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ONE POT SYNTHESIS OF POLYCYCLIC OXYGEN AROMATICS[1]

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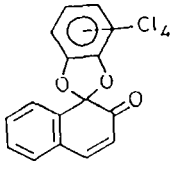
ABSTRACT: Reaction of 1-bromomethyl-2-(2-tetrahydropyranyloxy) naphthalene (5a) with tetrachlorocatechol in acetone in presence of anhydrous potassium carbonate resulted in the formation of compounds 7a, 8a and 9a, along with diastereomeric products to which (±) cis- and trans-8-chloro-10-hydroxy-10-(2-oxopropyl) spiro [11H-benzo[a]xanthen-11,2'(1'H) naphtho [2,1-b] furan]-9 (10H)-one (13a and 14a) structures were assigned based on spectral data. Similar reaction of the corresponding bromo compound (5b) using acetone or diethyl ketone as solvent gave the corresponding diastereomeric pair of compounds (13 and 14). X-ray crystal structure analysis of one of the trans compounds, 14c, further confirmed the assigned structure.

Oxidation[2] of 2-naphthol with o-chloranil results in the formation of isomeric spironaphthalenones 1 and 2 through an oxidative rearrangement of the oxydiphenol 3a. In connection with mechanistic studies on the unusual oxidative rearrangement of substituted 2-naphthols and oxydiphenols[3], it was envisaged to study the behaviour of 3b towards o-chloranil. With this in view, synthesis of 3b was undertaken and the interesting results obtained are discussed in this paper.



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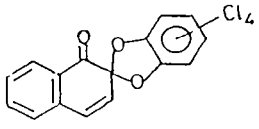

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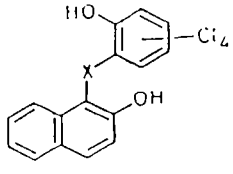

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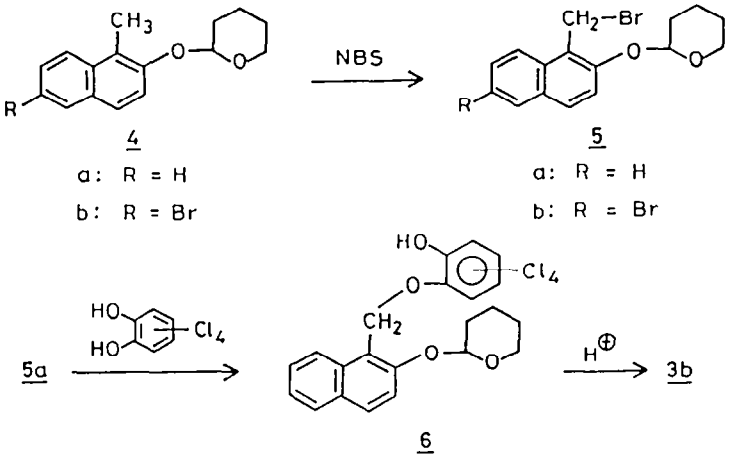
a: X = O

b: X = CH_2O

The projected synthesis of 3b, depicted in scheme I, involves N-bromosuccinimide (NBS) bromination of the pyranyl ether 4a followed by condensation of the resulting bromo compound 5a with tetrachlorocatechol in presence of base. It is essential to protect the hydroxyl of 1-methyl-2-naphthol in order to brominate the allylic methyl group[4]. The obvious choice was the pyranyl-

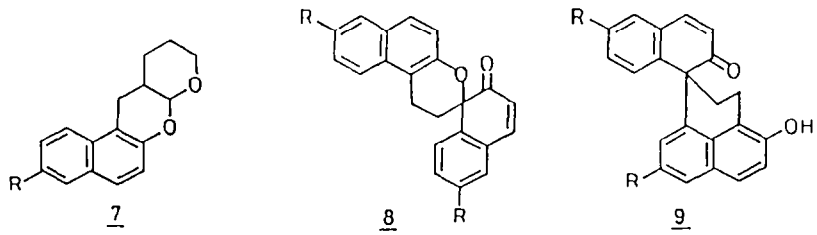


Scheme-I

ether which is stable to basic reaction conditions and could be cleaved under mild acidic conditions[5].

Tetrahydropyranyl ether 4a was prepared by the reaction of 1-methyl-2-naphthol with dihydropyran in dry methylene chloride in presence of catalytic amounts of pyridinium p-toluenesulfonate (PPTS). The presence of a broad triplet at δ 5.33 characteristic of the methine proton in ^{1}H NMR spectrum of 4a confirmed its formation. Bromide 5a, prepared by NBS bromination[6] (3 hrs) could not be isolated in pure form as it underwent rapid decomposition. However, ^{1}H NMR spectrum of a concentrated solution showed the presence of a singlet at δ5.0 corresponding to benzylic methylene protons. Subsequent reactions of 5a were carried out with the solution.

Condensation of 5a with tetrachlorocatechol was carried out in acetone in presence of anhydrous potassium carbonate under refluxing conditions for 24 hrs. The products obtained, after work up, were separated into alkali soluble and neutral fractions. The alkali extract, after neutralisation, gave mainly tetrachlorocatechol and no trace of the required pyranyl ether 6. The neutral fraction, on column chromatography followed by preparative TLC, led to five distinct compounds, of which the two least polar compounds and the most polar compound were characterised as the known pyranopyran 7a[7], the 1,2-naphthoquinone-1-methide dimer 8a[8] and the hydroxyspironaphthalenone 9a[9] respectively from spectral data and by comparison with authentic samples.

