Tetrahedron Vol. 49, No. 1, pp. 125-134, 1993
Printed in Great Britain

0040-4020/93 $5.00+.00

Reaction of Spironaphthalenones with Hydroxylamine: Part II. Structure of Product in the Reaction of 1'-Substituted Spironaphthalenone.

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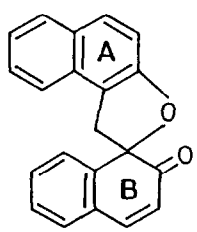
(*Received in UK 27 August* 1992)

Abstract: Reaction of 1'-aryl substituted spironaphthalenones **1a-d** with hydroxylamine hydrochloride in ethanol gave substituted cinnamic ester derivatives **4a-d**. Similarly, reaction of spironaphthalenone **1a** with different alcohols gave the corresponding esters **4i-m**. Reaction of unsymmetrical spironaphthalenones **1e-h** with hydroxylamine hydrochloride in presence of ethanol gave the respective esters **4e-h**. All the esters were characterised by their spectral data.

We have recently[1] adduced evidences to show that the mechanism proposed by Dean and coworkers[2] for the formation of pyrrolotropone 2 in the reaction of spironaphthalenone 1 with hydroxylamine hydrochloride is not correct. In continuation of this investigation, we have now subjected a number of 1'-aryl substituted spironaphthalenones to the same reaction with the hope of obtaining the corresponding dihydrotropones 3. The results obtained in this study are discussed below.



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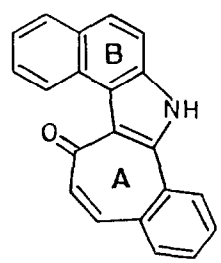

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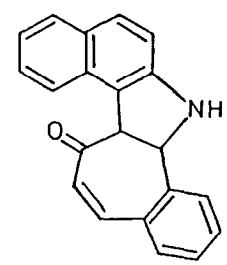
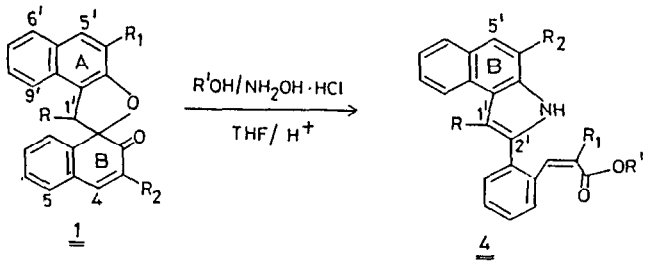


3

Preparation of spironaphthalenones 1a,b & d are already reported[3]. Spironaphthalenone **1c** was prepared by a two step process involving the condensation of p-nitrobenzaldehyde with β-naphthol in presence of acid. KOBr oxidation of the resulting bisnaphthol gave spironaphthalenone **1c** as the major product along with a small amount of the α-phenyl diastereomer which could be removed by repeated crystallisation.These two isomers could be differentiated by their ^{1}H NMR spectra[4]. Thus the spironapthalenone **1c**

exhibiting a signal at δ 6.1 for the α-enone proton (Table I) could be assigned the β-phenyl configuration. When the reaction of **1a** with NH_2OH in ethanol was carried out, we obtained in 80% yield, after purification, a yellow compound (M^+447) which showed IR absorptions at 3300 and 1710 cm^{-1}. The IR frequency of 1710 cm^{-1} was a little higher than that to be expected for the dihydrotropone 3. This compound exhibited in its ^1H NMR spectum (Table II) a doublet at δ 5.84 (J = 10.8 Hz) corresponding to the vinylic α-proton of an enone system. In addition, the compound also showed a NH signal at δ 8.8 (D_2O exchangeable). In the upfield region, the compound showed a three proton triplet at δ 1.2 (J = 7.2 Hz) and a quartet at δ 4.15 (J = 7.2 Hz,2H) indicating the presence of a $-OCH_2CH_3$ group. It may be mentioned that compound 3 is expected to show only a single peak in the upfield region of its ^1H NMR spectrum. Based on the IR, ^1H NMR and mass spectral data, this compound was assigned the substituted cinnamic ester structure **4a** (Scheme 1).



