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Oxidation of Spiroketones with DDQ - Synthesis of Tropone Derivatives and DDHQ Diesters

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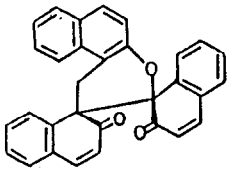
Abstract : Oxidation of spiroketones **3a-f** with DDQ in dry benzene gave tropone derivatives **4a-f** and DDHQ esters **5a-f** (cis-cis isomer **6a-f**, trans-trans isomer **7a-f**). While the aryl substituted spirokeone **17a** gave a 2:1 mixture of **19a** and the corresponding trans-trans isomer, the aryl substituted spiroketones **17b-d** gave exclusively cis-cis isomers **19b-d**. Heating acid chloride of acid **9c** with DDHQ resulted in compounds **4a** and **7a**, thus confirming the structures assigned. Mechanism of formation of these compounds has been rationalised. A detailed study of 2D ^{1}H-^{1}H COSY, ^{1}H-^{13}C COSY, HMBC and 2D NOESY of compound **7d** led to complete assignment of ^{1}H and ^{13}C NMR signals and its solution conformation.

Cur studies[2a-c] on the oxidation of naphthols and other substrates with high potential quinones, especially 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ), have led to the isolation and characterisation of compounds having novel structures (eg.1 & 2). In a preliminary communication[2d], we have reported the formation of tropone derivatives **4** in the reaction of spiroketones 3 with DDQ. In this paper, we discuss this reaction in detail, the characterisation of the other product formed and their syntheses.



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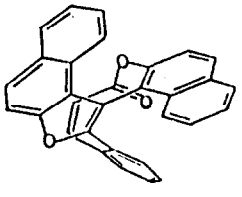

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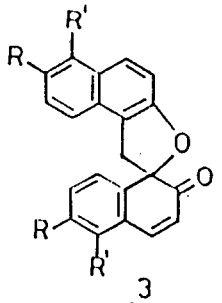
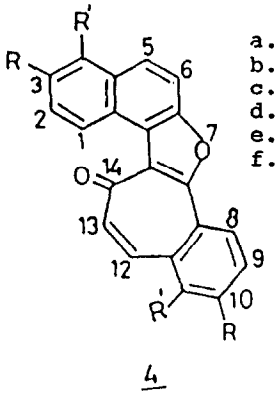


3

a. R = R' = H
b. R = OCH_3; R' = H
c. R = Br; R' = H
d. R = t-bu; R' = H
e. R = ; R' = H
f. R = H; R' = CH_3
g. R = CN, R' = H
h. R = H; R' = NO_2

Oxidation of 3a with DDQ was carried out by refluxing in benzene for 8 hrs.After the precipitated 2,3-dichloro-5,6-dicyano-hydroquinone (DDHQ)[3] was filtered, the filtrate gave on careful separation (column chromatography, preparative TLC) two compounds designated A and B. Compound A showed an IR frequency at 1628 cm^{-1} and analysed for $C_{21}H_{10}O_2$ (M^+ m/e 296) indicating it to be a dehydrogenated product. The significant ^1H NMR signals are the four one proton doublets at δ 7.05 (J=12.0 Hz), 7.48 (J=12.0 Hz), 8.68 (J=8.1 Hz) and 9.58 (J=9.4 Hz). Important signals in ^{13}C NMR are singlets at δ 183.7, 156.4, 152.8 and doublets at δ 111.3 and 137.4.

Hydrogenation of this compound with 10% Pd-C resulted in a dihydro derivative (M^+ m/e 298) exhibiting carbonyl stretching frequency at 1660 cm^{-1} indicative of loss of conjugation. The presence of a symmetrical multiplet (4 H) in the upfield region (δ 3.15) in its pmr spectrum (270 MHz) corroborated this fact. ^{13}C NMR confirmed the presence of a carbonyl group (δ 196.7) and two methylene groups (δ 29.7 and 44.2 as triplets) which was further supported by $NaBH_4$ reduction to the corresponding alcohol. On the basis of this data, structure 4a was assigned to this compound which was further confirmed by X-ray crystal structure analysis[2d]. The perspective view of this molecule is indicated in Fig.1.



a. R = R' = H
b. R = OCH_3; R' = H
c. R = Br; R' = H
d. R = t-bu; R' = H
e. R = ; R' = H
f. R = H; R' = CH_3

4

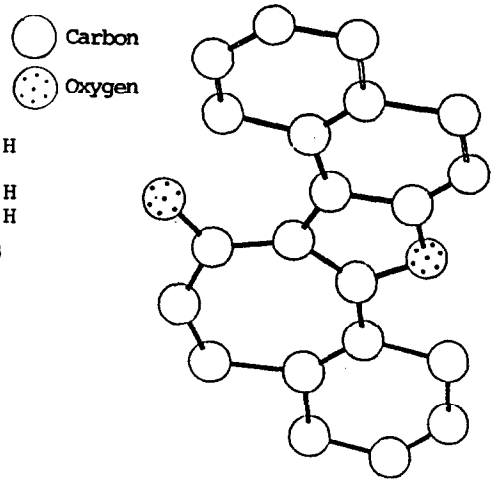
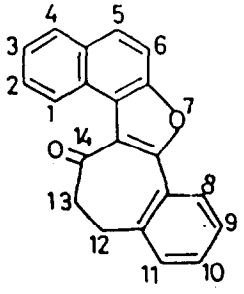


Fig.1 A perspective view of the molecule 4a

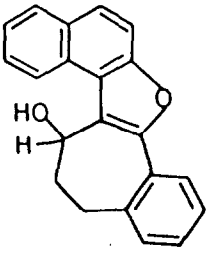
The significant spectral characteristics of this compound could be explained in terms of structure 4a. The low carbonyl stretching frequency (1628 cm^{-1}) in the IR spectrum is characteristic of tropone carbonyl[3]. The two mutually coupled doublets appearing at δ 7.05 (J=12.0Hz) and 7.48 (J=12.0 Hz) in ^1H NMR spectrum are respectively due to the C_{13} and C_{12} vinylic protons of the enone system in tropone. Th two doublets at δ 8.68

and 9.58 account for the highly deshielded protons at C_8 and C_1 respectively. This assignment is based on a careful analysis of the spectrum which showed meta coupling of the two doublets respectively with protons at C_{13} and C_3 which is absent in substituted tropone drivatives (vide infra). The singlets at δ 183.7, 156.4 and 152.8 in ^{13}C NMR obviously arise respectively from the carbonyl carbon and the two α - carbons of the furan ring. The doublets at δ11.3 and 137.4 are due to the α and β carbons of the enone system. The highly intense fragment at m/e 268 in the mass spectrum corresponds to loss of carbonyl resulting in a stable dinaphthofuran ion[4]. Formation of stable ions by ready loss of carbon monoxide is a characteristic feature in the mass spectra of tropones and benztropones[5].

The dihydro derivative and its borohydride reduction product could therefore be represented by structures **8a** and **8b** respectively.



