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ONE POT SYNTHESIS OF POLYCYCLIC OXYGEN AROMATICS.PART III[1a]

MECHANISM OF FORMATION

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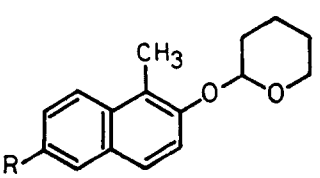
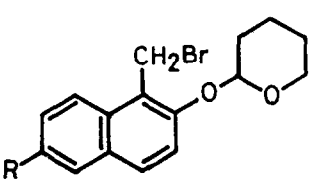
ABSTRACT: Reaction of 6-tert-butyl-1-bromomethyl-2-(2-tetrahydropyranyloxy)-naphthalene **2c** with tetrachlorocatechol (**TCC**) in acetone in presence of K_2CO_3 gave diastereomers **6c** and **7c**. A mechanism (Scheme-I) invoking the base[3] induced cleavage of the pyranyl ether **2** to 1,2-naphthoquinone-1-methide **8** as the first step has been postulated. The cleavage of the pyranyl ether linkage in **2** to give dimers **4** and **5** of 1,2-naphthoquinone-1-methide has been demonstrated with different bases. 1,2-Naphthoquinone-1-methide **8**, thus generated, undergoes Michael addition with **TCC** followed by elimination of chloride ions to give a diketone, which further undergoes aldolisation with acetone to give diastereomers **6** and **7**. Michael reaction of **8**, generated *in situ* from pyranyl ethers **2a-c**, with tetrabromocatechol (**TBC**) under similar reaction conditions gave the expected monobromo compounds **6h, 6i,6k,7m, 7n** and **7q**. The last step in the proposed mechanism, *viz.*, aldolisation has also been demonstrated using different ketonic solvents. Thus, reaction of **2a-c** with **TCC/TBC** in diethyl ketone/methyl ethyl ketone under similar reaction conditions gave the expected compounds **6** and **7**.

We have recently reported[1a] the formation of polycyclic oxygen aromatics **6a** and **7a** in the reaction of 1-bromomethyl-2-(2-tetrahydropyranyloxy)naphthalene **2a** with tetrachlorocatechol (**TCC**) in presence of K_2CO_3 and acetone. Structures of these types of compounds (**6b** and **7b**) have

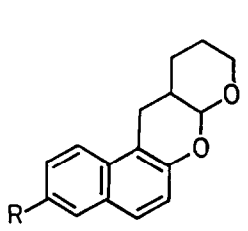


1a : R = H
1b : R = Br
1c : R = ^{t}Bu

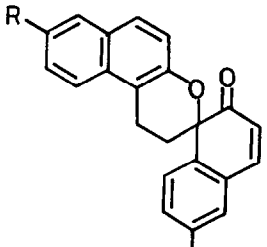


2a : R = H
2b : R = Br
2c : R = ^{t}Bu

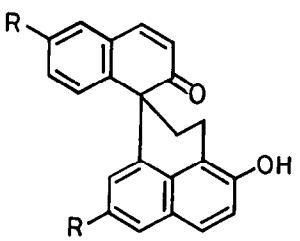
been confirmed by X-ray crystal structure analyses.[1a,1b] The sets of diastereomeric compounds could easily be differentiated[1a] by their characteristic ^{1}H and ^{13}C NMR signals (OH, $ArCH_2$ and $-CH_2-C=O$). When the reaction of 6-tert-butyl-1-bromomethyl-2-(2-tetrahydropyranyloxy)naphthalene **2c**[2] with **TCC** in acetone in presence of anhydrous K_2CO_3 was carried out, two diastereomers having spectral characteristics similar to those of **6a** and **7a** (Table - I) were obtained and these were assigned structures **6c** and **7c**. Similar diastereomeric products are also formed in the reaction of 2-bromomethyl-1-(2-tetrahydropyranyloxy)benzene with **TCC** in K_2CO_3 and acetone[4].