1

a) R = 4-OCH_3Ph ; $R_1 = R_2$ = H
b) R = Ph ; $R_1 = R_2$ = H
c) R = 4-NO_2Ph ; $R_1 = R_2$ = H
d) R = 2-OCH_3Ph ; $R_1 = R_2$ = H
e) R = Ph ; $R_1 = CH_3$; R_2 = H
f) R = Ph ; R_1 = H ; $R_2 = CH_3$
g) R = 2-OCH_3Ph ; $R_1 = CH_3$; R_2 = H
h) R = 2-OCH_3Ph ; R_1 = H ; $R_2 = CH_3$

4

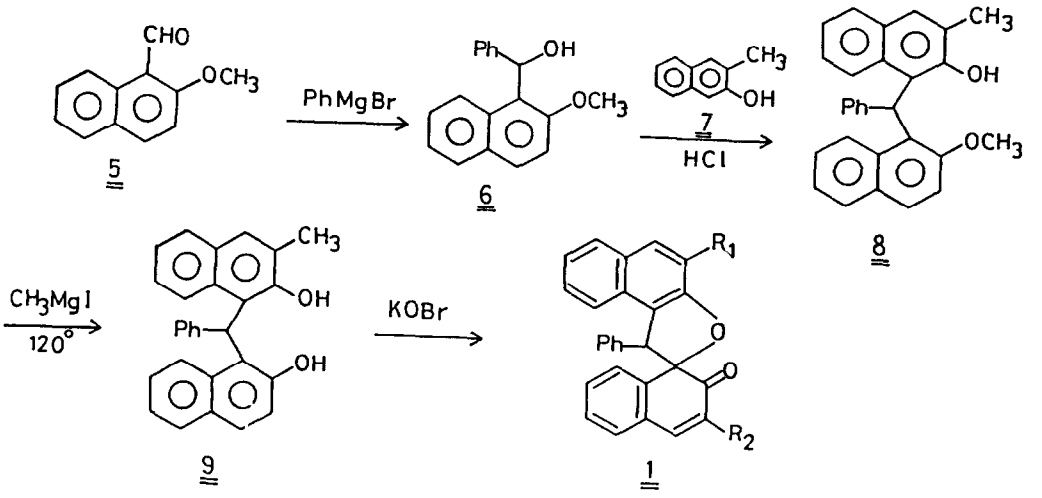
a) R = 4-OCH_3Ph ; $R_1 = R_2$ = H ; R' = Et
b) R = Ph ; $R_1 = R_2$ = H ; R' = Et
c) R = 4-NO_2Ph ; $R_1 = R_2$ = H ; R' = Et
d) R = 2-OCH_3Ph ; $R_1 = R_2$ = H ; R = Et
e) R = Ph ; $R_1 = CH_3$; R_2 = H ; R' = Et
f) R = Ph ; R_1 = H ; $R_2 = CH_3$; R' = Et
g) R = 2-OCH_3Ph ; $R_1 = CH_3$; R_2 = H ; R' = Et
h) R = 2-OCH_3Ph ; R_1 = H ; $R_2 = CH_3$; R' = Et
i) R = 4-OCH_3Ph ; $R_1 = R_2$ = H ; R' = CH_3
j) R = 4-OCH_3Ph ; $R_1 = R_2$ = H ; R' = i-Pr
k) R = 4-OCH_3Ph ; $R_1 = R_2$ = H ; R' = n-Pr
l) R = 4-OCH_3Ph ; $R_1 = R_2$ = H ; R' = n-Bu
m) R = 4-OCH_3Ph ; $R_1 = R_2$ = H ; R' = CH_2Ph

Scheme 1

The structure of **4a** was further substantiated by its ^{13}C NMR spectrum. The presence of a $-OCH_2CH_3$ group was evident from signals at δ 14.18(q) and δ 60.15(t). Further, signals were seen at δ 166.75 (ester carbonyl), 148.13 (d, β -carbon of enone) and 135.13 (s, C-3a carbon).It may be mentioned here that 1'-unsubstituted spironaphthalenone under the same reaction conditions did not form even a trace of the corresponding cinnamic ester derivative (HPLC).

In order to see the generality of this reaction, we subjected spironaphthalenones **1b-d** to reaction with NH_2OH in ethanol. In each case, the respective ethyl esters **4b-d** were obtained in good yields. When the spironaphthalenone **1a** was reacted with NH_2OH in different alcohols, the corresponding esters **4i-m** were obtained (Table II).