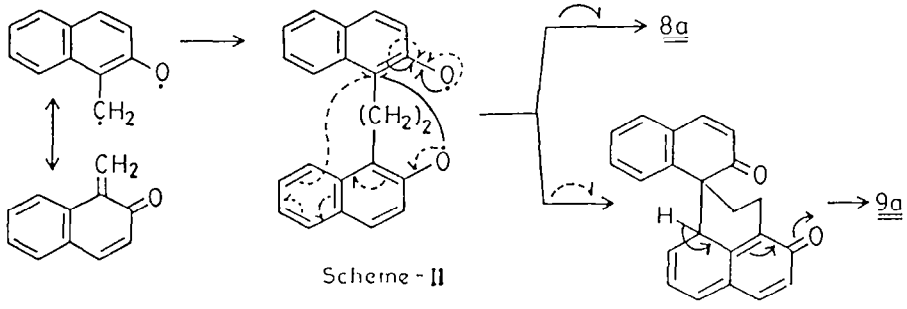


7
a: R = H
b: R = Br

8
a: R = H
b: R = Br

9
a: R = H
b: R = Br

The formation of 9a by dimerization of 1,2-naphthoquinone-1-methide, could be visualised as in scheme II.

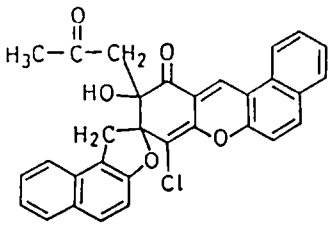


Scheme - II

The first medium polar compound, designated as A and which analysed for $C_{31}H_{21}ClO_5$ (HRMS, m/e calcd for $C_{31}H_{21}ClO_5$ 508.107741, found 508.107448), exhibited IR absorptions at 3350, 1715 and 1657 cm^{-1}, indicating the presence of a hydroxy and two carbonyl groups, one of which was conjugated. The characteristic features in ^1H NMR (270 MHz) spectrum are: a D_2O exchangeable broad singlet at δ 6.7, two AB quartets centred at 3.65 ($\Delta\nu_{AB}$ = 91.8 Hz, J_{AB} = 16.0Hz) and 2.79 ($\Delta\nu_{AB}$ = 124.2 Hz, J_{AB} = 16.0Hz) corresponding to two methylene groups with non-equivalent hydrogens and a three proton singlet at 2.32 ($COCH_3$). The mass spectrum exhibited a prominent peak at m/e 450 (M^+-58) corresponding to an elemental composition of $C_{28}H_{15}ClO_4$ resulting from loss of one molecule of acetone by McLafferty rearrangement from the molecular ion, thus confirming the presence of an acetonyl side chain. The IR spectrum of the other medium polar compound B [analysed for $C_{31}H_{21}ClO_5$: m/e 508 (M^+ ^{35}Cl)] shows absorptions at 3400, 1710 and 1670 cm^{-1}, indicative of a hydroxy and two carbonyl functions. The salient features in its ^1H NMR (270MHz) spectrum are: a three proton singlet at δ 2.20 ($COCH_3$), two AB quartets centred at 3.08 ($\Delta\nu_{AB}$ = 145.8 Hz, J_{AB} = 16.0Hz) and 3.72 ($\Delta\nu_{AB}$ = 202.5 Hz, J_{AB} = 16.0Hz); and a sharp D_2O exchangeable singlet at 4.80 (OH).

On the basis of spectral data, three alternate structures 10, 11 and 12 could be considered for these compounds. It was anticipated that the difference in conjugation in structures 10, 11 and 12 would be reflected in UV absorption

maxima. However, compounds **A** [λ_{max} (ε) ($CHCl_3$) 425(17,150)] and



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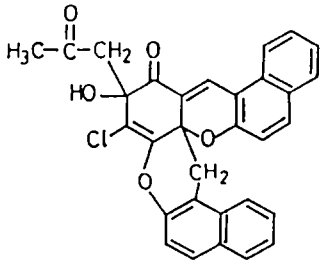

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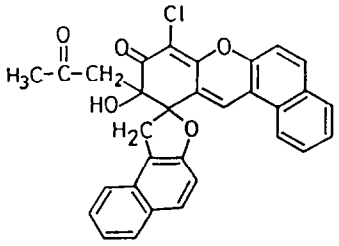


12

B [λ_{max} (ε) ($CHCl_3$) 427 (16,600)] showed very similar long-wavelength absorptions. Hence, it is likely that they are diastereomers of a particular structure rather than being represented by two different structures (**10**, **11** or **12**). Both the compounds **A** & **B** showed similar ^{13}C chemical shifts (Table-I) except for the $\underline{C}H_2Ar$, $\underline{C}H_2COCH_3$ and side chain carbonyl signals. Trichloro acetyl isocyanate (TAI), a useful *in situ* derivatising reagent for the ^{13}C NMR studies of alcohols, phenols and amines[10], immediately forms an urethane with alcohols and a study of the ^{13}C NMR of this gives information about the carbons in the vicinity of the hydroxy group. The ^{13}C NMR resonances in compounds **A** and **B** on TAI derivatisation are also listed in Table-I. In both the compounds **A** and **B**, the carbinol carbon signals at δ 82.98 and 80.19 are shifted downfield by 8.64 and 11.83 ppm respectively characteristic of saturated non-conjugated tertiary alcohols. This fact clearly ruled out the allylic alcohol structure **11**. The side chain carbonyl signals at δ 212.29 and 206.47 in compounds **A** and **B** have moved upfield by 8.1 and 4.69 ppm respectively, suggesting the presence of a stronger intramolecular hydrogen bonding in compound **A** relative to compound **B**. Similarity of UV, ^1H NMR and ^{13}C NMR (before and after TAI derivatisation) in these two compounds, further substantiates the conjecture that they could be diastereomers. Hence, both the compounds could be represented by a single structure (**10** or **12**). None of these compounds gave good crystals suitable for X-ray analysis.