3a : R = H
3b : R = Br
3c : R = ^{t}Bu

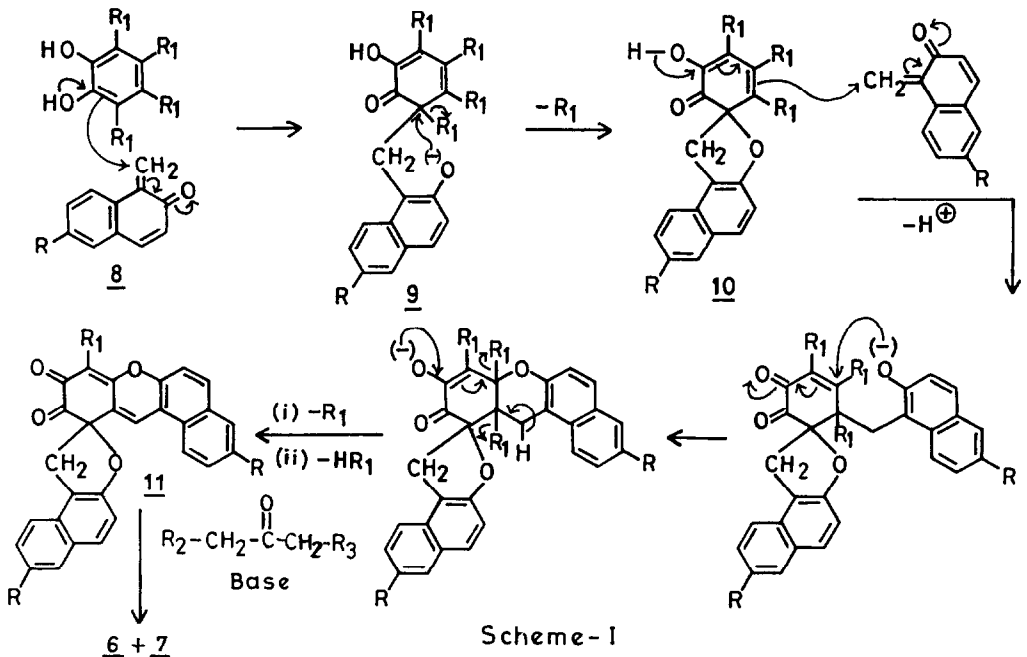


4a : R = H
4b : R = Br
4c : R = ^{t}Bu



5a : R = H
5b : R = Br
5c : R = ^{t}Bu

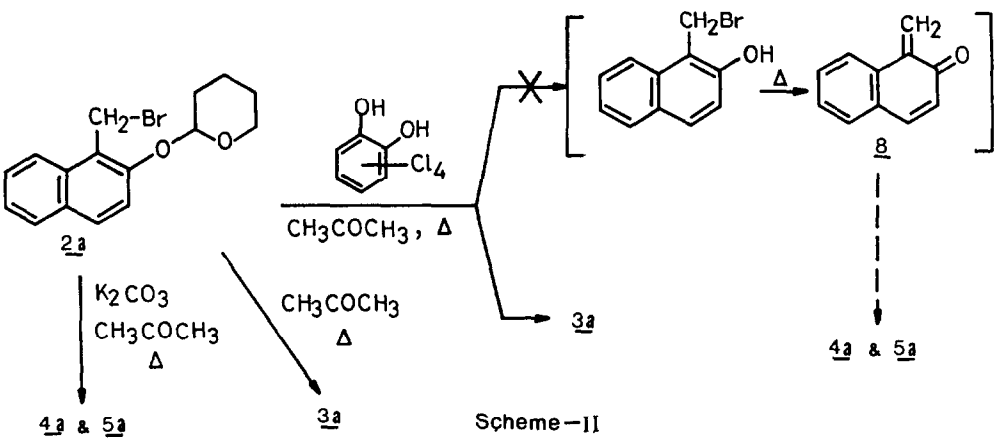
A probable mechanism of formation of the diastereomers **6** and **7** has been postulated (Scheme-I). Perhaps, two molecules of 1,2-naphthoquinone-1-methide **8**, initially generated, undergo Michael addition with **TCC** followed



Scheme-I

by stepwise removal of chloride ions to give the diketone **11**. Aldol condensation of the diketone with acetone gives the isomeric products.

Isolation of spironaphthalenones **4** and **5**,dimers of 1,2-naphthoquinone-1-methide (**8**), is a key evidence for the postulation of the cleavage of tetrahydropyranyl ether linkage in the bromide **2** under reaction conditions. As pyranyl ethers are sensitive to acids,[5] TCC present in the reaction mixture, was thought to be responsible for the cleavage to give 1-bromomethyl-2-naphthol which under thermal or base catalysed conditions could give **8** (Scheme-II). Thermolysis of 1-methoxymethyl-2-naphthol,[6] 1-hydroxymethyl-2-naphthol,[7] and 1-dimethylaminomethyl-2-naphthol[8] to quinone methide **8** are reported. However, refluxing bromide **2a** with TCC did not give **4a** and **5b**, but gave the known[9] pyranopyran **3a**. Thermal cleavage of pyranyl ether was ruled out on the basis of isolation of compound **3a** when bromide



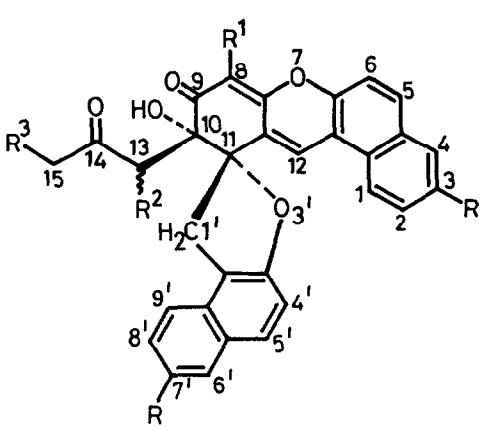
Scheme–II

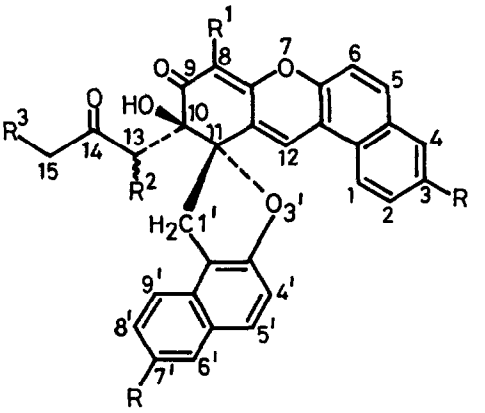
2a was refluxed in acetone. However, refluxing bromide **2a** in acetone in presence of K_2CO_3 yielded **4a** and **5a**. These studies revealed that the cleavage of tetrahydropyranyl ether linkage in the bromide **2a** to form quinone methide **8** is base induced. Isolation of compounds **4a** and **5a** in the reaction of **2a** with K_2CO_3-CH_3CN, Na_2CO_3-CH_3CN, $NaOCH_3$-CH_3CN and Et_3N-CH_3CN further supported this postulation. Formation of quinone methide could be the driving force for the unusual cleavage of pyranyl ether in **2a**[10] under basic conditions.

Addition of phenols to quinone methide is well established.[11] Michael addition of tetrachlorocatechol [C-3][12] to quinone methide **8** in presence of base could lead to **9** (Scheme-I). Cyclisation of the anion **9** by elimination of the chloride ion leads to **10**.[14] Further Michael addition of **10** to one more molecule of quinone methide **8** followed by expulsion of chloride ions leads to the diketone **11**. Aluminium oxide catalysed addition of acetone to o- and p- quinones to give acetonyl benzoquinols is known.[16] In the case of

substituted quinones, addition of acetone occurs preferentially at the more positive of the two carbonyls giving rise to only one of the two regio isomers. Accordingly, it can be presumed that the addition of acetone to diketone **11** takes place selectively on the unconjugated carbonyl carbon resulting in diastereomers **6** and **7**.

According to the proposed mechanism (Scheme-I), the reaction with tetrabromocatechol (**TBC**) instead of **TCC** should lead to the formation of isomeric compounds containing one bromine atom. In order to verify this, reaction of **2a** was repeated with **TBC** when spironaphthalenones **4a** and **5a**





6a : R = H, R_1 = Cl, R_2 = R_3 = H.
6b : R = Br, R_1 = Cl, R_2 = R_3 = H.
6c : R = ^{t}Bu, R_1 = Cl, R_2 = R_3 = H.
6d : R = H, R_1 = Cl, R_2 = α-CH_3, R_3 = CH_3
6e : R = H, R_1 = Cl, R_2 = H, R_3 = CH_3.
6f : R = Br, R_1 = Cl, R_2 = H, R_3 = CH_3
6g : R = ^{t}Bu, R_1 = Cl, R_2 = H, R_3 = CH_3
6h : R = H, R_1 = Br, R_2 = R_3 = H.
6i : R = R_1 = Br, R_2 = R_3 = H.
6j : R = R_1 = Br, R_2 = H, R_3 = CH_3.
6k : R = ^{t}Bu, R_1 = Br, R_2 = R_3 = H.