We have shown in our earlier work[1] that the ring B of spironaphthalenone 1 is converted into the aromatic ring of the naphthopyrrole, while the ring A in 1 forms the tropone ring in 2. In order to determine if such rearrangements also occur in the reaction of 1'-substituted spironaphthalenones with NH_2OH, we synthesised unsymmetrical spironaphthalenones **1e-g**. Reaction of 2-methoxynaphthalene-1-aldehyde (5) (Scheme 2) with phenylmagnesium bromide gave the alcohol 6 which on condensation with 3-methyl-2-naphthol (7) in ether in presence of HCl gave the monomethyl ether of bisnaphthol 8 in 55% yield. This was then



5 6 8 9 1

e) $R_1 = CH_3$; $R_2 = H$

f) $R_1 = H$; $R_2 = CH_3$

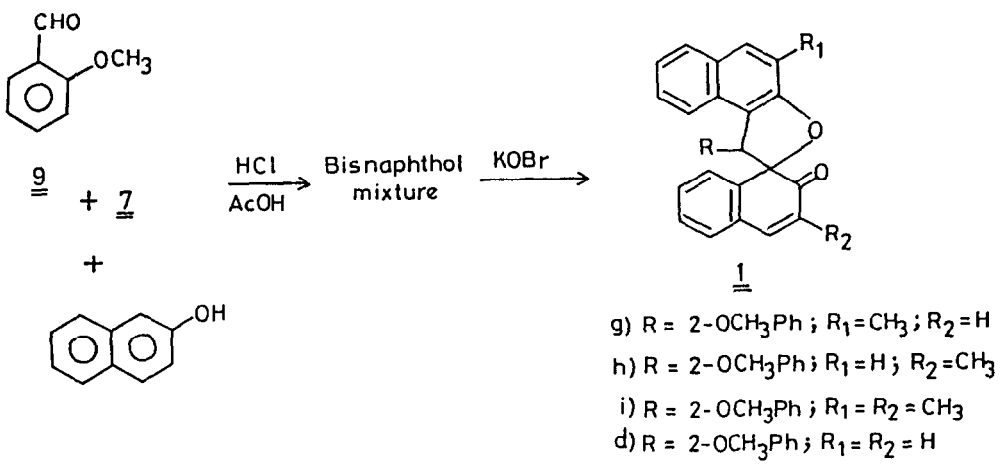
Scheme 2

Table I. ^{1}H NMR spectral data of spironaphthalenones

Compound number (config)#	^{1}H NMR data		
	C3	C1'	Rest of the signals
1c(1'R*,2'S*)	6.25 (d,J=10.1,1H,C3-H)	5.44(s)	6.8-8.0 (m,15H,ArH)
1e(1'R*,2'R*)	5.51 (d,J=10.8,1H,C3-H)	5.21(s)	2.61(s,3H,ArCH$_3$) 6.7-7.9(m,15H,ArH)
1f(1'R*,2'R*)	2.12 (d,J=1.2,3H,C3-CH$_3$)	5.22(s)	6.8-7.85 (m,16H,ArH)
1g(1'R*,2'S*)	6.20 (d,J=11.0,1H,C3-H)	5.85(s)	2.6(s,3H,ArCH$_3$) 3.55(s,3H,OCH$_3$) 6.3-7.85(m,14H,ArH)
1h(1'R*,2'S*)	2.10 (d,J=1.4,3H,C3-CH$_3$)	5.80(s)	3.50(s,3H,OCH$_3$) 6.4-8.0(m,14H,ArH)

All spectra were recorded at 90 MHz in $CDCl_3$, chemical shifts are in δ values; J values are in Hz; # See ref.3 for assignments of configuration based on α-enone proton signal.

demethylated with CH_3MgI at 120°C to give the bisnaphthol 9. KOBr oxidation of the bisnaphthol 9 gave a mixture of spironaphthalenones 1e & f which were separated by careful column chromatography. Structures of these isomeric spironaphthalenones were evident from their ^{1}H NMR data (Table I). While compound 1e showed a doublet at δ 5.51(J=10.8 Hz) for the α-proton of the enone, this was absent in compound 1f. On the other hand, compound