The reaction of the bromide **5b**, prepared from 6-bromo-1-methyl-2-naphthol by a procedure similar to that of **5a**, with tetrachlorocatechol in acetone in the presence of potassium carbonate gave, along with the compounds **7b**, **8b**[11] and **9b**[12], the isomeric products **C** [MS m/e 664 (M^+, ^{35}Cl, ^{79}Br); IR ν_{max} 3440, 1715, 1670 cm^{-1}; ^1H NMR (270 MHz)δ2.33 (s,3H), 2.73 (ABq, $\Delta\nu_{AB}$ = 129.6 Hz, J_{AB} = 16.2 Hz, 2H), 3.60 (ABq, $\Delta\nu_{AB}$ = 81.0 Hz, J_{AB} = 16.2 Hz, 2H), 6.75 (s,1H,OH)] and **D** [MS m/e 664 (M^+ ^{35}Cl, ^{79}Br); IR ν_{max} 3460, 1715, 1670 cm^{-1}, ^1H NMR (270 MHz) δ2.24(s,3H), 3.09 (ABq, $\Delta\nu_{AB}$ = 143.1 Hz, J_{AB} = 16.2 Hz, 2H), 3.71 (ABq, $\Delta\nu_{AB}$ = 191.7 Hz, J_{AB} = 16.2 Hz, 2H), 4.79 (s,1H,OH)]. X-ray crystal structure

Table I 13C NMR[a] of compounds A and B

Comp A	TAI derivative of A	Assignment (13a)	Comp B	TAI deriavtive of B	Assignment (14a)
29.35(t)	29.66	C(1')	31.94(q)	30.82	C(15)
32.22(q)	32.37	C(15)	37.19(t)	37.49	C(1')
38.07(t)	36.79	C(13)	47.40(t)	44.71	C(13)
82.98(s)	91.62	C(10)	80.19(s)	92.02	C(10)
90.59(s)	86.90	C(11)	91.77(s)	89.03	C(11)
103.76(s)	103.91	C(8)	103.27(s)	104.82	C(8)
111.77(d)	111.62	C(4')	111.35(d)	111.32	C(4')
114.33(s)	114.15	C(12a)	114.30(s)	113.91	C(12a)
116.10(d)	115.86	C(6)	116.16(d)	116.28	C(6)
116.25(s)	116.34	C(9'b)	117.20(s)	117.56	C(9'b)
121.65(d)	121.71	C(3)	121.62(d)	121.52	C(3)
122.47(d)	122.59	C(7')	122.59(s)	122.86	C(11a)
122.66(s)	124.27	C(11a)	123.35(d)	123.14	C(7')
123.93(d)	126.34	C(9')	123.60(d)	123.90	C(9')
126.16(d)	127.74	C(1)	126.37(d)	126.31	C(1)
127.47(d)	128.26	C(2)	127.10(d)	127.29	C(2)
128.08(d)	128.66	C(8')	128.29(d)	128.32	C(8')
128.60(d)	128.96	C(5')	128.51(d)	128.63	C(5')
128.87(d)	129.97	C(6')	128.69(d)	128.75	C(6')
128.87(d)	130.09	C(5)	128.90(d)	129.02	C(5)
129.76(s)	130.21	C(9'a)	129.69(s)	129.18	C(9'a)
130.34(s)	130.27	C(5'a)	129.81(s)	129.85	C(5'a)
130.52(s)	130.46	C(4a)	130.40(s)	130.15	C(4a)
130.67(s)	130.76	C(12b)	130.40(d)	130.70	C(4)
130.67(d)	130.91	C(4)	130.70(s)	130.70	C(12b)
132.59(d)	132.93	C(12)	133.08(d)	133.17	C(12)
150.76(s)	150.85	C(6a)	150.85(s)	150.97	C(6a)
156.12(s)	157.49	C(3'a)	155.88(s)	157.00	C(3'a)
159.99(s)	158.68	C(7a)	159.53(s)	158.68	C(7a)
188.58(s)	182.97	C(9)	189.50(s)	183.68	C(9)
212.29(s)	204.19	C(14)	206.47(s)	201.78	C(14)

[a]All spectra were measured in $CDCl_3$ (TMS as internal standard) at 25.03 MHz: s, singlet; d, doublet; t, triplet; q, quartet (in off-resonance decoupled spectra). Closely lying values are interchangeable.

analysis of compound C revealed[1a] the structure to be 13b in which the two oxygens on adjacent carbons C(10) and C(11) are in cis-configuration. The

crystals of isomeric compound **D** were not suitable for crystal structure analysis. Hence, compound D was, tentatively assigned[1a] the trans-structure **14b**. Accordingly, the desbromo compounds **A** and **B** whose spectral properties are similar to those of compounds **C** and **D**, were tentatively assigned the structures **13a** and **14a** respectively. A similar reaction of the bromide **5b** in diethyl ketone gave, in addition to **7b** and **8b**, three isomeric products, designated as **E**, **F** and **G**. A comparison of the important ^{1}H NMR signals of these compounds with those of compounds **A**, **B**, **C** and **D**, (Table II) revealed that compound **E** belongs to the cis series **13**, while compounds **F** and **G** belong to the trans series **14**. With a view to confirming the structure assigned to compounds of the type **14** unequivocally and also to assign stereochemistry of the C(13) methyl group, X-ray analysis of the highly crystalline compound **F** (14c) was undertaken.

