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A NEW AND EFFICIENT GENERAL METHOD FOR THE SYNTHESIS OF 2-SPIROBENZOPYRANS: FIRST SYNTHESIS OF CYCLIC ANALOGUES OF PRECOCENE I AND RELATED COMPOUNDS

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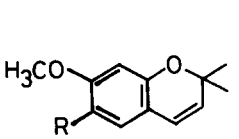
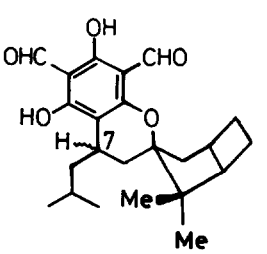
Abstract : A new synthesis of spirobenzopyran has been accomplished by Friedel- Crafts reaction of various m-dihydroxybenzenes and cycloalkylidene acetic acid in the presence of a Lewis acid.

Chromones, flavones and related heterocyclic compounds belonging to benzopyran family are widely distributed in nature and have been found to play an important role in a number of biological processes.[1-4] Precocene I and Precocene II are two anti-juvenile hormones possessing potential insecticidal activity.[5] Apart from these, a new class of compounds structurally related to benzopyrans has a spiro ring attached to the 2 position of the heterocyclic ring. Robustadial A and B are two representative natural products isolated recently from antimalarial Chinese herbal medicinal extract of Eucalyptus robusta leaves.[6]

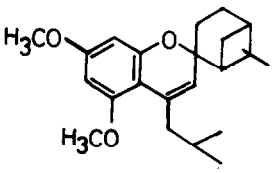




1a: R=H, Precocene I 2a, 7∝-H Robustadial A

1b: R=OCH3, Precocene II 2b, 7β-H Robustadial B

The presence of a spiro-ring system in these compounds coupled with photochromic properties exhibited[7] by spirochromenes make them attractive synthetic targets. A careful look at these structures indicates the presence of two or more hydroxy or alkoxy groups in the molecules.



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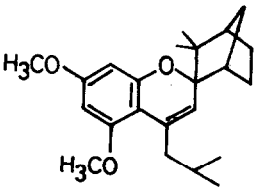

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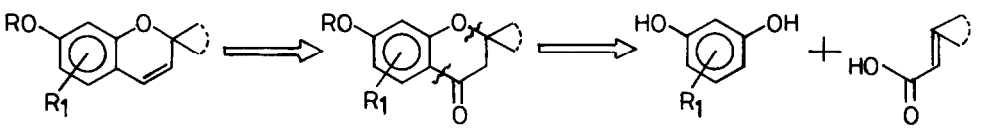
The synthesis of few spirochromenes which are important intermediates in the synthesis of analogues of (3) and (4) were reported by utilizing the methodology available in literature.[8] This route involves number of steps and a mixture of products is obtained. Another route recently described[9] yields spirochromenes in lower (35-38%) yields along with side products.

In order to circumvent these problems we sought to develop a more simple and general method for the synthesis of spirochromenes which is depicted in the Scheme I from retrosynthetic perspective.