1

g) R = 2-OCH_3Ph ; R_1=CH_3 ; R_2=H

h) R = 2-OCH_3Ph ; R_1=H ; R_2=CH_3

i) R = 2-OCH_3Ph ; R_1 = R_2 = CH_3

d) R = 2-OCH_3Ph ; R_1 = R_2 = H

Scheme 3

Table II. IR and ^{1}H NMR spectral data of pyrroloesters 4a-m

Compd. No.	IR cm^{-1}	^{1}H NMR data		
		∝-enone	NH	Rest of the signals
4a	3300 1707	5.84 (d,J=10.8)	8.80	1.20(t,J=7.2,$CH_2\underline{CH_3}$) 3.85(s,$\overline{OCH_3}$) 4.15(q,J=7.2,OCH_2CH_3) 6.8-8.0(m,15H,ArH)
4b	3300 1710	5.85 (d,J=12.0)	8.85	1.2(t,J=7.0,CH_2CH_3) 4.15(q,J=7.0,OCH_2CH_3) 7.1-8.0(m,15H,ArH)
4c	3300 1710	5.80 (d,J=11.0)	9.05	1.2(t,J=7.2,CH_2CH_3) 4.15(q,J=7.2,OCH_2CH_3) 7.2-8.3(m,14H,ArH)
4d	3352 1710	5.85 (d,J=12.0)	8.80	1.2(t,J=7.0,CH_2CH_3) 3.55(s,OCH_3) 4.15(q,J=7.0,OCH_2CH_3) 6.8-7.9(m,15H,ArH)
4e	3300 1707	—	9.00	1.05(t,J=7.0,CH_2CH_3) 1.98(d,J=1.6,∝-CH_3) 4.05(q,J=7.0,OCH_2CH_3) 6.48(m,1H,β-enone) 7.2-7.9(m,15H,ArH)
4f	3300 1710	5.88 (d,J=10.6)	9.00	1.18(d,J=7.0,CH_2CH_3) 2.6(s,C4-CH_3) 4.10(q,J=7.0,OCH_2CH_3) 6.9(d,J=10.6,β-enone) 7.1-7.9 (m,14H,ArH)
4g	3330 1708	—	8.9	1.0(t,J=7.0,CH_2CH_3) 1.96(d,J=1.3,∝-CH_3) 4.0(q,J=7.0,OCH_2CH_3) 6.5(m,β-enone) 7.2-7.98(m,14H,ArH)
4h	3322 1698	5.85 (d,J=12.0)	8.9	1.22(t,J=7.0,CH_2CH_3) 2.6(s,C4-CH_3) 3.6(s,OCH_3) 4.15(q,J=7.0,OCH_2CH_3) 6.8-8.25(m,14H,ArH)
4i	3300 1713	5.81 (d,J=10.8)	8.66	3.62(s,CO_2CH_3) 3.81(s,ArOCH_3) 6.78-8.00(m,15H,ArH)
4j	3300 1707	5.84 (d,J=10.8)	8.85	1.18[d,J=6.4,$CH(CH_3)_2$] 3.81(s,$\overline{OCH_3}$) 4.98[m,1H,$\overline{CH}(CH_3)_2$] 6.8-8.0(m,15H,ArH)
4k	3340 1710	5.83 (d,J=10.8)	8.80	0.82[t,J=6.8,$(CH_2)_2\underline{CH_3}$] 1.5(m,2H,-$CH_2\underline{CH_2}CH_3$) 3.94(s,OCH_3) 4.0(t,J=7.2,-OCH_2CH_2) 6.68-8.10(m,15H,ArH)
4l	3300 1709	5.81 (d,J=10.8)	8.80	0.9(t,J=6.0,CH_2CH_3) 1.1-1.6(m,$(CH_2)_2$) 3.8(s,OCH_3) 4.1(t,J=5.3,OCH_2CH_2)
4m	3320 1707	5.85 (d,J=10.8)	8.62	3.8(s,OCH_3) 5.11(s,OCH_2Ph) 6.78-8.0(m,20H,ArH)

All spectra were recorded at 90 MHz in $CDCl_3$ and chemical shifts are in δ values; J values are in Hz; NH signals are D_2O exchangeable.

1f showed a fine doublet ($\underline{J}$=1.8 Hz,allylic coupling) at δ 2.12 for the methyl proton. Unsymmetrical spironaphthalenones **1g & h** were prepared by a two step process. Condensation of o-anisaldehyde (9) with β-naphthol (Scheme 3) and 3-methyl-2-naphthol (7) in presence of acid resulted in a mixture of bisnaphthols. Oxidation of the bisnaphthols without further purification, yielded a mixture of spironaphthalenones **1g-j** which were then separated by careful column chromatography followed by preparative TLC. Structures of these compounds **1g-j** were confirmed from their ^{1}H NMR spectral data (Table I).