7a : R = H, R_1 = Cl, R_2 = R_3 = H.
7b : R = Br, R_1 = Cl, R_2 = β-CH_3, R_3 = CH_3
7c : R = ^{t}Bu, R_1 = Cl, R_2 = R_3 = H.
7d : R = H, R_1 = Cl, R_2 = α-CH_3, R_3 = CH_3.
7e : R = H, R_1 = Cl, R_2 = β-CH_3, R_3 = CH_3.
7f : R = H, R_1 = Cl, R_2 = β-CH_3, R_3 = H.
7g : R = H, R_1 = Cl, R_2 = H, R_3 = CH_3.
7h : R = Br, R_1 = Cl, R_2 = β-CH_3, R_3 = H.
7i : R = Br, R_1 = Cl, R_2 = H, R_3 = CH_3.
7j : R = Br, R_1 = Cl, R_2 = α-CH_3, R_3 = H.
7k : R = ^{t}Bu, R_1 = Cl, R_2 = β-CH_3, R_3 = H
7l : R = ^{t}Bu, R_1 = Cl, R_2 = H, R_3 = CH_3.
7m : R = H, R_1 = Br, R_2 = R_3 = H.
7n : R = R_1 = Br, R_2 = R_3 = H.
7o : R = R_1 = Br, R_2 = β-CH_3, R_3 = H.
7p : R = R_1 = Br, R_2 = H, R_3 = CH_3.
7q : R = ^{t}Bu, R_1 = Br, R_2 = R_3 = H.

along with diastereomers **6h** and **7m** with spectral characteristics (Table-I) similar to those of **6a** and **7a** were obtained. As expected,[17] the signal due to carbon atom attached to bromine in ^{13}C NMR is shifted upfield by 9.56 and 10.27 ppm in **6h** and **7m** relative to those in the corresponding chloro compounds.[1a] When this reaction was repeated with **2b** and 2c, the diastereomers **6i** & **7n**, and **6k** & **7q** were respectively formed, as apparent from their spectral (Table-1) characteristics.

As mentioned earlier, the last step in the postulated mechanism is the aldol condensation of acetone with diketone **11** generated in the reaction. Change of ketonic solvent in the reaction medium should result in the formation of corresponding aldol products. Accordingly, reaction of bromide **2a** with **TCC** in the presence of K_2CO_3 in diethyl ketone gave three someric compounds[18a] which analysed for $C_{33}H_{25}ClO_5$ and exhibited IR absorptions corrsponding to a hydroxy and two carbonyl groups. On the basis of the characteristic ^1H and ^{13}C NMR signals[1a] (Table-I), these compounds were tentatively assigned the structures **6d**, **7d** and **7e**.

Use of an unsymmetrical ketone as solvent in the above reaction should lead to the formation of products[18b] resulting by aldol condensation in two different ways. With this in view, reaction of bromide **2a** was carried out with **TCC** in methyl ethyl ketone in presence of K_2CO_3. The three isomeric compounds [MS: m/e 522 (M^+,^{35}Cl)] isolated were assigned the structures **6e**, **7f** and **7g** based on a detailed study of ^1H and ^{13}C spectral data (Table-I) and in analogy with those compounds isolated in acetone and diethyl ketone reactions. Similar reaction with bromides **2b** and 2c resulted in the formation of isomeric compounds **6f**, **7h**, **7i**, **7j**, and **6g**, **7k**, **7l** respectively. When reaction of bromide **2b** was carried out with **TBC** in methyl ethyl ketone in presence of K_2CO_3,three isomeric monobromo compounds to which structures **6j** , **7o**, and **7p** could be assigned were obtained.

It may be mentioned here that the postulated diketone intermediate **11** could not be isolated in any of the foregoing reactions. It was presumed that use of a non-ketonic solvent might stop the reaction at the diketone stage. However, when reaction of **2a** with **TCC** in acetonitrile containing K_2CO_3 was carried out, the only isolable products were the pyranopyran **3a** and dimers **4a** & **5a**

The generality as well as the probable mechanism of the base induced cleavage reaction of pyranyl ethers of 1-bromomethyl-2-naphthols 2 to give novel polycyclic oxygen aromatics has thus been demonstrated. Utility of this interesting one pot reaction in the synthesis of quinoline/isoquinoline analogues of these compounds is being further explored.

TABLE - I Characteristic Spectral Data

Compd. No.	^{1}H NMR (270 MHz, $CDCl_3$) Proton multiplicity: $ArCH_2$, AB_q ($\Delta\nu_{AB}$;J_{AB})Hz	HO, S	CH_2-CO-, AB_q ($\Delta\nu_{AB}$;J_{AB})Hz	CH_3 | CH-CO- q(J)Hz	^{13}C NMR (67.89 MHz, $CDCl_3$) Assignments of C_1', C_8, C_9, C_{13} and C_{14} carbons respectively	IR (Nujol) (cm^{-1}) ν_{OH}, >C=O and α,β-unsaturated >C=O	UV($CHCl_3$) (nm) λ_{max}
6c	3.60 (91.5;16.3)	6.75(br)	2.76 (129.5;16.7)	--	32.40,103.85,118.69 34.75,211.80	3340,1710, 1680	428(11,100),340(6,300) 280(7,250), 242(29.600)
7c	3.72 (203.0;15.5)	4.80	3.10 (146.1;14.5)	--	37.29,103.39,189.64 47.69, 206.23	3400,1705, 1685	435(19,500),341(12,350) 279(16,200),243(48,250)
6d	3.61 (110.7;16.0)	6.44(br)	--	3.25 (6.0)	--	3400,1720, 1680	430(8,450), 339(5,600) 267(13,250),251(44,250)
7d	3.76 (237.6;16.0)	4.51	--	3.42 (6.0)	--	3460,1710, 1670	431(13,400),344(15,100) 273(25,150),248(50,300)
7e	3.75 (205.2;16.0)	4.95	--	3.10 (6.0)	--	3450,1710, 1670	435(14,450),340(9,250) 267(20,600),249(67,000)
6e	3.64 (86.8;15.9)	6.88(br)	2.83-3.00 (m)	--	29.60,104.18,188.77 38.10,214.37	3340,1700, 1660	426(24,200),339(13,900) 289(10,300),242(48,200)
7f	3.72 (194.5;15.5)	4.67	--	3.01 (7.1)	--	3430,1705, 1660	432(18,250),338(8,950) 280(10,000),252(22,000)
7g	3.73 (198.2;15.6)	4.87	3.10 (143.6;14.6)	--	37.98,103.81,189.76 46.20,208.89	3430,1710, 1665	428(20,300),338(12,000) 287(10,700),242(33,200)
6f	3.61 (81.3;16.3)	6.88(br)	2.80-2.97 (m)	--	--	3330,1700, 1660	425(21,000),340(16,500) 280(17,100),247(50,250)
7h	3.69 (187.0;15.6)	4.67	--	2.99 (7.2)	38.76,103.74,189.18 51.52,210.40	3430,1700, 1660	426(19,600),341(13,400) 280(13,900),249(40,000)
7i	3.70 (193.1;15.0)	4.86	3.08 (143.6;15.0)	--	--	3420,1705, 1665	427(18,600),341(15.300) 280(15,250),249(36,750)