Table-II. Characteristic ^{1}H NMR (270 MHz) data

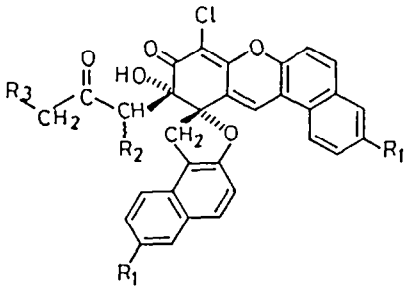
Proton Multiplicity		13a (A)	13b (C)	13c (E)	14a (B)	14b (D)	14C (F)	14d (G)
$ArCH_2$[13]	ABq	3.65	3.60	3.62	3.72	3.71	3.71	3.72
	($\Delta\nu_{AB}$, Hz)	(91.8)	(81.0)	(106.3)	(202.5)	(191.7)	(203.7)	(229.4)
OH	s	6.70	6.75	6.56	4.80	4.79	4.93	4.46
CH_2COCH_3	ABq	2.79	2.73	---	3.08	3.09	---	---
	($\Delta\nu_{AB}$, Hz)	(124.2)	(129.6)	---	(145.8)	(143.1)		

The perspective view of the molecule is shown in the Fig.1. The oxygen atoms O(19) and O(3') deviate significantly from the plane formed by C(9), C(10) and C(11) atoms by 1.174(6) and -0.060(6) Å respectively. The substituent oxygen atoms [O(19) and O(3')] at C(10) and C(11) respectively are thus in trans-orientation. This is unlike in the compound **13b**[1a] where O(19) and O(3') being in cis configuration, make displacements of -1.1354 and -0.093 Å respectively from the plane formed by C(9), C(10) and C(11). The X-ray crystallographic study, thus, unambiguously confirmed the trans structure **14c** for compound **F**.

From the torsional angle C(17)-C(13)-C(10)-O(19) = 55.3(9)°, it is evident that C(17) is cis to O(19) oxygen. That is, the C(13) methyl group in **14c** is in β-orientation. Compound **G**, having trans stereochemistry at C(10) and C(11) and isomeric with **14c** was assigned the epimeric C(13)-α-methyl structure **14d**.

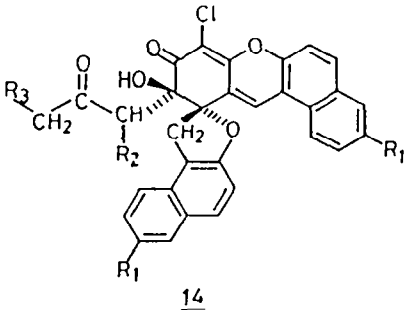
The diastereomeric nature of the set of compounds obtained in the above mentioned reactions, has thus been unequivocally demonstrated by X-ray crystal structure analysis.

Isolation of dimers **8** and **9** in this reaction is indicative of the formation of 1,2-naphthoquinone-1-methide by cleavage of the pyranyl ether



13

a: $R_1 = H$, $R_2 = R_3 = H$
b: $R_1 = Br$, $R_2 = R_3 = H$
c: $R_1 = Br$, $R_2 = \alpha$-Me, $R_3 = Me$



14

a: $R_1 = H$, $R_2 = R_3 = H$
b: $R_1 = Br$, $R_2 = R_3 = H$
c: $R_1 = Br$, $R_2 = \beta$-Me, $R_3 = Me$
d: $R_1 = Br$, $R_2 = \alpha$-Me, $R_3 = Me$

under basic reaction conditions. Perhaps, addition of tetrachlorocatechol to quinonemethide, followed by step wise cyclisation and elimination of chloride ions and finally, aldolisation is expected to give the diastereomeric products. A detailed investigation of the mechanism of this reaction is in progress.

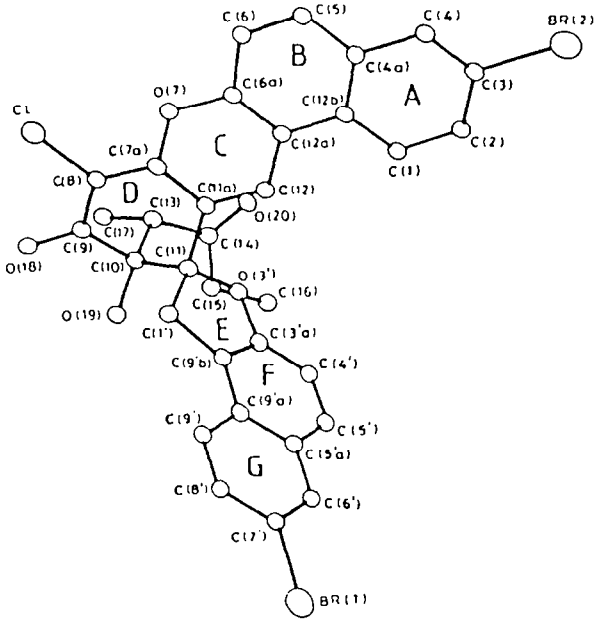


Fig. 1. Perspective view of compound 14c

EXPERIMENTAL SECTION

All melting points and boiling point are uncorrected. UV (nm)and IR (cm^{-1}) spectra were recorded on HITACHI Model 557 Double wavelength/Double beam and Perkin-Elmer Model 781 spectrometers respectively. NMR spectra were recorded on a Varian T-60 (60MHz) or a Bruker WH-270, 67.87 MHz (^{13}C) or a Jeol PS/PFT-100, 25.03 MHz (^{13}C) spectrometers with Me_4Si as internal standard (δ = 0 ppm). MS (70eV) were recorded on an Atlas CH-4 or a Jeol MS-DX 303 spectrometers. Analytical and preparative TLC were carried out using silica gel. Column chromatography was carried out using neutral/basic alumina.