Spironaphthalenone **1e** underwent reaction with NH_2OH in ethanol to give a single compound[5]. This compound showed in its ^{1}H NMR spectrum (Table II) a signal due to CH_3 on a double bond at δ 1.98(d,$\underline{J}$=1.6 Hz, allylic coupling). The compound also did not show any signal around δ 5.8 for the α-enone proton. Based on these spectral data, this compound was assigned the structure **4e**. Similarly, when the same reaction was carried out with **1f**, the ester having the methyl group at C-4 position was obtained as evident from the presence of a doublet for the α-proton of the enone in its ^{1}H NMR spectrum (Table II). Reaction of spironphthalenones **1g & h** resulted in the formation of the esters **4g & h**. These experiments clearly indicated that the ring A of the spironaphthalenone **1** is cleaved to form the α,β - unsaturated ester system of **4**, while ring B of **1** is converted to the aromatic ring of the naphthopyrrole moiety in **4**. These observations are in agreement with our earlier findings with 1'-unsubstituted spironaphthalenones[1].

It is clear from the present work that 1'-phenyl substituted and 1'-unsubstituted spironaphthalenones behave differently under the same reaction conditions to give exclusively either the pyrroloesters or pyrrolotropones respectively. Further work is in progress to establish the mechanism of these novel rearrangements.

EXPERIMENTAL SECTION

All m.ps reported are uncorrected. IR(cm^{-1}) spectra were taken on a Hitachi 270-50 double wavelength/double beam spectrometer. NMR spectra were recorded on a Jeol FX-90Q (90 MHz ^{1}H, 22.49 MHz ^{13}C) 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.

4-Nitrophenyl-bis(2-hydroxy-1-naphthyl)methane: Condensation of β-naphthol (6.9 gms) with 4-nitrobenzaldehyde in glacial acetic acid (50 ml) containing conc.HCl (2ml) resulted in the bisnaphthol (3.1 gm) : m.p.

>300°C; IR (nujol) 3100 cm^{-1}(br); ^1H NMR (90 MHz, DMSO-d_6) 6.9 (s, 1H,benzylic CH), 7.3-8.8 (m, 18H, ArH); Anal. Calcd. for $C_{27}H_{19}NO_4$: C, 76.95; H, 4.51; N, 3.31. Found C, 80.11; H, 4.32; N, 3.28%.

1'-(4-Nitrophenyl)-spiro{naphtho-1(2H),2'(1'H)-naphtho[2,1-b]furan}-2-one (1c) : To a solution of the above bisnaphthol (2 gm) in benzene (200 ml) was added KOBr (60 ml, prepared from 60 ml of 10% KOH and 4 gm Br_2) at 0°C with stirring. The mixture was allowed to remain at 5°C for 2 hrs and the benzene layer separated. Solvent removal followed by column chromatography (neutral alumina, benzene) gave 1c (1.1 gm); m.p.162°C(d); IR (nujol) 1690 cm^{-1}; MS ; m/e 419 (M^+,20), 402(100); Anal.Calcd. for $C_{27}H_{17}NO_4$: C, 77.32; H, 4.05; N 3.34. Found C, 77.58; H, 4.00; N, 3.4%.

Phenyl-(2-methoxy-1-naphthyl)methanol (6) : A solution of of 2-methoxy-2-naphthaldehyde (5,2 gm) in benzene– ether (40 ml,1:1) was added dropwise to phenylmagnesium bromide (prepared from 0.9 gm of bromobenzene and 0.52 gm of magnesium in 30 ml ether). The solution was stirred at 20°C for 2 hrs and then cooled to 0°C and quenched with aq.NH_4Cl. The organic layer was separated and solvent removal followed by column chromatography (silica gel, benzene) gave 6 (2.1 gm); m.p.92°C (benzene,hexane); IR 3200 cm^{-1} (br); ^1H NMR (90 MHz, $CDCl_3$) 3.8 (s, 3H,OCH_3), 4.05 (d, J = 9.0 Hz, 1H, D_2O exchangeable,OH), 6.71 (d, J = 9.0 Hz, 1H collapses to singlet on D_2O exchange,CHOH), 7.18-8.10 (m, 11H,ArH); MS ; m/e 264 (M^+, 100%). Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.81; H, 6.06. Found C,81.17; H,6.31 %.