Scheme I

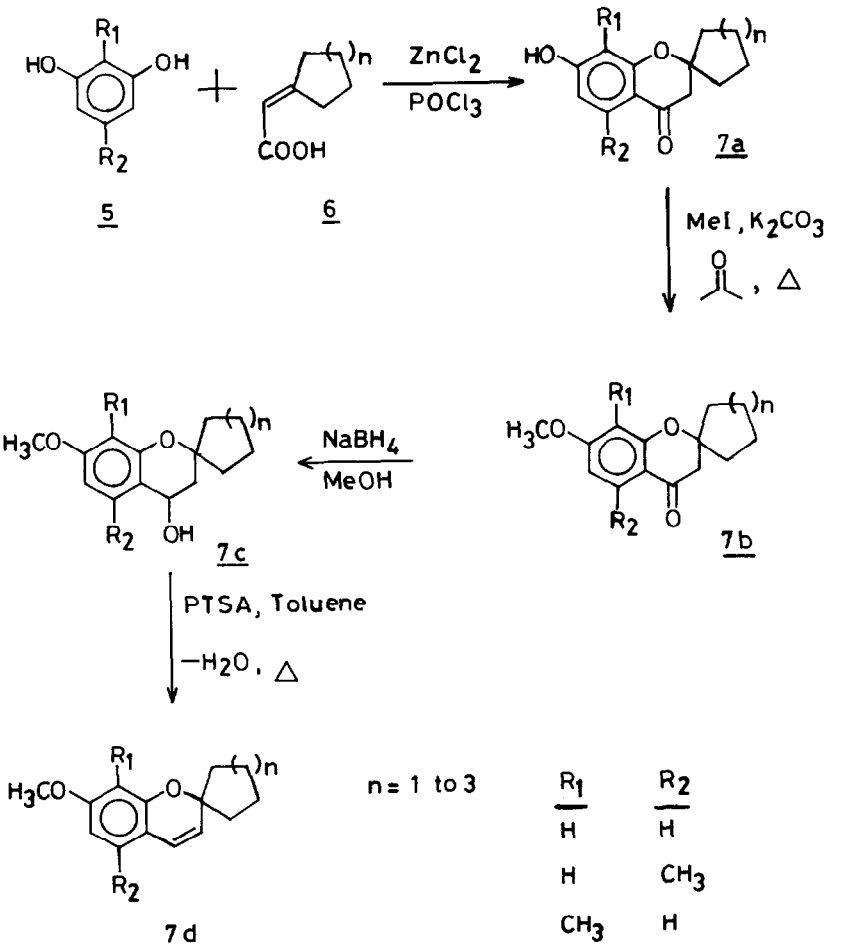


As per the envisaged route, resorcinol (5) was reacted with cyclohexylidene acetic acid (6a) in the presence of a Lewis acid i.e. $ZnCl_2$ + $POCl_3$. Only a single product (7a) was isolated in 68% yield. Its structure was established on the basis of spectroscopic data as well as its 2,4 dinitrophenylhydrazone derivative. IR spectrum of 7a clearly

showed the presence of a hydroxyl group at 3440 cm^{-1} and spiro benzopyran-4-one carbonyl at 1650 cm^{-1}. ^1H NMR confirmed the assigned structure with signal at δ2.6 as a singlet corresponding to methylene protons next to carbonyl group; the signal at δ7.71 as an AB pattern clearly established the regiochemistry of the product. Compound 7a was then converted to (7d) through the series of reactions depicted in the scheme II. It can thus be seen that this reaction sequence provides us a simple entry into 2-spiro benzopyran ring system with a facile synthesis of cyclohexyl analogue of precocene I.

In order to show the generality of this method, we have extended this reaction sequence to other m-dihydroxy benzenes having different substituents (Scheme II).

Scheme II



Having established the generality of the reaction as far as the m-dihydroxy substrates are concerned, we wanted to explore the possibility of increasing as well as decreasing the ring size of spiro ring system. To this extent, cycloheptylidene acetic acid (6b) and cyclopentylidene acetic acid (6c) were synthesized as reported in literature.[10]. Compound 6b on reaction with resorcinol under the conditions described above afforded a single product in 69% yield whose structure (8a) was deduced from its spectroscopic data. The latter was further transformed through a series of reactions to the cycloheptylidene analogue of Precocene I.

However, when cyclopentylidene acetic acid 6c was employed for condensation with resorcinol, the corresponding dihydroxy acylated product was obtained in 58% yield. It was then cyclized to the desired 2-spiro-benzopyran-4-(3H)-one by refluxing with sulphuric acid and ethanol. On the contrary 6c on reaction with orcinol under the same conditions afforded directly the cyclized product (9a) whose structure was confirmed on the basis of spectroscopic and analytical data.

In summary, we have shown a novel and versatile synthesis of 2-spiro benzopyrans by condensation of various dihydroxy benzenes with cycloalkylidene acetic acids. We have further converted the reaction products to cyclic analogues of Precocene I. Presently work on the synthesis of optically active 2-spiro benzopyrans as well as Robustadial A and B is in progress.

Experimental Section

Melting points (uncorrected) were determined using Toshniwal melting point apparatus. IR spectra were recorded on a Perkin-Elmer 781 spectrophotometer. ^1H NMR spectra were recorded on a Bruker AC-80 FT NMR. MS were obtained using Hewlett Packard GC/MS 5993 system. Elemental analysis was performed using Carlo Erba elemental analyser MOO-1106 instrument.