8a



8b

The intense m/e ion at 296 in the mass spectrum of compound B was earlier erroneously identified[2d] as the molecular ion, as no other ions were seen upto 500 mass units. Subsequent careful mass spectral studies indicated the occurence of weaker ions at m/e 524, 558 and 820. A chemical ionization mass spectrum of compound B showed the presence of an ion at m/e 821, suggesting the molecular weight to be 820. Careful separation of compound B resulted in two almost pure isomers B_1 and B_2.Both these isomers showed IR bands at 1756 cm^{-1}(strong) and 2230 cm^{-1} (very weak). While compound B_1 showed in its ^1H NMR signals at δ 6.2 (d, J=12.0 Hz,1H),7.34-7.63(m,6H),7.72(m,2H),7.95(d,J=8.0Hz,1H),7.99(d,J=8.0Hz ,1H),8.17(d,J=8.0Hz,1H),compound B_2 showed ^1H NMR signals at δ 6.71 (d, J=16.0 Hz, 1H), 7.38 (s,1H), 7.46-7.79 (m,8H), 7.96 (ddd,1H), 8.23 (d, J=8.0 Hz, 1H), 8.63 (d, J=16.0 Hz, 1H). The low coupling constant (J=12.0 Hz)of the doublet at δ 6.2 in compound B_1 suggested it to be a *cis* isomer,[11] while the high coupling constant (J=16 Hz) of the doublet at δ 6.7 in compound B_2 indicated it to be a *trans* isomer. Compound B_1 on standing for a long time is transformed to compound B_2.

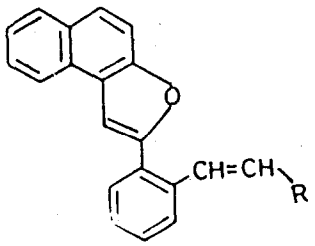
Compound B_1 on reduction with $NaBH_4$ in dry THF at room temperature gave a hydroxy compound [IR 3300-3400 cm^{-1}] with m/e 300. ^1H NMR spectrum of this compound showed a triplet (J=6.3 Hz) at δ 4.9 (D_2O exchangeable) integrating for one proton (-OH), an unsymmetrical triplet at δ 4.17 (J=6.3 Hz, 2H) due to methylene protons. A one proton triplet of doublet at δ 6.04 (J=10.0 and 6.3 Hz) and a doublet at δ 6.83 (J=10.0 Hz, 1H), are also seen. The presence of $-CH=CH-CH_2OH$ unit was inferred from double irradiation experiments. Acetylation with Ac_2O/Py gave a mono acetyl derivative (IR 1740 cm^{-1}) with m/e 343. ^1H NMR signals at δ 2.0 (s, 3H, $COCH_3$), 4.84 (d with small allylic coupling, J=8.0 Hz,2H), 6.02 (triplet of doublet, J=12.0 Hz and 8.0 Hz,1H), 6.98 (d with small allylic coupling, J=12.0 Hz, 1H) supported the presence of $-CH=CH-CH_2OAc$ moiety.

The borohydride reduction product on hydrogenation with 10% Pd-C in ethyl acetate gave a dihydro alcohol (IR 3400 cm^{-1}) with m/e 302. The ^1H NMR signals at δ 1.56-1.94 (m,2H), 2.45 (broad peak, 1H, D_2O exchangeable) 2.9 (t, J=7.5 Hz, 2H) and 3.54 (t, J=6.0 Hz,2H) confirmed the presence of $-CH_2CH_2CH_2OH$ moiety in the molecule.

Oxidation of the allylic alcohol with Pcc gave the known[6] aldehyde **9d** and hence, structure **9a** could be assigned to this alcohol. The allylic acetate and the dihydroalcohol could therefore be represented by structures **9b** and **10a** respectively. The presence of CH_2OH in this allylic alcohol suggested the presence of an ester rather than a lactone function in compound B_1. $LiAlH_4$ reduction of compound B_1 directly gave the alcohol **10a** by 1,4-reduction.

To confirm the presence of an ester moiety, compound B_1 was saponified by refluxing with 10% NaOH when an acid [IR 1700 cm^{-1}, M^+ m/e 314], identical with the acid **9c** formed by Ag_2O oxidation of the known aldehyde **9d** , was obtained

a. R = CH_2OH
b. R = CH_2OAc
c. R = COOH
d. R = CHO
e. R = COOMe



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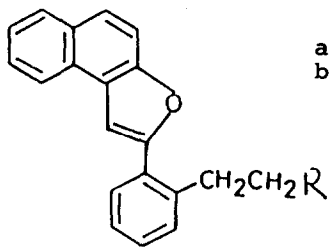
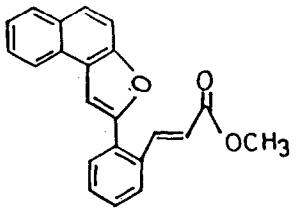


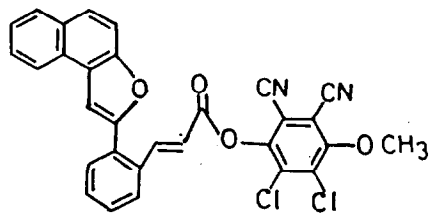
10

a. R = CH_2OH
b. R = COOH

Trans esterification of compound B_1 with dry MeOH resulted in two compounds. The less polar compound [IR 1740 cm^{-1}, ^1H NMR δ3.8 (s, 3H, OCH_3), 6.45 (d, J=16.0 Hz, 1H), 7.2-8.2 (m,11H), 8.3 (d, J=16.0 Hz, 1H)] *was identified as the methyl ester 11. The more polar compound was treated with CH_2N_2 to give, after purification, a compound with spectral data IR* 2250,1760,1630 cm^{-1}; ^1H NMR 4.1(s, 3H, OCH_3), 6.65 (d, J=16.0 Hz, 1H), 7.33 (s, 1H), 7.3-8.25 (m, 10H), 8.6 (d, J=16.0 Hz, 1H). This could be assigned the structure 12.

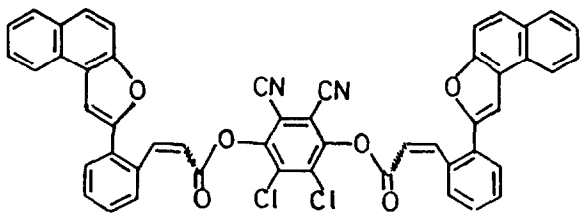


11



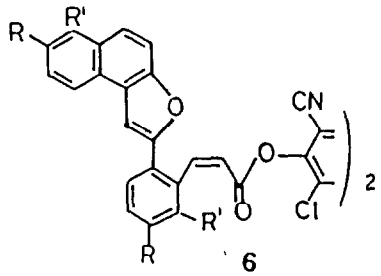
12

Based on the above chemical transformations and spectral data, the originally isolated compound B was tentatively assigned structure 5 [mixture of cis-cis (compoud B_1) and trans-trans (compound B_2) isomers].



