenones 1b-o with $NH_2OH.HCl$: $NH_2OH.HCl$ (3 mmol)[6] in ethanol (4.5 ml) was added to the spironaphthalenone (1 mmol) in THF (1.5 ml). A drop of conc.HCl was added and the mixture heated under reflux for 24 hrs. The solid that separated was washed with ethanol and recrystallised from DMF. All the compounds melted above 360°C.

3-10-Dibromo-14H-benzo[6,7]cyclohepta[1,2-b]naphtho[1,2-d]-indole-14-one (2b): Reaction of 1b with $NH_2OH.HCl$ gave 2b(250 mg) . Anal. Calcd. for $C_{21}H_{11}Br_2NO$: C, 54.86; H, 2.63; N, 2.82. Found C, 54.84; H, 2.85; N, 2.98%.

3,10-Dimethoxy-14H-benzo[6,7]cyclohepta[1,2-b]naphtho[1,2-d]indole-14-one (2c): Reaction of 1c gave 2c(250 mg).Anal.Calcd.for $C_{23}H_{17}NO_5$: C,77.75; H, 4.79; N, 3.94.Found C, 77.79;H, 4.86;N, 3.80%.

3,10-Di-(1-methylcyclohexyl)-14H-benzo[6,7]cyclohepta[1,2-b]naphtho[1,2-d] indole-14-one (2d) :Reaction of 1d gave 2d(255 mg);MS; m/e 487 (M^+, 39%). Anal. Calcd.for $C_{35}H_{37}NO$: C,86.24; H,7.60;N,2.87.Found C, 85.83; H, 7.73; N, 2.74%.

3,10-Di-t-butyl-14H-benzo[6,7]cyclohepta[1,2-b]naphtho[1,2-d]indole-14-one (2e): The reaction of 1e with $NH_2OH.HCl$ gave 2e(250 mg) .Anal.calcd.for $C_{29}H_{29}NO$: C, 85.51;H, 7.16;N, 3.42.Found C, 85.41; H,7.12; N, 3.48%.

4,11-Dimethyl-14H-benzo[6,7]cyclohepta[1,2-b]naphtho[1,2-d]indole-14-one (2f) : Reaction of 1f gave 2f(200 mg).Anal. Calcd.for $C_{23}H_{17}NO$: C, 85.42;H, 5.21;N, 4.38. Found C, 85.36; H, 5.25; N, 4.29%.

6,13-Dimethyl-14H-benzo[6,7]cyclohepta[1,2-b]naphtho[1,2-d]indole-14-one (2g): The reaction of spironaphthalenone 1g with $NH_2OH.HCl$ gave 2g(155 mg); MS ; m/e 323 (M^+,62), 295(100), 278(28) and 162 (57%). Anal.Calcd.for $C_{23}H_{17}NO$: C, 85.43; H, 5.32; N, 5.04.Found C, 85.67; H, 5.68; N, 5.22%.

6-Methyl-14H-benzo[6,7]cyclohepta[1,2-b]naphtho[1,2-d]indole-14-one (2h): Reaction of 1h gave 2h(195 mg) ;MS; m/e 309 (M^+,33), 295(8) 281(100), and 266(8%). Anal.Calcd.for$C_{22}H_{15}NO$ C, 85.41;H, 4.89; N, 4.53. Found C, 85.07; H, 4.69; N, 4.41%.

13-Methyl-14H-benzo[6,7]cyclohepta[1,2-b]naphtho[1,2-d]indole-14-One (2i): Reaction of 1i gave 2i(160 mg); MS; m/e 309 (M^+, 62), 281 (92), 155 (65), and 139 (100%). Anal.Calcd.for $C_{22}H_{15}NO$: C, 85.42; H, 4.89; N, 4.53. Found C, 85.08; H, 5.22; N, 4.91%.

10,13-Di-t-butyl-14H-benzo[6,7]cyclohepta[1,2-b]naptho[1,2-b]indole-14-one (2j): Reaction of 1j gave 2j(250 mg) ; MS; m/e 407 (M^+, 100), 392 (36) and 379 (25%). Anal.Calcd.for $C_{29}H_{29}NO$: C, 85.52; H, 7.11; N, 3.45. Found C, 85.38; H, 7.12; N, 3.46%.

11-Methyl-14H-benzo[6,7]cyclohepta[1,2-b]naphtho[1,2-d]indole-14-one (2k): Reaction of 1k gave 2k(220 mg). Anal.Calcd.for $C_{22}H_{15}NO$: C, 85.71; H, 4.82; N, 4.53. Found C, 85.60; H, 4.95; N, 4.11%.

6-Bromo-14H-benzo[6,7]cyclohepta[1,2-b]naphtho[1,2-d]indole-14-one (2l): Reaction of 1l gave 2l(160 mg); MS; m/e 375, 373 (M^+, 1:1, 73), 345 (100) and 264 (55%). Anal.Calcd.for $C_{21}H_{12}BrNO$: C, 67.36; H, 3.21; N, 3.70. Found C, 67.57; H, 3.02; N, 3.62%.

3,6,10-Tribromo-14H-benzo[6,7]cyclohepta[1,2-b]naphtho[1,2-d]indole-14-one (2m): The reaction of spironaphthalenone 1m with $NH_2OH.HCl$ gave 2m(180 mg); MS; m/e 529(M^+, 25%).Anal.Calcd.for $C_{21}H_{10}Br_3NO$: C, 47.3; H, 1.8; N, 2.64 Found C, 47.2; H, 1.8; N, 2.62%.

10-Bromo-14H-benzo[6,7]cyclohepta[1,2-b]naphtho[1,2-d]indole-14-one (2n): Reaction of 1n gave 2n(160 mg). Anal.Calcd.for $C_{21}H_{12}BrNO$: C, 67.37; H, 3.21; N, 3.70. Found C, 67.21; H, 3.19; N, 3.70%.

3-Bromo-14-H-benzo[6,7]cyclohepta[1,2-b]naphtho[1,2-d]indole-14-one (2o) : Reaction of spironaphthalenone 1o with $NH_2OH.HCl$ gave 2o(160 mg). Anal.Calcd.for $C_{21}H_{12}BrNO$: C, 67.37; H, 3.21; N, 3.70. Found C, 67.32; H, 3.15; N, 3.67%.

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