General procedure for the synthesis of 2-spiro-benzopyran-4(3H)-ones 7a/8a/9a:

A m-dihydroxy benzene (2 mmol), cycloalkylidene acetic acid (2 mmol), phosphoryl chloride (1.65 ml, 17.6 mmol) and zinc chloride (unfused, 0.380 gm, 2.8 mmol) were stirred at room temperature using $CaCl_2$ guard

tube for 6h. The reaction mixture was then poured over crushed ice. The solid that separated was filtered, washed with water, dried and recrystallised from diethyl ether/hexane as a colourless crystalline solid.

7a:R_1 =R_2 =H, n=2: 7-Hydroxy-spiro[2H-1-benzopyran-2,1'-cyclohexane]-4(3H)-one:

yield 68%; m.p. 168° C, IR(KBr) (ν,cm^{-1}):3440(-OH), 1650 (C=O), 1610, 1575 (Ar). ^{1}H NMR ($CDCl_3$) δ: 1.4-2 (br,m,10H), 2.59 (S,2H, $COCH_2$), 6.21 (br, S, 1H,OH), 6.42 (d, J=8.5Hz,Ar C6-H), 6.37(S, 1H,Ar C8-H) 7.71 (d, J=8.5Hz, 1H, Ar C5-H). Anal. Calc. for $C_{14}H_{16}O_3$: C, 72.41; H, 6.89. Found: C,72.49; H, 6.97.

7a:R_1 =H, R_2=CH_3, n=2: 7-Hydroxy-5-methyl-spiro[2H-1-benzopyran-2,1'-cyclohexane]-4(3H)-one:

yield 70%; m.p. 170° C, IR(KBr) (ν,cm^{-1}):3420(-OH), 1650 (C=O), 1590, 1570 (Ar). ^{1}H NMR ($CDCl_3$) δ: 1.4-2 (br,m,10H), 2.58 (S,3H, CH_3Ar), 2.62 (S,2H, $COCH_2$), 6.0 (br,S,1H,OH), 6.24 (S,2H,Ar C6 and C8-H). Anal. Calc. for $C_{15}H_{18}O_3$: C, 73.17; H, 7.31. Found: C,73.1; H, 7.22.

7a: R_1=CH_3, R_2=H, n=2: 7-Hydroxy-8-methyl-spiro[2H-1-benzopyran-2,1'-cyclohexane]-4(3H)-one:

yield 65%: m.p. 183° C, IR(KBr) (ν,cm^{-1}):3440(-OH), 1650 (C=O), 1605, 1585 (Ar). ^{1}H NMR ($CDCl_3$) δ: 1.4-2 (br,m,10H), 2.17 (S,3H, CH_3Ar), 2.65 (S, 2H,$COCH_2$), 3.98 (br,S,1H,OH), 6.47 (d, J=8.5Hz, 1H, Ar C6-H), 7.65 (d, J=8.5Hz, 1H, ArC5-H). Anal. Calc. for $C_{15}H_{18}O_3$: C, 73.17; H, 7.31. Found: C,73.21: H, 7.37.

8a: R_1=R_2=H. n=3: 7-Hydroxy-spiro[2H-1-benzopyran-2,1'-cycloheptane]-4(3H)-one:

yield69%; m.p. 152° C , IR(KBr) (ν,cm^{-1}): 3420(-OH), 1650(C=O), 1605, 1575 (Ar). ^{1}H NMR ($CDCl_3$) δ: 1.4-2 (br,m,12H), 2.66 (S,2H, $COCH_2$), 4.91 (br,S,1H,OH), 6.44(d, J=8.5Hz, Ar C6-H), 6.37 (S,1H,Ar C8-H),7.7(d,

J=8.5Hz, 1H, Ar C5-H). Anal. Calc. for $C_{15}H_{18}O_3$: C, 73.17; H, 7.31. Found: C,73.24; H, 7.34.

8a: R_1=H, R_2=CH_3, n=3: 7-Hydroxy-5-methyl-spiro[2H-1-benzopyran-2,1'-cycloheptane]-4(3H)-one:

yield 68%; m.p. 129° C, IR(KBr) (ν,cm^{-1}):3420(-OH), 1650 (C=O), 1600, 1580 (Ar). ^1H NMR ($CDCl_3$) δ: 1.4-2 (br,m,12H), 2.58 (S,3H, CH_3 Ar), 2.66(S,2H,$COCH_2$), 5.58 (br,S,1H,OH), 6.27 (S,2H,Ar C6 and C8-H). Anal. Calc. for $C_{16}H_{20}O_3$: C, 73.17; H, 7.31. Found: C,73.12; H, 7.26.