Phenyl-{2-hydroxy-2'-methoxy-3-methyl-bis(1-naphthyl)}methane (8): To a solution of 6(0.6 gm) in ether(120 ml) was added 3-methyl-2-naphthol (7,1.8 gm) along with 3 drops of HCl. The mixture was stirred at r.t. for 24 hrs. Solvent removal followed by column chromatography (5% EtOAc in benzene) gave 8 (0.5 gm); m.p.194°C (benzene-hexane); IR 3100 cm^{-1} (br); ^1H NMR (90 MHz, $CDCl_3$) 2.26 (s, 3H,$ArCH_3$), 3.4 (s, 3H,OCH_3), 5.3 (s, 1H,benzylic CH), 7.41 – 8.0 (m, 16H, ArH). Anal. Calcd for $C_{29}H_{24}O_2$: C, 86.13; H, 5.94. Found C, 85.67; H, 6.34%.

Phenyl-{3-methyl-bis(1-hydroxy-1-naphthyl)}methane (9): To methylmagnesium iodide (prepared from 0.6 gm magnesium, and 1.4 gm of methyl iodide in 60 ml ether) was added 8(0.7 gm). The mixture was stirred at r.t for 1 hr and then ether was removed and the residue heated at 120°C for 1 hr. Quenching with NH_4Cl followed by extraction with ether yielded 9 (425 mg); m.p. > 300°C; IR(nujol) 3000 cm^{-1} (br); ^1H NMR (90 MHz, $CDCl_3$) 2.41 (s, 3H,$ArCH_3$), 4 82 (s, 1H,benzylic CH), 7.2 – 8.2 (m, 17H, ArH). Anal. Calcd. for $C_{28}H_{22}O_2$: C, 86.15 ; H, 5.64 , Found C,86.34 ; H,5.57 %.

KOBr oxidation of 9 : To a solution of bisnaphthol(0.5 gm) in benzene(50 ml) was added KOBr (prepared from 15 ml of 10% KOH and 1 gm of Br_2) dropwise at 5°C. The mixture was stirred at 5°C for 2 hrs and the benzene

layer separated. Solvent removal followed by careful column chromatography (silica gel, benzene: hexane, 2:1) gave two fractions. The first fraction was identified as 4'-methyl-spiro{naphthalene-1(2H), 2'(1'H)naphtho[2,1-b] furan}-2-one (1e,145 mg); m.p. 231°C (benzene:hexane); Anal. Calcd. for $C_{28}H_{20}O_2$; C,86.59; H,5.15. Found C,86.21 ; H,5.17%. The more polar fraction was identified as 3-methyl-spiro{naphthalene-1(2H), 2'(1'H) naphtho[2,1-b] furan}-2-one (1f,160 gm); m.p. 218°C; IR 1690 cm^{-1}; Anal. Calcd for $C_{28}H_{20}O_2$: C, 86.59 ; H,5.15. Found C,86.34 ; H, 5.02%.

Preparation of spironaphthalenones 1d & g-i : A mixture of 3-methyl-2-naphthol (1.5 gm), 2-naphthol (1.44 gm), o-anisaldehyde(1.36 gm) and conc.HCl (0.5 ml) in AcOH(10 ml) was stirred at 0°C for 2 hrs and then at r.t for 8 hrs. The white solid that separated was filtered and dried (0.7 gm).

To the above solid (0.7 gm) in benzene 100ml was added KOBr (15 ml of 10% KOH containing 1 gm Br_2) at 0°C,the mixture was stirred at 5°C for 2 hrs and the benzene layer separated. Solvent removal followed by preparative TLC (benzene-hexane, 2:1) gave (i) 1'-(2-methoxyphenyl)-3,4'-dimethyl spiro{naphthalene-1(2H), 2'(1'H)-naphtho[2,1-b]furan}-2-one (1i, 12 mg); m.p. 101°C ($CHCl_3$-hexane); IR 1660 cm^{-1}; Anal. Calcd for $C_{30}H_{24}O_3$: C, 83.33; H, 5.55. Found C, 83.0; H, 5.4%. (ii) 1'-(2'-methoxyphenyl)-3-methyl-spiro{naphthalene-1(2H),2'(1'H)-naphtho[2,1-b]furan}-2-one (1h, 110 mg); m.p. 118°C ($CHCl_3$-hexane); IR (nujol) 1670 cm^{-1}; Anal. calcd for $C_{29}H_{21}O_3$ C, 83.25; H, 5.26. Found C, 83.01; H, 5.1%. (iii) 1'-(2-methoxyphenyl)-4'-methyl-spiro{naphthalene-1(2H),2'(1'H)-naphtho[2,1-b] furan}-2-one (1g,105 mg); m.p. 147°C($CHCl_3$-hexane); IR (nujol)1670 cm^{-1}; Anal. Calcd for $C_{29}H_{21}O_3$; C, 83.25; H, 5.25. Found C, 83.21; H, 5.19%. (iv) 1'-(2-methoxyphenyl)-spiro{naphthalene-1(2H),2'(1'H)-naphtho[2,1-b] furan}-2-one (1d,170 mg); m.p. 194°C (lit[3].194-196°C).