7j	3.71 (213.8;15.6)	4.40	--	3.29 (7.0)	--	3430,1710, 1660	427(10,250),340(8,200) 280(11,200),249(25,100)
6g	3.60 (93.0;16.2)	6.86(br)	2.82-2.99 (m)	--	33.70,103,87,188.69 37.99,212.80	3330,1700, 1660	430(17,000),340(10,450) 278(13,100),242(40,000)
7k	3.68 (202.4;15.4)	4.67	--	3.00 (6.7)	--	3340,1705, 1660	436(19,600),344(12,400) 282(14,600),244(48,000)
7l	3.70 (198.4;15.1)	4.85	3.08 (137.6;15.0)	--	--	3430,1700, 1665	433(16,750),341(11,600) 280(13,000),242(41,200)
6h	3.60 (108.0;16.0)	6.76(br)	2.76 (129.6;16.0)	--	29.00,94.20,189.00 38.40,212.00	3350,1710, 1680	425(7,250), 340(4,500) 271(10,250),249(36,700)
7m	3.75 (189.0;16.0)	4.80	3.10 (162.0;16.0)	--	37.39,93.00,190.01 47.80,206.10	3400,1710, 1675	426(10,600),342(5,300) 281(12,650),250(51,250)
6i	3.60 (81.0;16.4)	6.74(br)	2.74 (128.2;15.9)	--	--	3350,1710, 1660	429(14,100),342(11,100) 281(12,300),243(47,700)
7n	3.69 (191.4;15.4)	4.77	3.07 (142.0;14.8)	--	--	3410,1705, 1680	433(13,100),343(10,300) 282(11,200),244(43,400)
6j	3.60 (82.2;16.6)	6.89(br)	2.46-2.97 (m)	--	--	3340,1700, 1675	428(7,300), 341(6,950) 281(9,700), 243(44,400)
7o	3.67 (184.6;15.6)	4.65	--	2.97 (6.9)	--	3430,1710, 1680	433(9,900), 343(7.750) 282(11,100),244(51,100)
7p	3.69 (191.9;15.3)	4.83	3.07 (131.9;14.8)	--	--	3430,1700, 1665	431(13,000),342(11,200) 284(13,600),244(56,000)
6k	3.59 (92.5;16.5)	6.74(br)	2.76 (128.7;16.0)	--	32.56,93.99,188.95 34.76,212.40	3340,1710 1670	432(13,550),340(7,700) 291(6,800), 242(34,100)
7q	3.69 (202.4;15.5)	4.78	3.09 (143.0;14.4)	--	37.29,92.93,189.94 47.82,206.23	3410,1710 1675	436(15,200),341(9,700) 289(9.650), 242(36,350)

EXPERIMENTAL SECTION

All melting points are uncorrected. UV(nm) and IR (cm^{-1}) spectra were recorded on HITACHI Model 557 Double wave length/Double beam and Perkin-Elmer Model 781 spectrometers respectively. NMR spectra were recorded on a Varian T-60 (60 MHz) or a Jeol FX-90Q, 22.49 MHz (^{13}C) or a Bruker WH-270, 67.87 MHz (^{13}C) spectrometers with Me_4Si as internal standard (δ =0 ppm). MS (70 eV) were recorded on an Atlas CH-4 or a Jeol MS-DX 303 spectrometer fitted with a built-in direct inlet system. Analytical and preparative TLC were carried out using silica gel. Column chromatography was carried out using neutral/basic alumina. All Organic extracts were dried over anhydrous Na_2SO_4. Compounds (**6c-k** and **7c-q**) reported herein are racemic mixtures.

6-tert-Butyl-2-hydroxy-1-naphthaldehyde : To a mixture of 6-tert-butyl-2-naphthol[3] (10 gm, 0.05 mole) in ethanol (20 ml) and aq.NaOH (14.4 gm in 30 ml H_2O), $CHCl_3$ (6.1 ml) was added dropwise during 30 minutes maintaining the temp. at 70-80°C with constant stirring. Stirring was continued for one more hr by which time the sodium salt of phenolic aldehyde separated completely. Excess $CHCl_3$ and EtOH were distilled off. The solid was dissolved in water, the solution acidified with conc.HCl acid and extracted with ether (100 ml). The ether layer was washed with 10% aq.$NaHCO_3$ (2 x 30 ml), water (2 x 30 ml) and dried. Solvent was removed and purified by column chromatography (silica gel, hexane-benzene, 4:1) to give 6-tert-butyl-2-hydroxy-1-naphthaldehyde (5.24 gm,46%): m.p. 94°C (benzene-hexane); IR (nujol) 3098, 1668, 1620; ^1H NMR (60 MHz, $CDCl_3$) 1.4 (s, 9H), 7.00-8.02 (m, 5H), 10.76 (s, 1H), 12.99 (s, 1H, D_2O-exchangeable); MS; m/e 228 (M^+); Anal. calcd. for $C_{15}H_{16}O_2$: C, 78.94; H, 7.01. Found: C, 78.99; H. 7.11%.