8a: R_1 =CH_3 , R_2 =H, n=3: 7-Hydroxy-8-methyl-spiro[2H-1-benzopyran-2,1'-cycloheptane]-4(3H)-one:

yield 66%; m.p. 160° C, IR(KBr) (ν,cm^{-1}):3240(-OH), 1650 (C=O), 1610, 1585 (Ar). ^1H NMR ($CDCl_3$) δ: 1.4-2 (br,m,12H), 2.14 (S,3H, CH_3 Ar), 2.67(S,2H,$COCH_2$), 4.61 (br,S,1H,OH), 6.48 (d, J=8.0Hz, 1H, Ar C6-H), 7.65 (d, J=8.0Hz, 1H, Ar C5-H). Anal. Calc. for $C_{16}H_{20}O_3$: C, 73.17; H, 7.31. Found: C,73.29; H, 7.40.

9a: R_1 =R_2 =H, n=1: 7-Hydroxy-spiro[2H-1-benzopyran-2,1'-cyclopentane]-4(3H)-one:

yield 60%; m.p. 178° C, IR(KBr) (ν,cm^{-1}):3220(-OH), 1655 (C=O), 1595 (Ar). 1595 (Ar). ^1H NMR ($CDCl_3$) δ: 1.4-2 (br,m,8H), 2.76 (S,2H, $COCH_2$), 5.96 (br,S,1H,OH), 6.42 (d,J=8.5Hz, 1H, Ar C6-H), 6.34 (S,1H,Ar C8-H), 7.72 (d, J=8.5Hz, 1H, Ar C5-H). Anal. Calc. for $C_{13}H_{14}O_3$: C, 71.56: H, 6.42. Found: C.71.61; H, 6.48.

9a: R_1=H, R_2=CH_3, n=1: 7-Hydroxy-5-methyl-spiro[2H-1-benzopyran-2,1'-cyclopentane]-4(3H)-one:

yield 58%; m.p. 140° C, IR(KBr) (ν,cm^{-1}):3400(-OH), 1650 (C=O), 1600, 1590 (Ar). ^1H NMR ($CDCl_3$) δ: 1.4-2 (br,m,8H), 2.66 (S,3H, CH_3 Ar), 2.75(S,2H,$COCH_2$), 6.24 (S, 2H,Ar C6-H and C8-H) Anal. Calc. for $C_{14}H_{16}O_3$: C, 72.41; H, 6.89. Found: C,72.52; H, 6.94.

Typical procedure for the synthesis of the methyl ether of 7a/8a:

A mixture of 2-spiro-benzopyran-4(3H)-one 7a/8a (1.07 mmol), anhydrous potassium carbonate (0.295 gm, 2.14 mmol), methyl iodide (0.303 gm, 0.13 ml, 2.14 mmol) in dry acetone (25 ml) was refluxed for 17 h. The solvent was evaporated and the residue was taken up in water (25 ml) and extracted three times with dichloromethane (3x20ml). The combined organic extracts were dried (Na_2SO_4) and evaporated to yield a pale yellow oil.

7b: $R_1=R_2=H$, n=2: 7-Methoxy-spiro[2H-1-benzopyran-2,1'-cyclohexane]-4(3H)-one:

yield 91%; pale yellow oil, IR(Neat) (ν,cm^{-1}): 1680 (C=O), 1610, 1575 (Ar). ^1H NMR ($CDCl_3$) δ: 1.4-2 (br,m,10H), 2.64 (S,2H, $COCH_2$), 3.83(S,3H,OCH_3), 6.50 (d, J=8.8Hz, 1H, Ar C6-H; m, 1H,Ar C8-H), 7.76(d, J=8.8Hz, 1H, Ar C5-H).

7b: $R_1=H$, $R_2=CH_3$, n=2: 7-Methoxy-5-methyl-spiro[2H-1-benzopyran-2,1'-cyclohexane]-4(3H)-one:

yield 88%; pale yellow oil, IR(Neat) (ν,cm^{-1}): 1670 (C=O), 1605, 1565 (Ar). ^1H NMR ($CDCl_3$) δ: 1.4-2 (br,m,10H), 2.59 (S,3H,CH_3 Ar), 2.62(S,2H, $COCH_2$), 3.80(S,3H,OCH_3), 6.3 (S, 2H Ar C6 and C8-H).