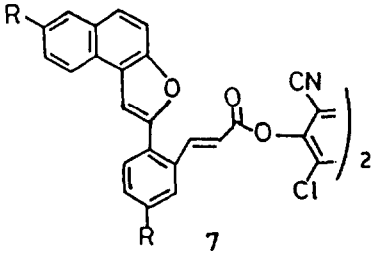
5

It is apparent that the initially formed cis isomer **6a** on standing for a long period is transformed to the more stable trans isomer **7a**.



6

a. R = R'=H
b. R = OCH_3; R'=H
c. R = Br; R'=H
d. R = t-bu; R'=H
e. R = R'=H
f. R = H; R'=CH_3



7

a. R = H
c. R = Br.
d. R = t-bu

When similar oxidation of spiroketones **3b-f** was carried out with DDQ, sets of two products **4b-f** and **6b-f** were respectively isolated. Only in the case of **3c** and **3d**,the trans compound **7c** and **7d** were obtained. Spiroketones **3g-h** failed to undergo any oxidation.

The tert.butyl compound **7d**, isolated in very pure state, was highly soluble in $CDCl_3$. Hence, a detailed ^1H & ^{13}C NMR analyses Which resulted in complete assignment of proton and carbon spectra could be undertaken.The ^1H NMR spectrum of **7d** at 400 MHz displayed 11 aromatic/olefinic protons (see Table 1). The ^1H NMR spin systems were assigned by using 2D ^1H-^1H COSY. A singlet at δ7.33 assigned to H-1 and a pair of doublets (J=15.8Hz each) at 6.73 and 8.63 assigned to H-17 and H-16 respectively were found to be the most striking signals in the ^1H NMR spectrum. ^{13}C NMR spectrum revealed 25 aromatic/olefinic signals. APT spectrum of **7d** revealed 11 aromatic/olefinic methine carbons and the remaining 14 as quaternaries. The one bond proton carbon attachment was established by a 2D ^1H-^{13}C COSY spectroscopy[7] and the data is summerized in Table 1. Due to the presence of 14 out of 25 carbons as quaternary centers, the assignment became very challenging. Most of these problems were resolved by using ^1H detected ^1H-^{13}C correlation spectroscopy (HMBC)[8]. The HMBC experiment (optimized for J_{CH}=7Hz) revealed many 2 and 3 bond correlations which are summarized in Table 1. Most important correlations were as follows:H-1 (δ7.33) gave strong 3 bond correlations to C-3a (δ152.89), C-9a (δ125.61) and a 2 bond correlation to C-9b (δ 124.15). Similarly, C-9b showed 3 bond correlations with H-4 and H-9; C-9a exhibited similar correlations with H-5, H-8 and H-6 and C-5a showed correlations with H-4. The lower half of the molecule also showed similar HMBC correlations. For example, both α and β hydrogens (H-17 and H-16) of the α, β- unsaturated ester showed correlations with ester

carbonyl. The attachment of C-16 to aromatic ring at C-15 was evident from the correlations of H-17 to C-15. Based on these and other HMBC correlations (see Table 1 and Fig.2) complete ^{1}H and ^{13}C NMR spectrum was assigned which was consistent with the proposed structure **7d**. Unfortunately, due to absence of any protons 2 to 3 bonds away from C-20, C-21 and C-22, these could not be connected to other part of the molecule. Due to some unforseen reason, under the experimental conditions employed for HMBC experiment, no correlations for C-2 and C-10 were observed. Due to lack of digital resolution in HMBC, poorly resolved carbon signals at 152.89 and 152.81 could not be independently assigned to C-3a or C-13. However, this did not have detrimental effect in confirming the structure. Solution conformation of **7d** was determined by the application of 2D NOESY optimized for 500 msec mixing time. NOE correlations of H-1 with H-16 and H-17 with H-14 demonstrate that the solution conformation of **7d** should be as drawn (Fig.3). In this conformation, H-1 and the substituted naphthyl ring are located on top of the α,β-unsaturated ester.

Table 1: High Resolution ^{1}H and ^{13}C NMR Assignment of 7d in $CDCl_3$ solutions.

Position	13C	1H	HMBC	NOE
1	106.56	7.33,s	----	H-1→H-9, H-16
2	147.58[a]	-----	----	----
3a	152.89[b]	-----	C-3a →H-1	----
4	128.71	7.68,d,8.8	----	H-4→ H-5
5	126.16	7.74,d,8.8	----	H-5→ H-4, H-6
5a	130.39	-----	C-5a →H-4, 9	----
6	124.03	7.89,d,1.6	C-6 → H-8	H-6→ H-5
7	152.04	-----	C-7 →H-6	----
8	125.44	7.73,dd,8.6,1.9	----	H-8→ H-9
9	123.40	8.17,d,8.8	----	H-9→ H-1
9a	125.61	-----	C-9a→ H-1,5,6,8,9	----
9b	124.15	-----	C-9b→H-1,4,9	----
10	128.97	-----	----	----
11	128.65	7.92,d,8.3	----	H-11→ H-12
12	112.08	7.64,dd,8.3.1.8	----	H-12→ H-11
13	152.81[b]	-----	C-13→H-11	----
14	124.73	7.79,d,1.8	----	H-14→ H-17
15	131.08	-----	C-15→ H-11,14,17	----
16	150.11	8.63,d,15.8	----	H-16→ H-1
17	115.6	6.73,d,15.8	----	H-17→ H-14
18	162.16	-----	C-18→ H-16,17	----
20	149.04[a]	-----	----	----
21	135.54	-----	----	----
22	110.97	-----	----	----

[a,b] in vertical column may be interchanged. They were either not correlated to any H or beyond the limit of digital resolution in HMBC. ***Tert*-butyl group**: 13C: 35.00, 29.75 (qC); 31.44,31.25 (CH_3). CN: 110.88.