6-tert-Butyl-1-methyl-2-naphthol : A mixture of amalgamated zinc, prepared from zinc (9.4 gm), and 6-tert-butyl-2-hydroxy-1-naphthaldehyde (5 gm, 0.05 mole) in ethanol (15.2 ml) containing water (6 ml) and conc.HCl acid (13.6 ml) was refluxed for 10 hrs and cooled. The solid residue was filtered and the filtrate was extracted with ether (2 x 50 ml). The ether extract was washed with 10% aq.$NaHCO_3$ (2 x 30 ml), water (2 x 30 ml) and dried. After removal of solvent, the residue was chromatographed (silica gel, benzene) to give 6-tert-butyl-1-methyl-2-naphthol (3.2 gm, 68%): m.p. 90°C (benzene-hexane); IR (nujol): 3410, 1620, 1600; ^1H NMR (60 MHz, $CDCl_3$) 1.30 (s, 9H), 2.43 (s, 3H), 4.72 (s, 1H, D_2O exchangeable), 6.81-7.81 (m, 5H); MS: m/e 214 (M^+); Anal. calcd. for $C_{15}H_{18}O$: C, 84.11; H, 8.41. Found: C, 83.75; H, 8.49%.

6-tert-Butyl-1-methyl-2-(2-tetrahydropyranyloxy)naphthalene (1c) : A solution of 6-tert-butyl-1-methyl-2-naphthol (5 gm) and dihydropyran (3.2 ml) in dry CH_2Cl_2 (80 ml) containing pyridinium-p-toluene sulfonate (584 mg) was stirred for 4 hrs at room temperature. The solution was washed with brine to remove catalyst, followed by ice-cold 10% aq.NaOH (2 x 40 ml), water (2 x 40 ml) and dried. The crude reaction mixture, after the removal of solvent and excess dihydropyran, was purified by column chromatography over basic alumina. Elution with hexane-benzene (1:1) gave the pyranyl ether **1c** (6.2 gm, 88.5%): m.p. 81°C (hexane); IR (nujol) 1620, 1600; ^1H NMR (60 MHz, $CDCl_3$) 1.40 (s, 9H), 1.52-2.04 (m, 6H), 2.52 (s, 3H), 3.40-4.02 (m, 2H), 5.36 (br.t, 1H), 6.96-7.92 (m, 5H); MS: m/e 298 (M^+); Anal. calcd. for $C_{20}H_{26}O_2$: C, 80.53; H, 8.72. Found: C, 80.17; H, 9.00%.

6-tert-Butyl-1-bromomethyl-2-(2-tetrahydropyranyloxy)naphthalene (2c) : A mixture of pyranyl ether **1c** (3.2 gm;0.0107 mole), N-bromo succinimide (**NBS**) (2.1 gm; 0.0118 mole) and dibenzoyl peroxide (29 mg; 0.0001 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% aq.NaOH (2 x 30 ml), water (2 x 30 ml) and dried.

The CCl_4 solution, concentrated to 1/4th of its original volume [IR(CCl_4) 1620, 1600; ^{1}H NMR (60 MHz, CCl_4), 1.36 (s, 9H), 1.50-2.15 (m, 6H), 3.4-4.15 (m, 2H), 4.98 (s, 2H), 5.48 (br.t, 1H), 7.00-8.04 (m, 5H)] and protected from light, was used in subsequent reaction, as attempts to purify resulted in decomposition.

Reaction of bromide 2a

a. **With TCC in acetone** : A solution of **2a**, prepared from pyranyl ether **1a**[1a] (0.61 gm; 0.0025 mole) was refluxed with **TCC** (0.62 gm, 0.0025 mole) in acetone (50 ml) for 24 hrs. The solvent was removed, residue dissolved in ether (50 ml), washed successively with 10% aq.NaOH (2 x 30 ml), water (2 x 30 ml) and dried. The solvent was removed and the resulting material was chromatographed. Elution with hexane-benzene (1:1) gave pyranopyran **3a** (115 gm; 19%): m.p. 77°c (lit.[9] m.p.78°C).

The same compound **3a** was obtained in the above experiment in the absence of **TCC**.

b. With different bases

(i) The product obtained by refluxing **2a**, prepared from **1a** (0.61 gm, 0.0025 mole), with anhydrous K_2CO_3 (0.52 gm, 0.0037 mole) in acetone (50 ml) for 24 hrs was chromatographed. Elution with benzene gave spironaphthalenone **4a** (80 mg; 20%): m.p. 142°C (lit.[19] m.p.141-142°C). Further elution with $CHCl_3$ gave hydroxy spironaphthalenone **5a** (65 mg; 16%): m.p.239-241° (lit.[20] m.p.242°C).

(ii) Reaction of **2a**, prepared from **1a** (0.61 gm) in CH_3CN (50 ml) containing K_2CO_3 (0.52 gm) gave **4a** and **5a** in 32% and 24% yield respectively. However, the same reaction in presence of Na_2CO_3-CH_3CN yielded much smaller yields (13% and 8%) of **4a** and **5a** respectively.

(iii) Reaction of **2a**,prepared from **1a** (0.61 gm) in CH_3CN (50 ml) containing NaOMe (0.16 gm) gave **4a** and **5a** in 38% and 25% yield respectively.

(IV) Reaction of **2a**, prepared from **1a** (0.61 g) in CH_3CN (50 ml) containing Et_3N (0.35 ml) gave **4a** and **5a** in 32% and 21% yield respectively.

c. With TCC in CH_3CN in presence of anhydrous K_2CO_3 : Reaction of **2a**, prepared from **1a** (1.21 gm; 0.005 mole), with **TCC** (1.24 gm, 0.005 mole) and K_2CO_3 (0.95 gm; 0.007 mole) in CH_3CN (75 ml), after usual workup and purification, gave pyranopyran **3a** (40 mg,3.4%), spironaphthalenones **4a** (170 gm; 21.5%) and **5a** (150 mg; 19%).