General Procedure for reaction of spironaphthalenones with $NH_2OH.HCl$ in alcohols: $NH_2OH.HCl$ (3 mmol) in alcohol (10 ml) was added to spironaphthalenone (3 mmol) in THF (6 ml), 4 drops of conc.HCl was then added and the mixture heated under reflux for 24 hrs. Solvent was removed and the residue purified by column chromatography (silica gel, $CHCl_3$).

Ethyl 2{1'-(4-methoxyphenyl)-naphtho[2,1-b]pyrrol-2'-yl}cinnamate (4a): The reaction of spironaphthalenone 1a with $NH_2OH.HCl$ in ethanol gave 4a (410 mg); m.p.98°C ($CHCl_3$; hexane); ^{13}C NMR (22.49 MHz, $CDCl_3$) 14.18 (q, $CH_2\underline{C}H_3$), 55.19 (q,OCH_3), 60.5 (t,$O\underline{C}H_2CH_3$), 113.02(d), 113.90(d), 118.65(s), 120.53(d), 123.30(d), 123.63(d), 125.40(s), 127.17(s), 128.94(s), 129.60(d), 130.04(s), 131.15(s), 132.47(s), 135.13 (s,C-3a carbon), 143.75

(d, β -enone carbon), 158.57 (s), 166.75 (s,C=O); MS; m/e 447 (M^+, 100); Anal. Calcd. for $C_{30}H_{25}NO_3$: C, 80,53; H, 5.59; N, 3.13. Found C, 80.67; H, 5.32; N, 3.11%.

Ethyl 2-(1'-phenyl-naphtho[2,1-b]pyrrol-2'-yl)cinnamate (4b): Reaction of **1b** with $NH_2OH.HCl$ in ethanol gave **4b**(400 mg); m.p.192°C; Anal. Calcd. for $C_{29}H_{23}NO_3$: C, 8.3.4; H, 5.5; N, 3.35. Found C, 82.9; H, 5.4; N 3.15%.

Ethyl 2-{1'-(4-nitrophenyl)-naphtho[2,1-b]pyrrol-2'-yl}cinnamate (4c): The reaction of **1c** with $NH_2OH.HCl$ in ethanol gave **4c** (480 mg); m.p.104°C(d) ($CHCl_3$; hexane); MS; m/e 462 (M^+, 55), 389(50); Anal. Calcd. for $C_{29}H_{22}N_2O_4$: C, 75.32; H, 4.76; N, 6.06. Found C, 75.28; H, 4.91; N, 6.42%.

Ethyl 2-{1'-(2-methoxyphenyl)-naphtho[2,1-b]pyrrol-2'-yl}cinnamate (4d): The reaction of **1d** with $NH_2OH.HCl$ in ethanol gave **4d**(420mg); m.p.78°C; Anal. calcd. for $C_{30}H_{25}NO_3$: C, 80.5; H, 5.59; N, 3.1. Found C, 79.9; H, 5.57; N, 2.95%.

Ethyl 2-(1'-phenyl-naphtho[2,1-b]pyrrol-2'-yl)-α-methylcinnamate (4e): The reaction of spironaphthalenone **1e** with $NH_2OH.HCl$ in ethanol gave **4e** (260 mg); m.p.146°C ($CHCl_3$, hexane); Anal. Calcd. for $C_{30}H_{25}NO_2$: C, 83.52; H, 5.80; N, 3.2. Found C, 83.38; H, 5.62; N, 3.18%.