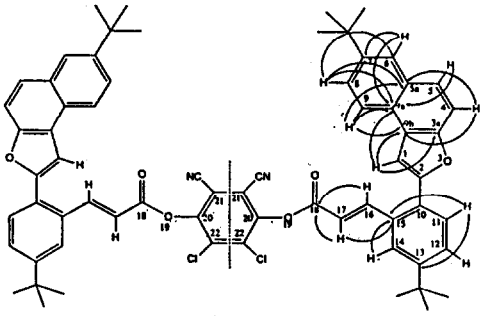


Fig.2 HMBC Correlations of 7d

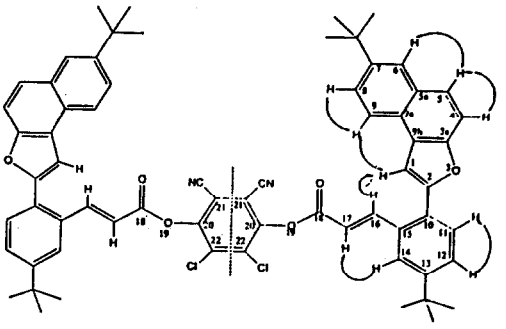
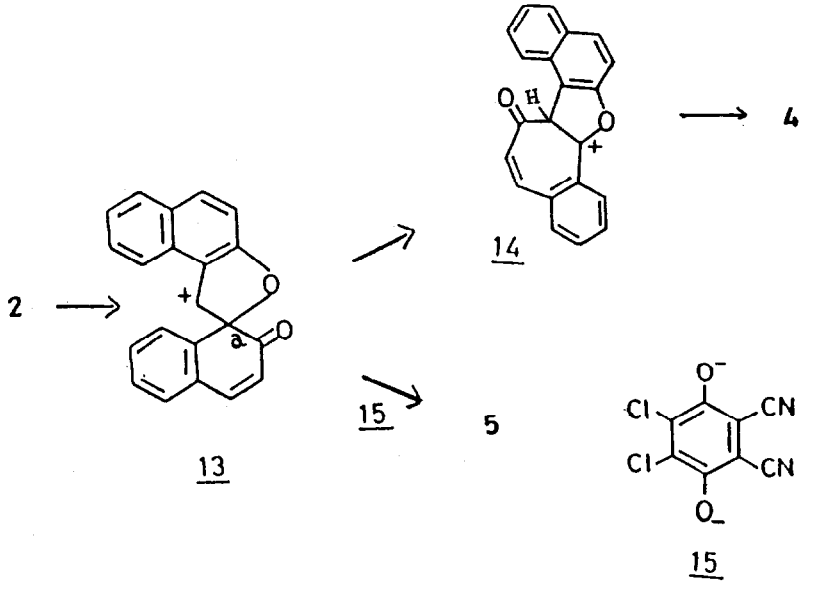


Fig.3 NOESY Correlations of 7d

Mechanism of formation of compounds 4 and 5

Formation of compounds **4** and **5** can be visualised through the intermediate [13] formed by removal of a hydrogen from **2**. Migration of bond 'a' followed by loss of proton results in the formation of **4**. Nucleophilic addition of hydroquinone dianion [15] to two units of [13] followed by breaking of bond 'a' gives the diester **5**.

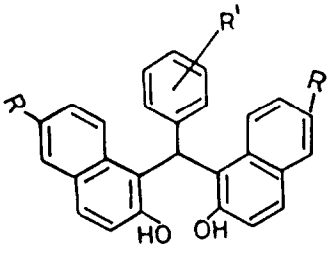


Scheme 1

Oxidation of aryl substituted spiroketones

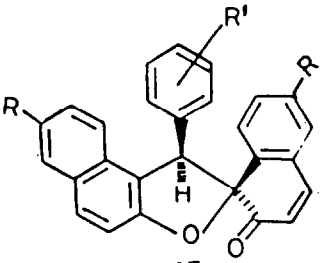
As seen from the foregoing mechanism, formation of tropone derivative (4) requires the presence of two hydrogens in the spironaphthalenone **3a**. DDQ oxidation of compounds **17a-e** in which one of the benzylic hydrogens has been replaced by aryl group should only result in the formation of compounds of the type **5**. With this in view, we have undertaken the oxidation studies of such compounds.

Oxidation of bis naphthols **16a-b** with KOBr following the general procedure of Dean and Coworker[9] gave mainly the respective β-aryl spiroketones **17** with traces of α-isomer **18** which could be separated by crystallisation.



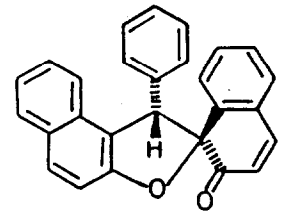
16

a. R = H; R' = 2,4-$(OCH_3)_2$
b. R = Br; R' = 2-OCH_3



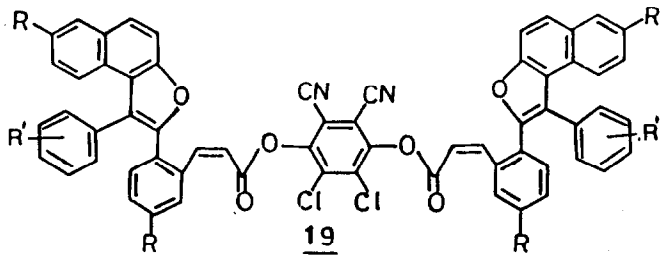
17

a. R = H; R'=H
b. R = H; R'=2-OCH_3
c. R = H; R'=2,4-$(OCH_3)_2$
d. R = Br; R'=2-OCH_3
e. R = H; R'=m-NO_2



18

Oxidation of compound **17a**[9] with DDQ (1:1.1 mol) in refluxing benzene was sluggish and even after three days, TLC showed the presence of starting material along with one more new product.The precipitated DDHQ was filtered off and the product was purified by column chromatography [silica gel,$CHCl_3$-hexane (1:1)]. The less polar product was identified as diester **19a** [I.R 2230,1760 cm^{-1}] from its spectral data along with its corresponding <u>trans</u> - <u>trans</u> isomer.



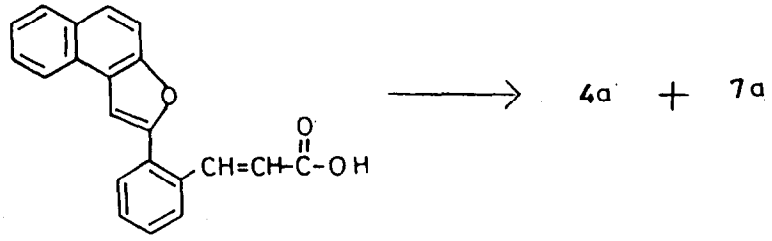
19

a. R = H; R' = H
b. R = H; R' = 2-OCH_3
c. R = H; R' = 2,4-$(OCH_3)_2$
d. R = Br; R' = 2-OCH_3
e. R = H; R' = m-NO_2

Oxidation of **17b-d** with DDQ was very facile.The reaction was complete within 12 hrs. and after purificatation gave good yields of the diesters **19b-c**. β-3-Nitrophenyl spironaphthalenone[9] **17e** failed to undergo any oxidation. High refluxing temperatures and even longer reaction time (7 days) also failed to induce any reaction. It is surprising that the aryl substitution at C-1 results in the exclusive formation of cis-cis diester (**19b-d**,except **19a**), unlike the unsubstituted spiroketones **3a-f**. It is obvious from the conformational studies of **7d** (NOESY,vide-supra) that the bulky phenyl substitution at C-1 does not favour the isomerisation of the initially formed cis-cis conformer **19b-d**. The observed differences in the behaviour of compounds with electron withdrawing and electron releasing groups in the phenyl ring on the course of the reaction (Scheme 1) is conceivable. Undoubtedly, presence of methoxy group on phenyl ring stabilizes the intermediate carbonium ion [13], thus facilitating the reaction.

Synthesis of compounds 4a and 7a

Structure assigned to diester **7a** was confirmed by an independent synthesis. The acid chloride obtained from acid **9c**, on heating with DDHQ gave two compounds, which were separated by preparative TLC. The less polar compound (m/e 820) with IR frequency at 1760 cm^{-1} was identified as the trans, trans diester **7a** mentioned above, while the more polar one was the expected tropone **4a** [Scheme 2].