1-Methyl-2-(2-tetrahydropyranyloxy) naphthalene (4a)

A solution of 1-methyl-2-naphthol[15] (5 gm) and dihydropyran (4.32 ml) in dry methylene chloride (80 ml) containing PPTS (795 mg) was stirred for 4 hrs at room temperature[16]. The solution was washed with saturated brine to remove the catalyst, followed by ice-cooled 10% aq. NaOH (50mlx4), water (50mlx4) and dried. The crude reaction mixture, after the removal of solvent and excess dihydropyran, was purified by column chromatography over basic alumina. Elution with benzene:hexane (1:1) gave the pyranyl ether 4a (6.0 gm; 84%), b.p. 140-142° C/2mm; IR (neat) 1620, 1600; ^1H NMR (60 MHz, CCl_4) 1.30-2.00 (m, 6H), 2.53 (s, 3H), 3.20-4.10 (m, 2H), 5.33 (br t, 1H), 7.10-7.90 (m, 6H), Anal. calcd. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.71. Found: C, 79.44; H, 7.71.

6-Bromo-1-methyl-2-(2-tetrahydropyranyloxy) naphthalene (4b)

A similar reaction of 6-bromo-1-methyl-2-naphthol[17] (5 gm) with dihydropyran (2.89 ml) in dry methylene chloride (80 ml) containing PPTS (532 mg) yielded the pyranyl ether 4b (5.5 gm; 81%), m.p. 80° C (benzene-hexane); IR(nujol) 1620, 1600; ^1H NMR (60 MHz, CCl_4) 1.30-2.13 (m,6H), 2.50 (s, 3H), 3.27-4.10 (m, 2H), 5.37 (br t, 1H), 7.17-7.87 (m, 5H). Anal. calcd. for $C_{16}H_{17}O_2$ Br: C, 59.83; H, 5.33. Found: C, 59.65; H, 5.30.

1-Bromomethyl-2-(2-tetrahydropyranyloxy) naphthalene (5a)

A mixture of pyranyl ether 4a (3.2 gm; 0.0132 mole), NBS (2.57 gm; 0.0145 mole) and dibenzoyl peroxide (32mg; 0.00145 mole) was refluxed in CCl_4 (40 ml) in dark till the NBS reacted completely (3 hrs). It was cooled, the separated succinimide was filtered off and the filtrate washed with ice-cold 10% aqueous NaOH (4x30ml) and water (4x30ml) and dried. The CCl_4 solution, concentrated to 1/4th of its original volume [IR 1620, 1600; ^1H NMR (60MHz) 1.40-2.30 (m, 6H), 3.30-4.00 (m,2H), 5.00 (s, 2H), 5.50 (br t, 1H), 7.10-8.00 (m, 6H)] and protected from light, was used in subsequent reactions.

6-Bromo-1-bromomethyl-2-(2-tetrahydropyranyloxy) naphthalene (5b)

The above reaction was repeated with the pyranyl ether 4b for 3 hrs to give the bromide 5b; IR (CCl_4) 1620, 1600; ^1H NMR (60MHz, CCl_4) 1.32-2.18 (m, 6H), 3.28-4.18 (m, 2H), 4.85 (s, 2H), 5.45 (br t, 1H), 7.08-7.85 (m, 5H).

Reaction of bromide 5 with tetrachlorocatechol in Ketonic solvents in presence of K_2CO_3

a) Reaction of 5a in acetone

A solution of bromide 5a in CCl_4 (25 ml), prepared from the pyranyl ether 4a (3.2 gm; 0.0132 mole) after dilution with acetone (25 ml), was added to a vigorously stirred refluxing solution of tetrachlorocatechol (3.27 gm; 0.0132 mole) in acetone (150 ml) containing anhydrous K_2CO_3 (2.73 gm; 0.0198 mole) over

a period of 4 hrs in dark. The reaction mixture was further refluxed for 24 hrs, cooled, K_2CO_3 filtered off and washed with little acetone. After the removal of acetone, the residue was taken in ether (150 ml) and washed successively with water (4x50 ml), 10% aqueous NaOH (4x50 ml), water (4x50 ml) and dried. Ether was removed and the residue chromatographed.