7b: $R_1=CH_3$, $R_2=H$, n=2: 7-Methoxy-8-methyl-spiro[2H-1-benzopyran-2,1'-cyclohexane]-4(3H)-one:

yield 90%; pale yellow oil, IR(Neat) (ν,cm^{-1}): 1680 (C=O), 1600 (Ar). ^1H NMR ($CDCl_3$) δ: 1.4-2 (br,m,10H), 2.14 (S,3H,CH_3 Ar), 2.62 (S,2H, $COCH_2$), 3.88(S,3H,OCH_3), 6.55 (d, J=8.8Hz, 1H, Ar C6-H), 7.78 (d, J=8.8Hz,1H,Ar C5-H).

8b: $R_1=R_2=H$, n=3: 7-Methoxy-spiro[2H-1-benzopyran-2,1'-cycloheptane]-4(3H)-one:

yield 86%; pale yellow oil, IR(Neat) (ν,cm^{-1}): 1675 (C=O), 1610, 1575

(Ar). ^{1}H NMR ($CDCl_3$) δ: 1.4-2 (br,m,12H), 2.67 (S,2H, $COCH_2$), 3.82(S,3H,OCH_3), 6.48 (d, J=8.5Hz,1H,Ar C6-H; m,1H, Ar C8-H), 7.73(d, J=8.5Hz, 1H, Ar C5-H).

8b: R_1=H, R_2=CH_3, n=3: 7-Methoxy-5-methyl-spiro[2H-1-benzopyran-2,1'-cycloheptane]-4(3H)-one:

yield 88%; pale yellow oil, IR(Neat) (ν,cm^{-1}): 1675 (C=O), 1605, 1570 (Ar). ^{1}H NMR ($CDCl_3$) δ: 1.4-2 (br,m,12H), 2.59 (S,3H,CH_3 Ar), 2.62 (S,2H, $COCH_2$), 3.81(S,3H,OCH_3), 6.31 (m, 2H,Ar C6 and C8-H).

8b: R_1 =CH_3,R_2=H, n=3: 7-Methoxy-8-methyl-spiro[2H-1-benzopyran-2,1'-cycloheptane]-4(3H)-one:

yield 90%: pale yellow oil, IR(Neat) (ν,cm^{-1}): 1675 (C=O), 1595, (Ar). ^{1}H NMR ($CDCl_3$) δ: 1.4-2 (br,m,12H), 2.14 (S,3H,CH_3 Ar), 2.65 (S,2H, $COCH_2$), 3.82(S,3H,OCH_3), 6.54 (d, J=8.0Hz, 1H, Ar C6-H), 7.73 (d, J=8.0Hz, 1H, Ar C5-H).

General procedure for the $NaBH_4$ reduction of 2-spiro-benzopyran-4(3H)-one 7c/8c:

Sodium borohydride (0.148 gm, 4 mmol) was added to a solution of 2-spirobenzopyran-4(3H)-one 7b/8b (2 mmol) in dry methanol (20 ml). The mixture was stirred for 3 h. at room temperature. The solvent was removed and the residue was taken up in water (20 ml) extracted with dichloromethane (3x20 ml). The combined organic extracts were dried and concentrated the viscous oil that separated was chromatographed over silica gel, using hexane/EtOAC (90:10) as eluent.

8c: R_1 =R_2 =H, n=2: 3,4-Dihydro-7-methoxy-spiro[2H-1-benzopyran-2,1'-cyclohexane]-4-ol:

yield 85%; colourless viscous oil, IR(Neat) (ν,cm^{-1}): 3380 (-OH), 1610, 1580 (Ar). ^{1}H NMR ($CDCl_3$) δ: 1.4-2 (br,m,12H), 3.76 (S,3H,OCH_3), 4.81 (T,1H, CHOH), 6.48(d, J=8.5Hz,1H, Ar C6-H; m,Ar C8-H), 7.27 (d, J=8.5Hz, 1H, Ar C5-H).