9c

Scheme 2

This is the first report of the formation of DDHQ esters in oxidations using DDQ. To the best of our knowledge, DDHQ esters are also not reported in literature. Chemistry of such esters could be of interest and we are presently looking into this aspect.

EXPERIMENTAL SECTION

All melting points are uncorrected, IR (ν_{max}) spectra were recorded on Perkin Elmer Model 781 spectrometer. NMR spectra were recorded on a JEOL FX-90Q, 22.49 MHz (^{13}C) are a Buker WH-270, 67.87 MHz, (^{13}C) spectrometers 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 carriedout using silica gel. Column chromatography was carried out using silica-gel. All organic extracts were dried over anhydrous Na_2SO_4.

Preparation of bisnaphthols

Preparation of 16a : 2,4 dimethoxy - benzaldehyde (6 gm) and 2-naphthol (11.6 gm) were taken in acetic acid and cooled to 0°C. Conc.HCl was added carefully and the mixture was stirred for 12 hrs. The solid separated was filtered, washed with plenty of water, dried at room temperature and crystallised from acetic acid to give **16a** (13 gm, 77%) m.p. 206-8°C ; IR(nujol) 3320 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) 3.7 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 5.95 (bs, 2H, D_2O exchangeable) 6.75 (s, 1H), 6.95 (d with further coupling, J = 9.0 Hz, 2H), 7.4 (d, J = 7.0 Hz, 1H), 7.2 - 7.45 (m, 5H), 7.65 - 7.90 (m, 7H). Analysis calcd. for $C_{29}H_{24}O_4$ C, 79.8; H, 5.5. Found : C, 79.5; H, 5.4%.

Preparation of 16b : Similar condensation of o-anisaldehyde (3.6 gm) and 6-bromo-2-naphthol (11.0 gm) gave the bis naphthol **16b** (10 g, 63%) m.p. 195-7°C; IR (nujol) 3325 cm^{-1}; ^1H NMR (90 MHz, DMSO-D_6) 3.3 (s, 3H, OCH_3), 6.3-8.1 (m, 15H), 9.4 (bs, 2H, D_2O exchangeable). Analysis calcd. for $C_{28}H_{20}O_3Br_2$ C, 59.6; H, 3.55. Found C, 59.3; H, 3.52%.

Oxidation of bisnaphthols with KOBr :

a. Oxidation of 16a : To a solution of bis naphthol **16a** (4.0 gm) in benzene (400 ml) at 0°, bromine (8 gm) in 10% KOH (120 Ml) was added gradually during 30 min. and the mixture was stirred at the same temp. for another 1 hr. The benzene layer was separated, washed with water and dried. Removal of solvent followed by purification by column chromatography [neutral alumina, benzene] gave **17b** (3.2 gm, 80%) m.p 132°C (Chloroform-pet.ether); IR (nujol) 1689, 1635 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) 3.5 (bs, 3H, OCH_3), 3.65 (s, 3H, OCH_3), 5.3 (s, 1H, methine), 6.25 (d, J = 10.0 Hz, 1H), 7.0-7.6 (m, 13H), 7.9 (d, J = 10.0 Hz, 1H); MS m/e (relative intensity) 434 (M^+, 100), 417(90), 403 60), 291(45), 189(25); HRMS Calcd. for $C_{29}H_{22}O_4$ 434.1581, found 434.1510.

b. Oxidation of 16b : Similar oxidation of **16b** (5 g) in benzene (400 ml) with bromide (7 gm) in 10% KOH (105 ml) gave 17C (3.5 gm, 70%), m.p. 196-8° (chloroform-pet.ether);IR (nujol) 1683, 1630 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) 3.6 (s, 3H, OCH_3), 5.84 (s, 1H, methine), 6.2-6.65 (m, 5H),6.90 - 7.15 (m, 4H), 7.30-7.44 (m, 2H), 7.50 (s, 1H), 7.80 (d, J = 7.0 Hz, 1H), 8.04 (d, J = 2.0 Hz, 1H); MS m/e 564, 562, 560 (M^+, 7, 14, 7), 547, 545, 543 (M-17, 8, 16, 8), 533, 531, 529 (55, 100, 50). HRMS calcd. for $C_{28}H_{18}O_3Br_2$ 559.9623, found 559.9660.

Oxidation of spiroketone (3a-f) with DDQ :

General Procedure : A solution of spiroketone (1 mmol) and DDQ (1.1 mmol) in dry benzene (50 ml) was refluxed for 24 hrs. The precipitated DDHQ was filtered off, the filtrate concentrated and the residue obtained was chromatographed [silica gel]. Elution with chloroform gave yellow compounds were further purified by preparative tlc [chloroform-pet.ether 3:1].

Oxidation of 3a : gave **4a** (more polar, 120 Mg, 40%) m.p.180° (chloroform); IR(nujol) 1628 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) 7.05 (d, J = 12.0 Hz, 1H), 7.48 (d, J = 12.0 Hz, 1H), 7.52-7.76 (m, 6H), 7.9-7.97 (m,2H), 8.68 (d, J = 8.1 Hz, 1H), 9.58 [d, J = 9.4 Hz, 1H); MS m/e 296(M^+). Analysis calcd. for $C_{21}H_{12}O_2$ C, 85.12; H,4.08. Found C, 85.23;H, 4.15%: **6a** (less polar, 65 Mg, 15%) m.p. 219-21° IR (nujol) 1760 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) 6.2 (d, J = 12.0 Hz, 1H), 7.34-7.63 (m, 7H), 7.72 (m, 2H),7.95 (d,J=8.0Hz,1H), 7.99 (d, J = 8.0 Hz, 1H), 8.17 (d, J = 8.0 Hz,1H); MS m/e 820 (M^+,1), 524(50), 297(44), 296(40), 268(100), 239(56). Analysis calcd. for $C_{50}H_{26}O_6N_2Cl_2$ C, 73.08; H, 3.16; Found C,72.7; H, 3.10.and **7a** (less polar, 70 mg, 16%), m.p.135-7°C; IR(nujol) 2230, 1760, 1630 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) 6.71 (d, J = 16.0 Hz, 1H), 7.38 (s, 1H), 7.46-7.79 (m, 8H), 7.96 (ddd, 1H), 8.23 (d, J = 8.0 Hz, 1H), 8.63 (d, J = 16.0 Hz, 1H), MS m/e 820 (M^+,1), 524(50), 297(42), 296(40), 268(100), 239(56). Analysis calcd.for $C_{50}H_{26}O_6N_2Cl_2$ C,73.08;H,3.16.Found C,72.6; H,3.0%.