Elution with hexane-benzene (1:1) gave the pyranopyran 7a (45 mg: 1.4%), m.p. 77°C (benzene-hexane) (lit[7], m.p. 78°C). Further elution with benzene gave the spironaphthalenone 8a (370 mg; 18.0%), m.p. 142°C (benzene-hexane) (lit[8], m.p. 141-142°C). The material obtained by further elution with chloroform and chloroform:ethyl acetate (19:1) was separated into three compounds by preparative TLC (chloroform:ethyl acetate 19:1). The less polar compound was shown to be (±) cis-8-chloro-10-hydroxy-10-(2-oxopropyl)spiro [11H-benzo [a] xanthen-11,2'(1'H)-naphtho [2,1-b] furan]-9 (10H)-one 13a (135 mg: 4.0%), m.p. 241°C (benzene-hexane): UV ($CHCl_3$), 425(17,150), 405(17,900), 355(9,700), 338(10,900), 325(8,900), 278 (12,500), 262(16,500), 257(20,000), 242(39,400): MS m/e (relative intensity) 510, 508 (M^+, 20,56), 473(17), 451(37), 450(42), 433(38), 423(100), 405(28), 387(46), 352(27), 296(54), 295(42), 294(74), 268(57). Anal. calcd. for $C_{31}H_{21}ClO_5$: C, 73.15; H, 4.16. Found: C, 73.40; H, 4.50. The medium polar compound was identified as (±) trans-8-chloro- 10-hydroxy-10-(2-oxopropyl) spiro [11H-benzo [a] xanthen-11,2' (1'H)-naphtho [2,1-b] furan]-9 (10H)-one **14a** (215 mg; 6.4%), m.p. 238-239°C (acetone): UV ($CHCl_3$) 427(16,600), 410(17,300), 356(8,800), 338(10,400), 325(8,800), 278(12,150), 262 (16,000), 256(18,100), 242(36,400): MS m/e (relative intensity) 510, 508 (M^+, 11, 34), 473(19), 451(25), 450(32), 433 (24), 423(100), 405(22), 387(36), 352(45), 296(45), 295(41), 294(86), 268(34). Anal. calcd.for $C_{31}H_{21}ClO_5$: C,73.15; H, 4.16. Found: C, 73.40, H,4.20 and the most polar compound was characterised as 2',3'-Dihydro-4'-hydroxyspiro[naphthalene-1(2H),1'(1H) phenalen]-2-one 9a (205mg; 9.9%), m.p. 239-241°C (acetone-petroleum ether) (lit[9], 242°C).

b) Reaction of bromide 5b in acetone

The product obtained by reaction of bromide 5b, prepared from 4b (3.2 gm; 0.01 mole), with tetrachlorocatechol (2.48 gm; 0.01 mole) in acetone (150 ml) containing anhydrous K_2CO_3 (2.07 gm; 0.015 mole), was chromatographed. Elution with hexane-benzene (1:1) and benzene afforded cis-3-bromo-7a, 10, 11, 11a-tetrahydro-9H, 12H-naphtho [2,1-b] pyrano [3,2-e] pyran 7a (50 mg; 3.1%): m.p. 115-116°C (benzene-hexane); IR (nujol) 1620, 1600; ^1H NMR (270 MHz, $CDCl_3$) 1.63-1.82 (m,4H), 2.26-2.40 (m, 1H), 2.93 (dd, J = 17.0, 4.3 Hz, 1H), 3.16 (dd, J = 17.0, 6.6 Hz, 1H), 3.74-3.81 (m, 1H), 4.05-4.12 (m, 1H), 5.40 (d, J = 2.5Hz, 1H), 7.13 (d, J = 8.9Hz, 1H), 7.51-7.56 (m, 2H), 7.64(d, J = 8.9Hz, 1H) 7.90 (d, J = 1.9Hz, 1H). Anal. calcd.for $C_{16}H_{15}O_2Br$: C, 60.18; H, 4.74, Found: C, 60.27; H,4.63. and spironaphthalenone 8b (390 mg; 16.6%) m.p. 176°C (benezne-hexane) (lit[11], 177° C). Further elution with chloroform:ethyl acetate (19:1) gave (±)cis - 3,7'-dibromo-8-chloro-10-hydroxy-10-(2-oxopropyl) spiro [11H-benzo [a] xanthen-11,2' (1' H)-naphtho [2,1-b] furan]-9(10H)-one 13b (140 mg: 4.2%), m.p. 278°C (benzene-hexane): UV ($CHCl_3$) 427 (12,800), 406 (13,700), 358(9,000), 340(9,750), 326(6,500), 290(8,100), 278(10,400), 256(23,200), 244(43,750): ^{13}C NMR (Table-III): MS m/e (relative intensity) 670, 668, 666, 664, (M^+ 6, 18,25,12), 609(13), 608(24), 581(71), 374(100), 348(36). Anal. calcd.for $C_{31}H_{19}ClBr_2O_5$: C, 55.85, H, 2.85. Found: C, 55.95; H; 2.87 and (±) trans-3,7',- dibromo-8-chloro-10-hydroxy-10-(2-oxopropyl) spiro [11H-benzo [a] xanthen-11,2'(1' H)-naphtho [2,1-b] furan]-9 (10H)-one 14b (210 mg: 6.3%) m.p 262°C (benzene-hexane): UV ($CHCl_3$) 435(17,450), 418(18,400), 360(11,900), 344(13,800), 328(10,000), 293(11,700), 284(13,800) 256(32,000), 247(40,900): ^{13}C NMR (Table-III); MS m/e (relative intensity) 670, 668, 666, 664 (M^+ 5,16,26,12), 609(18), 608(27), 581(60), 374(100), 348(41). Anal calcd.for $C_{31}H_{19}ClBr_2O_5$, C, 55.85; H,2.85 Found: C, 55.47; H, 3.12 and 6,8'-Dibromo-2',3'-dihydro-4'-hydroxyspiro[naphthalene-1 (2H),1'(1H)phenalen]-2-one 9b (220mg, 9.4%), m.p. 272°C (EtoAchexane) (lit[12], 273°C).

c) Reaction of bromide 5b in diethyl ketone

The product obtained by the reaction of bromide 5b prepared from pyranyl ether 4b (3.2 gm; 0.01 mole), with tetrachlorocatechol (2.48 gm ; 0.01mole), in diethyl ketone (150 ml) containing anhydrous K_2CO_3 (2.07 gm,0.015 mole), was chromotographed. Elution with hexane:benzene (1:1) and benzene afforded pyranopyran 7b (40 mg; 1.3%) and spironaphthalenone 8b (220 mg; 9.4%). The fraction obtained by further elution with chloroform was separated into two fractions by repeated preparative TLC (benzene).