Reaction of bromide 2 with TCC/TBC in Ketonic solvents in presence of K_2CO_3

General Procedure: A solution of bromide **2** in CCl_4 (25 ml), prepared from pyranyl ether **1** after dilution with ketonic solvent (25 ml), was added to a vigorously stirred refluxing solution of **TCC** or **TBC** in Ketonic solvent (150 ml) containing anhydrous K_2CO_3 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 ether. After the removal of solvent, the residue was taken in ether (150 ml) and washed successively with water (4 x 50 ml), 10% aq.NaOH (4 x 50 ml), water (4 x 50 ml) and dried. Ether was removed and the residue chromatographed.

a. **Reaction of bromide 2c in acetone** : The product obtained by reaction of **2c**, prepared from **1c** (3.2 gm, 0.0107 mole), with **TCC** (2.66 gm, 0.0107 mole) and K_2CO_3 (2.22 gm; 0.016 mole) in acetone (150 ml) was chromato-

graphed. Elution with benzene gave spironaphthalenone **4c** (270 mg; 11.2%): m.p. 217°C (lit.[21] m.p.218°C) and cis-3-tert-butyl-7a,10,11,11a-tetrahydro-9H, 12H-naphtho[2,1-b]pyrano[3,2-e]pyran **3c** (30 mg; 0.9%): m.p. 132°C (benzene-hexane); IR (nujol) 1620, 1600. ^{1}H NMR (90 MHz, $CDCl_3$) 1.40 (s, 9H), 1.60-1.79 (m, 4H), 2.20-2.42 (m, 1H), 2.90 (dd, J = 16.9, 4.2 Hz, 1H), 3.21 (dd, J = 17.1, 6.2 Hz, 1H), 3.64-3.88 (m, 1H), 3.92-4.20 (m, 1H), 5.39 (d, J = 2.6 Hz, 1H), 7.08 (d, J = 8.8 Hz, 1H), 7.50-7.79 (m, 4H); MS: m/e 296 (M^+); Anal. calcd. for $C_{20}H_{24}O_2$; C, 81.08; H, 8.10. Found: C, 80.89; H, 8.07%.

The material obtained by further elution with $CHCl_3$ - EtOAc (19:1) was separated into three compounds by repeated PTLC ($CHCl_3$). The less polar compound was shown to be cis-3,7'-di-tert-butyl-8-chloro-10-hydroxy-10-(2-oxopropyl)spiro [11H-benzo[a]xanthen-11,2'(1'H)-naphtho[2,1-b] furan]-9(10H)-one **6c** (135 mg; 4.1%): m.p. 138-140°C (d) ($CHCl_3$-hexane); MS: m/e 620 (M^+); Anal. calcd. for $C_{39}H_{37}ClO_5$; C, 75.48; H, 5.96. Found: C, 75.31; H, 6.07%.

The medium polar compound was identified as trans-3,7'-di-tert-butyl-8-chloro-10-hydroxy-10-(2-oxopropyl)spiro[11H-benzo[a]xanthen-11,2'(1'H)-naphtho[2,1-b]-furan]-9(10H)-one **7c** (210 mg; 6.3%): m.p. 162-164°C (d) ($CHCl_3$-hexane); MS: m/e 620(M^+); Anal. calcd. for $C_{39}H_{37}ClO_5$; C, 75.48; H, 5.96. Found: C, 75.17; H, 6.10%.

The most polar compound was characterised as **5c** (225 mg; 7.8%): m.p.160°C (lit.[22], m.p.160-162°C).

b. Reaction of bromide 2a in diethyl ketone : The product obtained by reaction of **2a**, prepared from **1a**[18] (3.2 gm; 0.013 mole), with **TCC** (3.22 gm; 0.013 mole) and K_2CO_3 (2.69 gm; 0.019 mole) in diethyl ketone (150 ml) was chromatographed. Elution with benzene afforded **3a** (30 mg, 1.0%) and **4a** (250 mg; 12.3%). Further elution with $CHCl_3$-EtOAc (19:1) gave a mixture of compounds, which was separated into two fractions by PTLC ($CHCl_3$ - hexane, 9:1). Fraction (i) was identified as cis-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 **6d** (85 mg; 2.4%); m.p.158-160°C(d) ($CHCl_3$); MS:m/e 536(M^+); Anal. calcd. for $C_{33}H_{25}ClO_5$: C, 73.81; H, 4.69. Found : C, 73.61; H, 4.79%.

Fraction (ii) was further separated (PTLC) into two compounds. One of them was identified as trans-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 **7d** (95 mg; 2.7%): m.p. 178-180°C ($CHCl_3$-hexane); MS : m/e 536(M^+); Anal. calcd. for $C_{33}H_{25}ClO_5$: C, 73.81; H, 4.69. Found: C, 73.55; H, 4.72%. The other compound was identified as trans-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 **7e** (110 mg; 3.25%); m.p.188-190°C(d) ($CHCl_3$-hexane); MS : m/e 536(M^+); Anal. calcd. for $C_{33}H_{25}ClO_5$; C, 73.81; H, 4.69. Found : C, 74.01; H, 4.65%.

C. Reaction of bromide 2a in methyl ethyl ketone : The product obtained by reaction of 2a, prepared from **1a** (3.2 gm,0.013 mole), with **TCC** (3.22 gm, 0.013 mole) and K_2CO_3 (2.69 gm, 0.019 mole) in methyl ethyl ketone was chromatographed. Elution with benzene afforded **3a** (45 mg; 1.4%) and **4a** (250 mg; 12.3%). Further elution with $CHCl_3$ - EtOAc (19:1) gave a mixture of compounds, which was separated into three fractions by repeated PTLC ($CHCl_3$). Fraction (i) was identified as cis-8-chloro-10-hydroxy-10-(2-oxobutyl)spiro [11H-benzo[a]xanthen-11,2'(1'H)-naphtho[2,1-b]furan]-9(10H)-one **6e** (145 mg; 4.3%): m.p.278-279°C(d) ($CHCl_3$-hexane): MS: m/e 522 (M^+); Anal. calcd. for $C_{32}H_{23}ClO_5$: C, 73.49; H, 4.43. Found : C, 73.29; H,4.26%.

Fraction (ii) was separated into two compounds (PTLC). The first compound was identified as trans-8-chloro-10-hydroxy-10-(1β-methyl-2-oxopropyl)spiro[11H-benzo[a]xanthen-11,2'(1'H)-naphtho[2,1-b]furan]-9(10H)-one **7f** (80 mg; 2.45%); m.p. 268-270°C(d) ($CHCl_3$); MS: m/e 522(M^+); Anal. calcd. for $C_{32}H_{23}ClO_5$: C, 73.49, H, 4.43. Found: C, 73.75; H, 4.61%. The

other compound was the trans-8-chloro-10-hydroxy-10-(2-oxobutyl)spiro[11H-benzo[a]xanthen-11,2'(1'H)naphtho[2,1-b]furan]-9(10H)-one **7g** (140 mg;4.1%); m.p. 158-160°C ($CHCl_3$); MS : m/e 522(M^+); Anal. calcd. for $C_{32}H_{23}ClO_5$: C, 73.49; H, 4.43. Found: C, 73.18; H, 4.75%.