Oxidation of 3b : gave **4b** (more polar, 165 mg, 46%) m.p.232-4°C (chloroform); IR (nujol) 1628 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) 3.96 (s, 3H, OMe), 3.96 (s, 3H, OMe), 7.05 (d, J = 12.7 Hz, 1H), 7.16-7.36 (m, 4H), 7.42 (d, J = 12.7 Hz, 1H), 7.71 (d, J = 8.9 Hz, 1H), 7.82 (d, J = 8.9 Hz, 1H), 8.64 (d, J = 8.9 Hz, 1H), 9.6 (d, J = 8.9 Hz, 1H); MS m/e 354(M^+). Analysis calcd. for $C_{23}H_{16}O_4$ C, 77.51; H, 4.53. Found C, 77.40; H, 4.38%. **6b** (less polar,120mg) m.p.196°C,IR (nujol) 1760 cm^{-1}, ^1H NMR (270 MHz, DMSO-D_6) 3.87 (s, 3H, OCH_3), 3.96 (s, 3H, OCH_3), 6.47 (d, J = 12.0 Hz, 1H), 7.07 (metacoupled doublet, J = 9.0 Hz, 1H), 7.18 (meta coupled singlet, 1H), 7.28 (d, J = 8.0 Hz, 1H), 7.36 (s, 1H), 7.65 (s, 1H), 7.76 (meta coupled doublet, J = 8.0 Hz, 1H), 7.9 (d, J = 8.0 Hz, 1H), 8.1 (d, J = 9.0 Hz, 1H) Analysis calcd. for $C_{54}H_{34}O_{10}N_2Cl_2$ C, 68.86; H, 3.61; Found C, 68.5; H, 3.55%.

Oxidation of 3c: gave **4c** (more polar, 170 Mg, 37%) m.p. > 300°C, IR (nujol) 1628 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$), 7.08 (d, J = 14.0 Hz, 1H), 7.8 (d, J = 14.0 Hz, 1H), 7.84 (d, J = 13.0 Hz, 1H), 8.05 - 8.44 (m, 5H), 8.6 (d, J = 7.0 Hz, 1H), 9.47 (d, J = 8.0 Hz, 1H); MS m/e 454(M^+). Analysis calcd.for $C_{21}H_{10}O_2Br_2$ C, 55.55; H, 2.23. Found C, 55.62; H, 2.28%. and 4:1 mixture of **6c** and **7c**, m.p. 238-9°C, IR (nujol) 1760 cm^{-1}, ^1H NMR (270 MHz, DMSO-D_6) 6.24 (d, J = 10.0 Hz, 1H), 6.6 (d, J = 12.0 hz, 1H), 7.35 (d, J = 8.0 Hz), 7.61 - 7.94 (m), 8.15 (d, J = 12.0 Hz), 8.36 - 8.41 (m) (aromatic, 32H). Anal. Calcd. for $C_{50}H_{22}O_6N_2Cl_2Br_4$ C, 52.77; H, 1.93, Found C, 52.3, H, 1.80%.

Oxidation of 3d; gave **4d** (more polar, 150 mg, 37%), m.p.294-6°C; IR (nujol) 1628 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$), 1.37 (s, 9H, t-bu), 1.43 (s, 9H, t-bu), 7.0 (d, J = 12.0 Hz, 1H), 7.4 (d, J = 12.0 Hz, 1H), 7.6-7.95 (m, 6H), 8.53 (d, J = 8.0 Hz, 1H), 9.54 (d, J = 9.0 Hz, 1H); MS m/e 408(M^+). Analysis calcd. for $C_{29}H_{28}O_2$ C, 85.26; H, 6.91. Found C, 85.39; H, 7.05%. **6d** (less polar, 120 mg, 23%) m.p.156-8°C, IR (nujol) 1760 cm^{-1}, ^1H NMR (270 MHz, $CDCl_3$), 1.29 (s, 9H), 1.40 (s, 9H), 6.34 (d, J = 10.0 Hz, 1H), 7.13 (s, 1H), 7.45 (d, J = 7.0 Hz, 1H), 7.55-7.70 (m, 5H), 7.75-7.85 (m, 2H), 8.08 (d, J = 10.0 Hz, 1H). Analysis calcd. for $C_{66}H_{58}O_6N_2Cl_2$ C, 75.78; H, 5.55; Found C, 75.34; H, 5.90%.**7d** (less polar, 80 mg, 15%) m.p. IR (nujol) : 1757 cm^{-1}, ^1H NMR (400 MHz, $CDCl_3$), 6.73 (d, J = 15.8 Hz, 1H) 7.33 (s, 1H), 7.64 (dd, J = 8.3 and 1.8 Hz, 1H), 7.68 9d, J = 8.8 Hz, 1H), 7.73 (dd, J = 8.6 Hz and 1.9 Hz, 1H), 7.74 (d, J = 8.8 Hz, 1H), 7.79 (d, J = 1.8 Hz, 1H), 7.89 (d, J = 1.6 Hz, 1H), 7.92 (d, J = 8.3 Hz, 1H), 8.17 (d, J = 8.8 Hz, 1H), 8.63 (d, J = 15.8 Hz, 1H). Analysis calcd. for $C_{66}H_{58}O_6N_2Cl_2$ C, 75.78, H, 5.55. Found C, 75.62; H, 5.51%.

Oxidation of 3e; gave **4e** (more plar, 165 mg, 33.6%) m.p. 272-4°C; IR(nujol) 1628 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) 1.28 (s, 6H, CH_3x2), 1.2-2.4 (m, 20H), 7.05 (d, J = 13.0 Hz, 1H), 7.53 (d, J = 13.0 Hz, 1H), 7.70-7.97 (m, 6H), 8.67 (d, J = 9.0 Hz, 1H), 9.56 (d, J = 9.0 Hz, 1H). Analysis

calcd. for $C_{37}H_{36}O_2$ C, 86.02, H, 7.43. Found C, 85.8; H, 7.32%.**6e** (less polar, 205 mg, 34%) m.p. 145°, IR (nujol) 1755 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) 1.15 (s,3H), 1.2 (s, 3H), 1.1-2.3 (m, 20H), 6.35 (d, J = 12.0 Hz, 1H), 7.15-7.9 (m, 9H), 8.1 (d, J = 8.0 Hz, 1H). Analysis calcd. for $C_{78}H_{74}O_6N_2Cl_2$ C, 77.6; H, 6.14. Found C, 77.1; H, 6.0%.

Oxidation of 3f[10] ; gave 4f (more polar, 100 mg, 30%) m.p.180°C ($CHCl_3$); IR(nujol) 1629 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) 2.54 (s, 3H, CH_3), 2.69 (s, 3H, CH_3), 7.07 (d, J = 13.0 Hz, 1H), 7.43 - 7.85 (m, 6H), 8.15 (d, J = 9.0 Hz, 1H), 8.58 (d, J = 7.5 Hz, 1H), 9.39 (d, J = 7.5 Hz, 1H). MS m/e 324 (M^+,100), 296 (M-28, 85). Analysis calcd. for $C_{23}H_{16}O_2$ C, 85.15; H, 4.93. Found C, 84.80; H, 4.81%.**6f** (less polar, 150 mg, 34%) 2.67 (s, 3H, CH_3), 2.74 (s, 3H, CH_3), 6.50 (d, J = 11.4 Hz, 1H), 6.91 (s, 1H), 7.15 - 8.05 (m, 9H). Analysis calcd. for $C_{54}H_{34}O_6N_2Cl_2$ C, 73.90; H, 3.88. Found C, 73.73; H, 3.80%.