Fraction (i) was identified as (±) cis-3,7'-dibromo-8-chloro-10-hydroxy-10-(1-methyl-2-oxobutyl) spiro [11H-benzo[a]xanthen-11,2' (1'H) naphtho [2,1-b] furan]-9(10H)-one 13c (80 mg; 2.3%), m.p. 204-205°C (benzene-hexane); UV ($CHCl_3$) 426(19,400), 406(20,150), 358(13,200), 341(14,000), 328(10,000), 290(11,800) 280(15,350), 246(52,400); IR (nujol) 3330, 1700, 1660; ^1H NMR (270MHz, $CDCl_3$)1.14 (t, J = 7.2Hz,3H), 1.21 (d, J =7.1 Hz, 3H), 2.57-2.68 (pair of quartets, 1H), 2.98-3.10 (pair of quartets, 1H) (both together forming an ABq, J_{AB} = 18.7 Hz, 2H), 3.17(q, J = 7.1Hz, 1H), 3.62 (ABq, $\Delta\nu_{AB}$ = 106.3Hz, J_{AB} = 16.5Hz, 2H), 6.56 (s, 1H, D_2O exchangeable), 7.37 (d, J = 8.8 Hz, 1H), 7.48 (d, J = 9.0Hz, 1H), 7.55 (d, J = 9.0Hz,1H), 7.56 (dd, J = 8.8, 2.0Hz, 1H), 7.63 (dd, J = 9.1, 1.8Hz, 1H), 7.78-7.90 (m, 4H), 8.00 (d, J = 1.8Hz,1H), 8.03 (d, J = 1.7Hz,1H); ^{13}C NMR (Table-III); Anal. calcd. for $C_{33}H_{23}ClBr_2O_5$: C, 57.04; H,3.34. Found C, 57.44; H,3.36.

Table-III. ^{13}C NMR DATA (67.89 MHz, $CDCl_3$)

Compound				
13b	13c	14b	14c	14d
29.73(t)	7.56(q)	31.85(q)	7.96(q)	7.52(q)
32.15(q)	12.95(q)	37.32(t)	13.36(q)	13.60(q)
38.11(t)	35.22(t)	47.55(t)	34.16(t)	36.16(t)
82.80(s)	38.20(t)	80.39(s)	38.74(t)	39.10(t)
91.06(s)	43.07(d)	92.11(s)	49.60(d)	51.43(d)
104.59(s)	84.56(s)	104.24(s)	83.52(s)	81.94(s)
112.97(d)	92.01(s)	112.53(d)	92.66(s)	92.82(s)
114.65(s)	104.51(s)	114.69(s)	104.37(s)	105.39(s)
116.65(s)	113.07(d)	115.32(s)	112.26(d)	112.45(d)
117.68(d)	114.79(s)	117.47(s)	114.97(s)	114.67(s)
120.37(s)	117.11(s)	117.61(d)	115.33(s)	117.43(s)
121.93(d)	117.63(d)	117.80(s)	117.56(d)	117.77(d)
123.52(d)	120.33(s)	120.62(s)	118.07(s)	120.59(s)
124.25(d)	121.88(d)	122.62(d)	120.68(s)	122.02(d)
127.42(s)	123.48(d)	123.53(d)	122.52(d)	123.42(d)
128.93(s)	124.26(d)	124.44(d)	123.78(d)	124.49(d)
129.03(d)	127.45(s)	127.36(s)	124.50(d)	127.32(s)
129.86(d)	129.24(s)	129.17(s)	127.45(s)	129.11(s)
130.52(s)	130.06(d)	129.17(d)	129.15(s)	129.11(d)
131.04(d)	131.04(s)	130.62(d)	129.15(d)	130.58(d)
131.54(d)	131.51(d)	130.86(d)	130.63(d)	130.83(d)
132.04(s)	132.04(d)	131.13(d)	130.86(d)	131.16(s)
151.00(s)	132.63(s)	131.21(s)	131.10(d)	131.16(d)
156.66(s)	150.92(s)	131.72(d)	131.77(d)	131.72(d)
159.63(s)	156.20(s)	132.01(d)	131.92(d)	131.90(d)
188.62(s)	158.92(s)	132.08(s)	132.15(s)	132.28(s)
221.89(s)	190.17(s)	151.08(s)	151.06(s)	151.01(s)
---	217.84(s)	156.45(s)	156.20(s)	156.55(s)
---	---	159.22(s)	159.55(s)	159.75(s)
---	---	189.61(S)	188.67(s)	190.14(s)
---	---	206.17(s)	213.28(s)	212.04(s)