8c: R_1 =H, R_2 =CH_3 , n=2: 3,4-Dihydro-7-methoxy-5-methyl-spiro[2H-1-benzopyran-2,1'-cyclohexane]-4-ol:

yield 87%; colourless viscous oil, IR(Neat) (ν,cm^{-1}): 3360 (-OH), 1610, 1590 (Ar). ^{1}H NMR ($CDCl_3$) δ: 1.4-2 (br,m,12H), 2.36 (S,3H,CH_3Ar), 3.75 (S,3H, OCH_3), 4.96 (q, 1H, CHOH), 6.38, 6.42 (2xd, 2H, Ar C6 and C8-H).

8c: R_1 =CH_3 , R_2 =H, n=2: 3,4-Dihydro-7-methoxy-8-methyl-spiro[2H-1-benzopyran-2,1'-cyclohexane]-4-ol:

yield 85%; colourless viscous oil, IR(Neat) (ν,cm^{-1}): 3360 (-OH), 1610, 1585 (Ar). ^{1}H NMR ($CDCl_3$) δ: 1.4-2 (br,m,12H), 2.10 (S,3H,CH_3 Ar), 3.8 (S,3H, OCH_3), 4.85(q, 1H, CHOH), 6.49 (d, J=8.0Hz, 1H, Ar C6-H), 7.23 (d, J=8.0 Hz, 1H, Ar C5-H).

9c: R_1 =R_2 =H, n=3 : 3,4-Dihydro-7-methoxy-spiro[2H-1-benzopyran-2,1'-cycloheptane]-4-ol:

yield 84%; colourless viscous oil, IR(Neat) (ν,cm^{-1}): 3360 (-OH), 1620, 1580 (Ar). ^{1}H NMR ($CDCl_3$) δ: 1.4-2 (br,m,14H), 3.77 (S,3H,OCH_3), 4.82 (T,1H, CHOH), 6.43(d, J=8.0Hz, 1H, Ar C6-H; m,Ar C8-H), 7.28 (d, J=8.0Hz, 1H, C5-H).

9c: R_1 =H,R_2 =CH_3 , n=3: 3,4-Dihydro-7-methoxy-5-methyl-spiro[2H-1-benzopyran-2,1'-cycloheptane]-4-ol:

yield 88%; m.p. 79° C, IR(KBr) (ν,cm^{-1}): 3340 (-OH), 1610, 1585 (Ar). ^{1}H NMR ($CDCl_3$) δ: 1.4-2 (br,m,14H), 2.38 (S,3H,CH_3Ar), 3.74 (S,3H,OCH_3), 4.85(q, 1H, CHOH), 6.35 (2xd, 2H, Ar C6 and C8-H).

9c: R_1 =CH_3, R_2 =H, n=3: 3,4-Dihydro-7-methoxy-8-methyl-spiro[2H-1-benzopyran-2,1'-cycloheptane]-4-ol:

yield 85%; colourless viscous oil, IR(Neat) (ν,cm^{-1}): 3360 (-OH), 1615, 1595 (Ar). ^{1}H NMR ($CDCl_3$) δ: 1.4-2 (br,m,14H), 2.08 (S,3H,CH_3Ar), 3.81 (S,3H, OCH_3), 4.81(q, 1H, CHOH), 6.52 (d, J=8.0Hz, 1H, Ar C6-H), 7.25 (d, J=8.0Hz, 1H, Ar C5-H).

Procedure for the synthesis of spiro 2H-1-benzopyran 7d/8d:

A mixture of 2-spiro-benzopyran-4-ol 7c/8c (1.048 mmol) and p-toluene sulphonic acid (12 mgs, 0.063 mmol) in toluene (50 ml) was refluxed for 5h. with azeotropic removal of water. The reaction mixture was washed with $NaHCO_3$ solution, dried (Na_2SO_4) and removal of solvent yielded a pale yellow viscous oil which was purified by column chromatography over silica gel, using hexane/EtOAC (99:1) as eluent.

7D: R_1=R_2=H, n=2: 7-Methoxy-spiro[2H-1-benzopyran-2,1'-cyclohexane].

yield 87%; colourless viscous oil, IR(Neat) (ν,cm-1): 1635 (CH=CH), 1620, 1570 (Ar). ^{1}H NMR ($CDCl_3$) δ: 1.4-2 (br,m,10H), 3.77 (S,3H,OCH_3), 5.51 (d, J=9.6Hz, 1H, C3-H), 6.28 (d, J=9.6Hz, 1H, C4-H), 6.34 (d, J=8Hz, 1H, Ar C6-H), 6.42 (S, 1H, Ar C8-H), 6.85 (d, J=8Hz, 1H, Ar C5-H). MS : (m/z, 70ev) = 230 (M^+).