Ethyl 2-(1'-phenyl-4'-methyl-naphtho[2,1-b]pyrrol-2'-yl)cinnamate (4f): The Reaction of spironphthalenone **1f** with $NH_2OH.HCl$ in ethanol gave **4f** (280 mg); m.p.180°C ($CHCl_3$, hexane); Anal. Calcd. for $C_{30}H_{25}NO_2$: C, 83.52; H, 5.80; N 3.24. Found C, 83.41; H,5.61; N, 3.02%.

Ethyl 2-{1'-(2-methoxyphenyl)-naphtho[2,1-b]pyrrol-2'-yl}-α-methyl cinnamate (4g): Reaction of **1g** with $NH_2OH.HCl$ gave **4g**(310 mg); m.p.76°C; Anal. calcd for $C_{31}H_{27}NO_3$: C, 80.86; H, 5.85; N, 3.02. Found C, 80.4; H, 5.62; N, 2.84%.

Ethyl 2-{1'-(2-methoxyphenyl)-4'-methyl-naphtho[2,1-b]pyrrol-2'-yl} cinnamate (4h): The reaction of spironaphthalenone **1h** with $NH_2OH.HCl$ gave **4h**(320 mg); m.p. 123°C; Anal. Calcd. For $C_{31}H_{27}NO_3$: C, 80.86; H, 5.85; N, 3.03. Found C, 80.3; H, 5.71; N, 2.90%.

Methyl 2-{1'-(4-methoxyphenyl)-naphtho[2,1-b]pyrrol-2'-yl}cinnamate (4i): Reaction of spironaphthalenone **1a** with $NH_2OH.HCl$ in methanol gave **4i** (550 mg); m.p.83°C; Anal. Calcd. for $C_{29}H_{23}NO_3$: C, 80.69; H, 5.85; N, 3.23. Found C,80.48; H,5.42;N, 3.18%.

i-Propyl 2-{1'-(4-methoxyphenyl)-naphtho[2,1-b]pyrrol-2'-yl}cinnamate (4j): Reaction of **1a** with $NH_2OH.HCl$ in isopropyl alcohol gave **4j** (350 mg) ; m.p.73°C; Anal. Calcd. for $C_{31}H_{27}NO_3$: C, 80.69; H, 5.85; N, 3.30. Found C, 80.58; H, 5.64; N, 3.04%.

n-Propyl 2-{1'-(4-methoxyphenyl)-naphtho[2,1-b]pyrrol-2'-yl}cinnamate (4k): Reaction of spironaphthalenone **1a** with $NH_2OH.HCl$ in n-propyl alcohol gave

4k (400 mg); m.p.78°C; Anal. Calcd. for $C_{31}H_{27}NO_3$: C, 80.69; H, 5.85; N, 3.03. Found C, 80.42; H, 5.71; N, 2.98%.

n-Butyl 2-{1'-(4-methoxyphenyl)-naphtho[2,1-b]pyrrol-2'-yl}cinnamate (41): Reaction of **1a** with $NH_2OH.HCl$ in n-butyl alcohol gave **41**(300 mg); m.p.81°C; Anal. Calcd. for $C_{32}H_{29}NO_3$: C, 80.84; H, 6.10; N, 2.94. Found C, 80.62; H, 6.10; N, 2.58%.

Benzyl 2-{1'-(4-methoxyphenyl)-naphtho[2,1-b]pyrrol-2'-yl}cinnamate (4m): Reaction of **1a** with benzyl alcohol gave **4m**(280 mg);m.p.94°C; Anal.Calcd.for $C_{34}H_{31}NO_3$: C,81.43; H,6.18; N,2.71. Found C, 81.03; H, 6.08; N, 2.71%.

ACKNOWLEDGMENTS

We thank Dr. A. Sarkar, NCL, PUNE for a few analyses reported herein. Financial assistance from Council of Scientific and Industrial Research and Indian National Science Academy, New Delhi is gratefully acknowledged.

REFERENCES AND NOTES

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4. β -phenyl spironaphthalenones exhibit the signal for the α -enone proton in ^1H NMR around δ 6.1 ,while the corresponding α -phenyl isomers show a shielded signal around δ 5.4 for the same proton (see reference 3. for assignments).
5. TLC ($CHCl_3$) of the crude product showed the presence of only one product.HPLC also indicated the presence of only **4e** (retention time 4 min on a Waters Microbondapack C18 column with $CHCl_3$ as the eluent); the isomeric ester **4f** had a retention time of 4.25 min on the same column.^1H NMR spectra of the crude and the purified compound were identical.