Oxidation of 17a[9] : gave 2:1 mixture of **19a** and its corresponding trans - trans isomer (less polar,160 mg, 33%); IR(nujol) 1760 cm^{-1}; ^1H NMR (DMSO - D_6) 5.85 (d, J = 12.4 Hz), 6.35 (d, J = 16.0 Hz, 7.22 - 8.05 (m, 32H). Analysis calcd. for $C_{62}H_{34}O_6N_2Cl_2$ C, 76.46, H, 3.5. Found C, 76.2; H, 3.33%, and the starting material (100 mg)

Oxidation of 17b[9] : gave **19b** (less polar, 300 mg, 72%) m.p. 171-2°C; IR(nujol) 2250, 1767 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) 3.62 (s, 3H, OCH_3), 5.84 (d, J = 12.0 Hz, 1H), 6.95-7.07 (m, 2H), 7.19-7.98 (m, 13H); ^{13}C NMR (270 MHz, $CDCl_3$) positive signals at 110.88, 111.03, 115.23, 119.34, 122.56, 131.09, 131.21, 133.01, 135.36, 148.78, 150.12, 152.72, 158.06, 160.82. Negative signals at 55.37, 111.54, 112.45, 114.51, 115.31, 121.32, 123.35, 124.41, 126.06, 126.30, 128.16, 128.43, 128.88, 129.63, 130.08, 130.22, 132.55, 150.41; MS m/e (relative intensity) 1032 (M^+, 5), 629(12), 403(100), 374(25), 361(10), 343(22). Analysis calcd. for $C_{64}H_{38}N_2O_8Cl_2$ C, 74.3; H, 3.67; Found C, 73.9; H, 3.7%.

Oxidation of 17c : gave **19c** (less polar, 420 mg, 76%), m.p. 175-7°C; IR(nujol) 2250, 1765 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$), 3.76 (s, 3H), 3.96 (s, 3H), 6.10 (d, J = 14.0 Hz, 1H), 6.9-7.05 (m, 2H), 7.3-8.05 (m, 12H). Analysis calcd. for $C_{66}H_{40}O_{10}N_2Cl_2$ C, 72.7; H, 3.85. Found C, 72.4; H, 3.78%.

Oxidation of 17d : gave **19d** (less polar, 450 mg, 67%); m.p.195-7°C; IR(nujol) : 2250, 1767 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$), 3.7 (s, 3H), 5.9 (d, J = 12.0 Hz, 1H), 6.98-7.31 (m, 4H), 7.33-7.54 (m, 5H), 7.64-7.84 (m,3H), 8.05-8.07 (m,1H). Analysis calcd. for $C_{64}H_{38}O_8N_2Cl_2$ C, 56.9; H, 2.52. Found C, 56.8; H, 2.59%.

Hydrogenation of 4a : A solution of tropone **4a** (200 mg) in dry THF (60 ml) was stirred with 10% Pd-C catalyst (35 mg) in an atmosphere of hydrogen till the hydrogen uptake ceased (10 hrs). After filtering off the catalyst from the colourless filtrate, solvent was removed in vacuo and the residue crystallize to give dihydrotropone **8a** (185 mg, 92%). m.p. 150° (benzene-pet.ether); IR(nujol) 1660 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) 3.1-3.2 (Sym. multiplet, 4H, $-CH_2CH_2-$), 7.26-8.15 (m, 9H), 9.22 (d, J =9.0 Hz, 1H); ^{13}C NMR (270 MHz, $CDCl_3$) 196.7 (s, C=O), 158.4(s), 152.4(s), 140.6(s), 131.8(s), 130.2(d), 129.2(s), 128.96(d), 128.87(d), 128.71(s), 128.43(d), 128.06(d), 127.41(d,2xC), 126.6(d), 125.24(d), 111.60(d), 44.24(t), 29.76(t); MS m/e 298 (M^+). Analysis calcd. for $C_{21}H_{14}O_2$: C, 84.54; H, 4.73. Found : C, 84.60; H, 4.85%.

Reduction of this compound **8a** (100 mg) with $NaBH_4$ (20 mg) in methanol (20 ml) gave the alcohol **8b** (85 mg, 84%), m.p. 125° ($CHCl_3$); IR(nujol) 3300-3400 cm^{-1} (-OH); ^1H NMR (270 MHz, $CDCl_3$), 1.8-2.6 (m, 2H), 3.1 (t, 2H), 5.5 (s, 1H, -OH), 5.65 (t, 1H), 7.2-8.3 (m, 9H), 8.8 (d, J =10.0 Hz,

1H), MS m/e 300(M^+). Analysis calcd. $C_{21}H_{16}O_2$: C, 83.98; H, 5.37. Found: C, 83.84; H, 5.30%.

$NaBH_4$ Reaction of 6a : Compund **6a** (1 g) in dry THF (400 ml) was stirred with $NaBH_4$ (100 mg) at room temperature for 24 H. The residue obtained after complete removal of THF in vacuo was stirred with saturated NH_4Cl solution and extracted with $CHCl_3$. The dried extract was concentrated and purified by preparative TLC (chloroform) to give 3-[2'-(2-(naphtho[2,1-b]-furanyl)Phenyl]-1-propanol **9a** (550 mg, 75%); m.p. 105° ($CHCl_3$-Pet.ether); IR(nujol) 3300-3400 cm^{-1} (-OH); ^1H NMR (270 MHz, $CDCl_3$) 4.17 (dd, 1H), 4.9 (t, J = 6.3 Hz, 1H, D_2O exchangeable, 6.04 (triplet of doublet, J = 10.0 and 6.3 Hz, 1H), 6.83 (d, J = 10.0 Hz, 1H), 7.34-7.99 (m, 9H), 8.6 (d, J = 7.2 Hz, 1H), 8.36 (d, J = 8. Hz, 1H); ^{13}C NMR (270 MHz, $CDCl_3$), 150.0(s), 152.0(s), 134.2(s), 131.5(d,2xC), 130.54(d), 128.8(d), 127.8(d,2xC), 127.62(d), 126.37(d), 125.57(d), 125.18(s), 124.64(d), 123.53(d), 112.2(d), 105.5(d), 59.7(t); MS m/e 300(M^+). Analysis calcd. for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37. Found : C, 84.05, H, 5.48%.

Acetylation of this compound (200 mg) with Ac_2O/Py gave the monoacetate **9b** (180 mg), IR (thin film) 1740 cm^{-1} (C=O); ^1H NMR (270 MHz, $CDCl_3$). 2.0 (s, 3H, $OCOCH_3$), 4.84 (doublet with allylic coupling, J = 8.0 Hz, 2H), 6.02 (triplet of doublet, J = 12.0 and 8.0 Hz, 1H), 6.98 (doublet with allylic coupling, J = 12.0 Hz, 1H), 7.2-8.3 (m, 11H); MS m/e 342(M^+). Analysis calcd. for $C_{23}H_{18}O_3$; C, 80.68; H, 5.30. Found: C, 80.55; H, 5.18%.