7D: R_1=H, R_2=CH_3, n=2: 7-Methoxy-5-methyl-spiro[2H-1-benzopyran-2,1'-cyclohxane].

yield 84%; pale yellow oil, IR(Neat) (ν,cm-1): 1635 (CH=CH), 1610, 1575 (Ar). ^{1}H NMR ($CDCl_3$) δ: 1.4-2 (br,m,10H), 2.23 (S,3H,CH_3 Ar), 3.73 (S,3H,OCH_3), 5.51(d,J=10Hz,1H,C3-H), 6.26 (S,2H, Ar C6 and C8-H), 6.41 (d, J=10Hz, 1H, C4-H). MS : (m/z, 70ev) = 244 (M^+).

7D: R_1 =CH_3,R_2=H, n=2: 7-Methoxy-8-methyl-spiro[2H-1-benzopyran-2,1'-cyclohexane].

yield 82%; pale yellow solid, m.p. 58° C; IR(KBr): (ν,cm^{-1}): 1640 (CH=CH), 1610, 1580 (Ar). ^{1}H NMR ($CDCl_3$) δ: 1.4-2 (br,m,10H), 2.18 (S,3H,CH_3 Ar), 3.79 (S,3H,OCH_3), 5.45 (d, J= 9.6Hz, 1H,C3-H), 6.28 (d, J=9.6Hz,1H, C4-H), 6.35 (d, J=8Hz, 1H, Ar C6-H), 6.76 (d, J=8Hz, 1H, Ar C5-H). Anal. Calc. for $C_{16}H_{20}O_3$ C, 78.68 H, 8.19 Found C,78.74, H,8.24 MS : (m/z, 70ev) = 244 (M^+).

8D: R_1=R_2=H, n=3: 7-Methoxy-spiro[2H-1-benzopyran-2,1'-cycloheptane].

yield 82%; colourless viscous oil, IR(Neat) (ν,cm^{-1}): 1635 (CH=CH), 1615, 1580 (Ar). ^1H NMR ($CDCl_3$) δ: 1.4-2 (br,m,12H), 3.77 (S,3H,OCH_3), 5.53 (d, J=9.6Hz, 1H, C3-H), 6.30(d,J=9.6Hz,1H,C4-H), 6.35 (d,J=8Hz,1H,Ar C6-H), 6.42(S,1H,Ar C8-H), 6.85(d,J=8Hz,1H Ar C5-H). MS :(m/z, 70 ev) = 244 (M^+).

8D: R_1=H, R_2=CH_3, n=3: 7-Methoxy-5-methyl-spiro[2H-1-benzopyran-2,1'-cycloheptane].

yield 85%; colourless viscous oil, IR(Neat) (ν,cm^{-1}): 1635 (CH=CH), 1610, 1575 (Ar). ^1H NMR ($CDCl_3$) δ: 1.4-2 (br,m,12H), 2.24 (S,3H,CH_3 Ar), 3.77 (S,3H,OCH_3), 5.53(d, J=10Hz, 1H,C3-H), 6.25 (S, 2H, Ar C6 and C8-H) 6.42 (d, J=10 Hz, 1H, C4-H). MS : (m/z, 70ev) = 258 (M^+).

8D: R_1=CH_3, R_2=H, n=3: 7-Methoxy-8-methyl-spiro-[2H-1-benzopyran-2,1'-cycloheptane].

yield 87%; colourless viscous oil, IR(Neat) (ν,cm^{-1}): 1640 (CH=CH), 1610, 1590 (Ar). ^1H NMR ($CDCl_3$) δ: 1.4-2 (br,m,12H), 2.12 (S,3H,CH_3 Ar), 3.79 (S,3H,OCH_3), 5.56(d, J=9.6Hz,1H,C3-H), 6.29 (d, J=9.6Hz, 1H,C4-H), 6.37(d,J=8Hz,1H,Ar C6-H), 6.78 (d, J=8Hz,1H,Ar C5-H). MS: (m/z, 70ev) = 258 (M^+).

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