Fraction (iii) was identified as **5a** (90 mg; 4.4%).

d. Reaction of bromide 2b in methyl ethyl ketone : The product obtained by reaction of **2b**, prepared from **1b**[1a] (3.2 gm; 0.01 mole), with **TCC** (2.48 gm, 0.01 mole) and K_2CO_3 (2.07 gm; 0.015 mole) in methyl ethyl ketone (150 ml) was chromatographed.[3] Elution with benzene gave **3b** (40 mg; 1.3%); m.p.115°C (lit.[1a] 115-116°C) and **4b** (275 gm, 11.7%): m.p.176°C (lit.[23] 177°C). Further elution with $CHCl_3$ - EtOAc (19:1) gave a mixture of compounds which was separated into three fractions by PTLC ($CHCl_3$ - hexane, 4:1). Fraction (i) was identified as cis-3,7'-dibromo-8-chloro-10-hydroxy-10-(2-oxobutyl)spiro[11H-benzo[a]xanthen-11,2'(1'H)naphtho[2,1-b]furan]-9(10H)-one **6f** (145 mg;6.6%): m.p.249°C ($CHCl_3$-hexane); MS : m/e 678(M^+); Anal. calcd. for $C_{32}H_{21}ClBr_2O_5$: C, 56.45; H, 3.11. Found: C, 56.64; H, 2.97%.

Fraction (ii) was further separated into two compounds by PTLC ($CHCl_3$ - hexane, 4:1). One of them was identified as trans-3,7'-dibromo-8-chloro-10-hydroxy-10-(1β-methyl-2-oxopropyl)spiro[11H-benzo[a]xanthen-11,2'(1'H)-naphtho[2,1-b]furan]-9(10H)-one **7h** (75 mg; 3.4%): m.p. 243-245°C(d) ($CHCl_3$-hexane); MS : m/e 678(M^+); Anal. calcd. for $C_{32}H_{21}ClBr_2O_5$: C, 56.45; H, 3.11. Found: C, 56.62; H, 3.02%. The other was identified as trans-3,7'-dibromo-8-chloro-10-hydroxy-10-(2-oxobutyl)spiro[11H-benzo[a]xanthen-11,2'-(1'H)naphtho[2,1-b]furan]-9(10H)-one **7i** (100 mg; 4.5%): m.p. 198°C ($CHCl_3$-hexane); MS: m/e 678(M^+); Anal. Calcd. for $C_{32}H_{21}ClBr_2O_5$; C, 56.45; H, 3.11. Found : C, 56.23; H, 3.15%.

Fraction (iii) was identified as trans-3,7'-dibromo-8-chloro-10-hydroxy-10-(1α-methyl-2-oxopropyl)spiro[11H-benzo[a]xanthen-11,2'(1'H)-naphtho[2,1-b]furan]-9(10H)-one **7j** (20 mg; 1%); m.p.194-196°C ($CHCl_3$-hexane); MS : m/e 678(M^+); Anal. calcd. for $C_{32}H_{21}ClBr_2O_5$: C, 56.45; H, 3.11. Found : C, 56.12, H, 2.98%.

e. Reaction of bromide 2c in methyl ethyl ketone : The product obtained by reaction of **2c**, prepared from **1c** (3.2 gm; 0.0107 mole), with **TCC** (2.66 gm, 0.0107 mole) in methyl ethyl ketone (150 ml) containing K_2CO_3 (2.22 gm; 0.016 mole), was chromatographed. Elution with benzene gave **3c** (35 mg; 0.9%) and **4c** (280 mg; 13.1%). The fraction obtained by further elution with $CHCl_3$-EtOAc (19:1) was separated into three fractions by repeated PTLC ($CHCl_3$ - hexane, 4:1). Fraction (i) was characterised as cis-3,7'-di-tert-butyl-8-chloro-10-hydroxy-10-(2-oxobutyl)spiro[11H-benzo-[a]xanthen-11,2' (1'H) naphtho[2,1-b]furan]-9(10H)-one **6g** (130 mg; 3.8%): m.p.176°C(d) ($CHCl_3$-hexane); MS : m/e 634(M^+); Anal.calcd. for $C_{40}H_{39}ClO_5$: C, 75.70; H, 6.15. Found: C, 75.26; H, 6.14%.

Fraction (ii) was further separated into two compounds by PTLC ($CHCl_3$ -hexane, 9:1). One of them was identified as trans-3,7'-di-tert-butyl-8-chloro-10-hydroxy-10-(1β-methyl-2-oxopropyl)spiro[11H-benzo[a]xanthen-11,2'(1'H)naphtho[2,1-b]furan]-9(10H)one **7k** (85 mg; 2.5%): m.p.176°C(d) ($CHCl_3$-hexane): MS : m/e 634(M^+); Anal. calcd. for $C_{40}H_{39}ClO_5$: C, 75.70; H, 6.15. Found: C, 75.42; H, 6.30%. The other was identified as trans-3,7'-di-tert-butyl-8-chloro-10-hydroxy-10-(2-oxobutyl)spiro[11H-benzo[a]xanthen-11,2'(1'H)-naphtho[2,1-b]furan]-9(10 H)-one **7l** (190 mg; 5.6%); m.p.164°C(d) ($CHCl_3$-hexane); MS : m/e 634(M^+); Anal. calcd. for $C_{40}H_{39}ClO_5$: C, 75.70; H, 6.15. Found: C, 75.63; H, 6.37%.

Fraction (iii) was characterised as **5c** (170 mg; 7.5%).

f. Reaction of bromide 2a in acetone : The product obtained by reaction of **2a**, prepared from **1a** (3.2 gm; 0.013 mole), with **TBC** (5.50 gm; 0.013 mole) and K_2CO_3 (2.69 gm; 0.019 mole) in acetone (150 ml) was

chromatographed. Elution with benzene gave **3a** (30 mg, 1.0%) and **4a** (300 mg; 14.8%). The material obtained by further elution with $CHCl_3$ - EtOAc (19:1) was separated into three compounds by repeated PTLC ($CHCl_3$). The less polar compound was characterised as cis-8-bromo-10-hydroxy-10-(2-oxopropyl)spiro-[11H-benzo[a]xanthen-11,2'(1'H)naphtho[2,1-b]furan]-9(10H)-one **6h** (305 mg; 8.5%); m.p.205°C(d) ($CHCl_3$); MS : m/e 552(M^+); Anal.calcd. for $C_{31}H_{21}BrO_5$: C, 67.28; H, 3.82. Found : C, 66.90; H, 4.00%.