Hydrolysis of 6a : A mixture of compound **6a** (500 mg) and 10% NaOH (100 ml) were refluxed until the yellow colour of the solid disappeared (48 hrs). The white solid was filtered off and dried at 60°C. The dried solid was stirred with 10% HCl (50 ml) for 1 hr. The solid was extracted with ethylacetate (100 ml), washed with water (25 ml x 3) and dried. Removal of ethyl acetate gave Cis-3-[2'-(2-(naphtho[2,1-b]-furanyl)}phenyl]-1-propenoic acid **9c** (275 mg, 72%), m.p.202° ($CHCl_3$): IR(nujol) 1700, 1625 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$), 6.19 (d, J = 12.0 Hz, 1H), 7.34 (s, 1H), 7.37-7.63 (m, 5H), 7.72 (m, 5H), 8.17 (d, J = 8.0 Hz, 1H); MS m/e (relative intensity) 314 (M^+, 85), 296 (M-18, 25), 269(100), 239(70). Analysis calcd. for $C_{21}H_{14}O_3$: C, 80.25; H, 4.45.Found: C, 79.82; H, 4.41%.

Esterification of this acid **9c** (200 mg) with $MeOH/H_2SO_4$ gave methyl ester **9e** (160 mg, 78%) m.p. 82°C, IR(thin film) 1728, 1630 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$), 3.56 (s, 3H, OCH_3), 6.0 (d, J = 12.0 Hz, 1H), 7.1-8.1 (m, 11H); MS m/e 328(M^+). Analysis calcd. for $C_{22}H_{16}O_3$: C, 80.47; H, 4.91. Found : C, 80.6; H, 5.08%.

Hydrogenation of 9c : Hydrogenation **9c** (200 mg) in ethylacetate (25 ml) with 10% Pd-C (35 mg) followed by usual work up gave dihydro acid **10b** (170 mg, 85%), m.p. 132° ($CHCl_3$-Pet.ether); IR(nujol) 1700 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) 2.76 (t, J = 7.6 Hz, 2H), 3.34 (t, J = 7.5 Hz, 2H), 7.35 (d, J = Hz, 2H), 7.42 (s,1H), 7.46-7.82 (m,6H), 7.95 (d, J = 8.0 Hz, 1H), 8.18 (d, J = 8.2 Hz, 1H); ^{13}C NMR (90 MHz, $CDCl_3$), 179.37(s), 155.3(s), 152.39(s), 138.2(s), 130.50(d,2xC), 129.96(s), 129.31(d), 128.99 (d, 2xC), 127.69(s), 127.04(s), 126.499d), 125.41(d), 124.65(d), 124.22(s) 123.579d), 112.41(d), 103.96(d), 35.37(t), 29.74(t); MS m/e (relative intensity) 316(M^+,100), 269(30), 257(20), 239(18). HRMS calcd. for $C_{21}H_{16}O_3$ 316.1100. Found 316.1113%.

Ag_2O Oxidation of 9d : To a solution of **9d** (50 mg) in ethanol (10 ml) was added $AgNO_3$ (80 mg) in water (1 ml). To this a solution of 2% NaOH (5 ml) was added and the mixture stirred over night. The precipitate was filtered off, most of the ethanol removed and extracted with ethyl acetate. The ethyl acetate extract was washed with water and dried. Removal of solvent gave **9c** (40 mg, 76%), m.p. 202°C.

Hydrogenation of 9a : Hydrogenation of **9a** (200 mg) with 10% Pd-C (35 mg) in ethyl acetate (25 ml) gave the alcohol **10a** (190 mg, 95%). IR(neat) 3400 cm^{-1} (br, -OH); ^1H NMR (270 Mhz, $CDCl_3$) 1.56-1.94 (m, 2H), 2.45 (bs, D_2O exchangeable, 1H), 2.9 (t, J = 7.5 Hz, 2H), 3.54 (t, J = 6.0 Hz, 2H), 7.1-8.1 (m, 11H); MS m/e 302(M^+). Analysis calcd. for $C_{21}H_{18}O_2$: C, 83.42; H, 6.0. Found : C, 83.42; H, 6.0%.

The same alcohol (85 mg, 41%) was also obtained by reduction of **6a** (200 mg) with $LiAlH_4$ (20 mg) in THF followed by work up and purification.

Trans esterification of 6a : Compound **6a** (500 mg) was taken in dry MeOH (500 ml) and heated to reflux for three days. Methanol was removed completely and the product was separated by column chromatography (silica gel, $CHCl_3$-pet.ether 2:1) to give less polar methyl ester **11** (240 mg, 64%) m.p.62°C; IR(nujol) 1740 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) 3.8 (s, 3H, OCH_3), 6.45 (d, J = 16.0 Hz, 1H), 7.2-8.2 (m, 11H), 8.3 (d, J = 16.0 Hz, 1H). Analysis calcd. $C_{22}H_{16}O_3$ C, 80.47, H, 4.91. Found : C, 80.2; H, 4.82%.

Further elution with $CHCl_3$-EtOAc 4:1 gave phenolic material which on treatment with CH_2N_2 gave, after purification ($CHCl_3$-pet.ether 2:1) **12** (130 mg, 38%) m.p. 95°C ; IR(nujol) 2250, 1760, 1630 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) 4.1 (s, 3H, OCH_3), 6.65 (d, J = 16.0 Hz, 1H), 7.33 (s, 1H), 7.3-8.25 (m, 10H), 8.6 (d, J = 16.0 Hz, 1H). Analysis calcd. for $C_{30}H_{16}O_4N_2Cl_2$. C, 66.8; H, 3.0. Found C, 66.4; H, 2.92%.

Preparation of DDHQ diester of acid 9c : A mixture of acid **9c** (1 g) and thionyl chloride (0.22 ml) was heated at 90°C for 2 hrs. DDHQ (0.21 g) was added gradually over a period of 15 min. and the mixture heated again for 2 h. The cooled reaction mixture was extracted with benzene (50 ml x 3) and the benzene extract was washed repeatedly with water (50 ml x 5) and dried. The residue obtained after removal of benzene was chromatographed to give trans, trans diester **7a** (less polar, 250 mg) m.p. 135.7°C; and tropone **4a** (125 mg).

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3. When precipitated DDHQ was washed with acetone to remove DDHQ, an yellow solid was left behind. This was insoluble in common organic solvents. This also showed ^1H NMR signals similar to compound B, but in the mass spectrum, it showed ions beyond m/e 820. An osmometric determination of molecular weight of this solid indicated it to be polymeric. Further investigation was not carried out on this material. We are thankful to Dr.R.A.Kulakarni and Dr.Amithabha Sarkar for this determination.

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11. It was very difficult to get a 100% pure cis compound as it was always contaminated with trans isomer.