Fraction (ii) was separated into two compounds by repeated preparative TLC (methylene chloride) and identified as (±) trans-3,7'-dibromo-8-chloro-10-hydroxy-10-(1β-methyl-2-oxobutyl) spiro[11H-benzo[a] xanthen-11, 2' (1'H)-naphtho [2,1-b]furan]-9(10H)-one **14c** (200 mg; 6.0%): m.p. 240-242°C (chloroform hexane); UV ($CHCl_3$) 428(22,300), 410(23.000), 358(13,400), 340(15,600), 327(11,200), 290(14,300), 281(17,000), 256(40,800), 247(57,900), IR(nujol) 3410, 1700, 1655, ^1H NMR (270 MHz, $CDCl_3$) 1.04 (d, J = 7.2Hz, 3H), 1.20 (t, J = 7.1Hz, 3H), 2.58-2.88 (two pairs of quartets forming an ABq, J_{AB} = 18.9 Hz, 2H), 3.07 (q, J = 7.1 Hz, 1H), 3.71 (ABq, $\Delta\nu_{AB}$ = 203.7 Hz, J_{AB} = 15.6Hz, 2H) 4.93(s, 1H, D_2O exchangeable), 7.26(d, J = 8.9Hz, 1H), 7.32 (d, J = 8.8Hz, 1H), 7.49(dd, J = 8.8, 1.9Hz, 1H), 7.57(d, J = 9.1Hz, 1H), 7.67(dd, J = 8.9, 1.8Hz, 1H), 7.70(d, J = 9.1Hz, 1H), 7.87(s, 1H), 7.88(d, J = 8.8Hz, 1H), 7.971(d, J = 8.9Hz, 1H), 7.972(d, J = 1.9Hz, 1H), 8.02 (d, J = 1.8Hz, 1H); ^{13}C NMR (Table-III): Anal. calcd. for $C_{33}H_{23}ClBr_2O_5$: C, 57.04, H 3.34: Found: C, 56.82; H, 3.24. and (±) trans- 3,7'-dibromo-8-chloro-10-hydroxy-10-(1α-methyl-2-oxobutyl)spiro [11H-benzo[a] xanthen-11,2' (1'H)-naphtho [2,1-b]furan]-9(10H)-one **14d** (80mg; 2.3%), m.p. 263-265°C (chloroform-hexane): UV ($CHCl_3$) 428(20,750), 410(21,250), 359(13,250), 340(15,000), 327(10,450), 290(13,350), 282(15,900), 256(33,600), 245(62,200); IR(nujol) 3450, 1705,1655; ^1H NMR (270 MHz, $CDCl_3$) 0.85 (t, J = 7.1Hz, 3H), 1.37 (d, J = 6.9Hz, 3H), 2.36-2.51 (pair of quartets, 1H), 2.52-2.66(pair of quartets, 1H) (both together forming an (ABq, J_{AB} = 18.6Hz, 2H), 3.39(q, J = 6.9Hz, 1H), 3.72 (ABq, $\Delta\nu_{AB}$ = 229.4 Hz, J_{AB} = 15.7Hz, 2H) 4.46 (s, 1H, D_2O exchangeable), 7.33(d, J = 8.8Hz, 1H), 7.42(d, J = 8.8Hz, 1H), 7.50(dd, J = 8.8, 1.7 Hz, 1H), 7.58(d, J = 9.1Hz, 1H), 7.68(dd, J = 9.1, 1.9Hz, 1H), 7.73(d, J = 8.8Hz, 1H), 7.84(s, 1H), 7.88(d, J = 9.1Hz, 1H), 7.95(d, J = 9.1Hz, 1H), 7.98(d, J = 1.7Hz, 1H), 8.04(d, J = 1.9Hz, 1H); ^{13}C NMR (Table-III); Anal. calcd.for $C_{33}H_{23}ClBr_2O_5$: C, 57.04; H.3.34. Found C, 56.97; H, 3.25.

X-ray analysis of compound 14C

$C_{33}H_{23}ClBr_2O_5$, M_r = 694.8, Triclinic, P $\bar{1}$, a = 8.142(3), b = 11.797 (3), c = 16.481(4) Å, V = 1555.95 Å^3, α = 97.79(2), β = 95.66(2), γ = 93.60(3) , Z = 2, D_x = 1.491 Mgm^{-3}, λ (CuKα) = 1.5418 Å, μ = 36.8 mm^{-1}, F(000) = 696, T = 293 K. Final R = 0.086 for 3462 unique reflections with $I \geq 3\sigma(I)$.

The crystals suitable for X-ray diffraction were grown from chloroform and methanol solution by slow evaporation. Intensity data were collected on a CAD-4 diffractometer with Ni-filtered CuKα radiation using a crystal of dimensions 0.22 X 0.27 X 0.33 mm up to $\sin\theta/\lambda$ = 0.562 Å^{-1} using $\omega - 2\theta$ scan. Lorentz and polarisation corrections were applied. A total of 3673 reflections were measured for $0 \leq h \leq 8$, $-13 \leq k \leq 13$, $-18 \leq l \leq 18$ of which 3462 reflections have $I \geq 3\sigma(I)$.

The statistics for the normalised structure factors favours the space group P 1. The positions of bromine and chlorine atoms were located using direct methods (MULTAN 11/82 [18]) and Patterson syntheses. Successive weighted and difference Fourier synthesis revealed the positions of the rest of the non-H atoms. The hydrogen atoms were fixed from geometric considerations. The structure was refined using anisotropic temperature factors for non-H atoms and fixed isotropic temperature factors for hydrogen atoms. The final R = 0.086 and wR = 0.097. The residual electron density in the final difference Fourier was in between +1.24 and -1.38 e/Å^3.

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