The medium polar compound was identified as trans-8-bromo-10-hydroxy-10-(2-oxopropyl)spiro[11H-benzo[a]xanthen-11,2'(1'H)naphtho[2,1-b]furan]-9(10H)-one **7m** (345 mg; 10.1%). m.p 198-200°C(d) ($CHCl_3$-hexane): MS : m/e 552(M^+); Anal. calcd. for $C_{31}H_{21}BrO_5$: C, 67.28; H, 3.82. Found : C, 67.10; H, 3.80%.

The most polar compound was the spironaphthalenone **5a** (200 mg, 9.9%).

g. **Reaction of bromide 2b in acetone** : The product obtained by reaction of **2b**, prepared from **1b** (3.2 gm; 0.01 mole), with **TBC** (4.22 gm; 0.01 mole) and K_2CO_3 (2.07 gm; 0.015 mole) in acetone (150 ml) was chromatographed. Elution with benzene gave **3b** (40 mg; 1.3%) and **4b** (280 mg; 12%). The material obtained by further elution with $CHCl_3$ - EtOAc (19:1), separated into three components by PTLC ($CHCl_3$). The least polar compound was characterised as cis-3,7',8-tribromo-10-hydroxy-10-(2-oxopropyl)spiro[11H-benzo[a]xanthen-11,2'(1'H)naphtho[2,1-b]furan]-9(10H)-one **6i** (280 mg;7.9%). m.p.268°C ($CHCl_3$-hexane); MS : m/e 710 (M^+); Anal. calcd.for $C_{31}H_{19}Br_3O_5$: C, 52.54; H, 2.68. Found : C, 52.44; H, 2.70%.

The medium polar compound was identified as trans-3,7',8-tribromo-10-hydroxy-10-(2-oxopropyl)spiro[11H-benzo[a]xanthen-11,2'(1'H)naphtho[2,1-b]-furan]-9(10H)-one **7n** (365 mg; 10.3%); m.p.228°C(d) ($CHCl_3$-hexane); MS : m/e 710(M^+); Anal. Calcd for $C_{31}H_{19}Br_3O_5$: C, 52.54; H, 2.68. Found: C, 52.09; H, 2.52%.

The most polar compound was the **5b** (240 mg; 10.3%) m.p.272°C (lit.[22] 273°C).

h. **Reaction of bromide 2b in methyl ethyl ketone** : The product obtained by reaction of **2b**, prepared from **1b** (3.2 gm; 0.01 mole), with **TBC** (4.22; 0.01 mole) and K_2CO_3 (2.07 gm; 0.015 mole) in methyl ethyl ketone (150 ml) was chromatographed. Elution with benzene afforded **3b** (30 mg; 0.9%) and **4b** (260 mg; 11.1%). Further elution with $CHCl_3$ - EtOAc (19:1) gave a mixture of compounds, which was separated into three fractions by repeated PTLC ($CHCl_3$ - hexane 4:1). Fraction (i) was identified as cis-3,7',8-tribromo-10-hydroxy-10-(2-oxobutyl)spiro[11H-benzo[a]xanthen-11,2'(1'H)naphtho[2,1-b]furan]-9(10H)-one **6j** (145 mg; 4.0%): m.p.150°C(d) ($CHCl_3$); MS: m/e 724(M^+); Anal. calcd. for $C_{32}H_{21}Br_3O_5$; C, 53.18; H, 2.90. Found: C, 53.34; H, 3.10%.

Fraction (ii) was separated into two compounds by PTLC ($CHCl_3$-hexane, 9:1). One of them was identified as trans-3,7',8-tribromo-10-hydroxy-10-(1β-methyl-2-oxopropyl)spiro[11H-benzo[a]xanthen-11,2'(1'H)naphtho[2,1-b]-furan]-9(10H)one **7o** (80 mg; 2.2%): m.p.165°C(d) ($CHCl_3$-hexane); MS: m/e 724(M^+); Anal.calcd. for $C_{32}H_{21}Br_3O_5$: C, 53.18; H, 2.90. Found : C, 52.75; H. 2.94%. The other compound was shown to be trans-3,7',8-tribromo-10-hydroxy-10-(2-oxobutyl)spiro[11H-benzo[a]xanthen-11,2'(1'H)naphtho[2,1-b]-furan]-9(10H)-one **7p** (195 mg; 5.4%): m.p.190°C ($CHCl_3$): MS : m/e 724(M^+); Anal. calcd. for $C_{32}H_{21}Br_3O_5$: C, 53.18; H, 2.90. Found: C, 53.02; H, 2.93%.

Fraction (iii) was the dimer **5b** (165 mg; 7.1%).

i. **Reaction of bromide 2c in acetone** : The product obtained by reaction of **2c**, prepared from **1c** (3.2 gm; 0.0107 mole), with **TBC** (4.52 g; 0.0107 mole) and K_2CO_3 (2.21 gm;0.016 mole) in acetone was chromatographed. Elution with benzene afforded **3c** (30 mg; 0.9%) and **4c** (250 mg, 11.2%). The material obtained by further elution with $CHCl_3$ - EtOAc (19:1) was separated into three components by PTLC ($CHCl_3$ - hexane, 9:1). The least

polar compound was shown to be cis-3,7'-di-tert-butyl-8-bromo-10-hydroxy-10-(2-oxopropyl)spiro[11H-benzo[a]xanthen-11,2'(1'H)naphtho[2,1-b]furan]-9(10H)-one **6k** (250 mg; 7.0%): m.p. 186°C(d) ($CHCl_3$-hexane); MS : m/e 666(M^+); Anal. calcd. for $C_{39}H_{37}BrO_5$: C, 70.48; H, 5.57. Found : C, 70.08; H, 5.55%.

The medium polar compound was identified as trans-3,7'-di-tert-butyl-8-bromo-10-hydroxy-10-(2-oxopropyl)spiro[11H-benzo[a] xanthen-11,2'(1'H)-naphtho[2,1-b]furan]-9(10H)-one **7q** (335 mg; 9.4%): m.p.181°C (d) ($CHCl_3$-hexane); MS : m/e 666(M^+); Anal. calcd for $C_{39}H_{37}BrO_5$; C, 70.48; H, 5.57. Found : C, 70.05; H, 5.70%.

The most polar compound was the dimer **5c** (220 mg, 9.3%).

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REFERENCES AND NOTES

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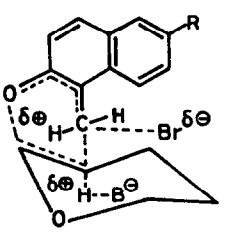

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