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NOVEL "ONE-POT" PREPARATION OF TETRAHYDRO-BENZODIPYRAN-4-ONES. APPLICATION TO THE SYNTHESIS OF PRECOCENE ANALOGUES WITH CONDENSED DIHYDROPYRAN RINGS

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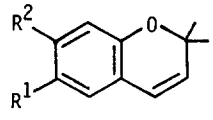
Abstract—A novel one-pot preparation of tetrahydrobenzodipyran-4-ones **5** and **6** involving the sequential condensation of resorcinols **7** with 3,3-dimethylacrylic acid (**8**) and 1,3-dichloro-3-methylbutane (**10**) in the presence of methanesulphonic acid (which acts as solvent and catalyst) and further conversion of tetrahydrobenzodipyran-4-ones to the corresponding dihydrobenzodipyrans **3** and **4**, which are precocene analogues, is described.

Since the isolation of precocenes I and II (**1** and **2**) from *Ageratum houstonianum*,[1] several analogs have been synthesized in different laboratories[2] to establish insect anti-juvenile hormone (AJH) activity structure relationships for potential application in insect control.

These studies have shown that the presence of a C-7 alkoxy substituent in the 2H-chromene skeleton is an important requirement to elicit AJH activity. However, results of precocene metabolism in different insect species revealed that cleavage at this group is one of the detoxification mechanisms observed.[3] Accordingly, we anticipated that possible enhancement of the AJH activity could follow from prevention of such a cleavage, by building up of steric hindrance at this C-7 site.

Putative candidates to achieve this aim were dihydrobenzodipyrans **3** and **4**, in which a dihydrobenzopyran ring is formed between that position and C-6 or C-8. Obvious intermediates for preparation of **3** and **4** were the corresponding tetrahydrobenzodipyran-4-ones **5** and **6**, which by LAH reduction and dehydration would easily afford the desired compounds. A preliminary literature search, however, revealed that the synthesis of such condensed systems, with different functionalization in each one of the two pyran rings, had not been reported heretofore.

In the present paper, we describe a one-pot procedure for preparation of compounds **5** and **6**, which implies a combination of two methods, recently developed in our laboratory, for the synthesis of 2,2-dimethylchroman-4-ones[4] and 2,2-dimethylchromans.[5] As shown in Scheme 1, this novel procedure involves the sequential condensation of an appropriate resorcinol **7** with 3,3-dimethylacrylic acid (**8**), followed by chromanylation of the resulting 7-hydroxychroman-4-one **9** with a prenylating reagent, such as 1,3-dichloro-3-methylbutane (**10**). Both reactions were carried out in methanesulphonic acid,



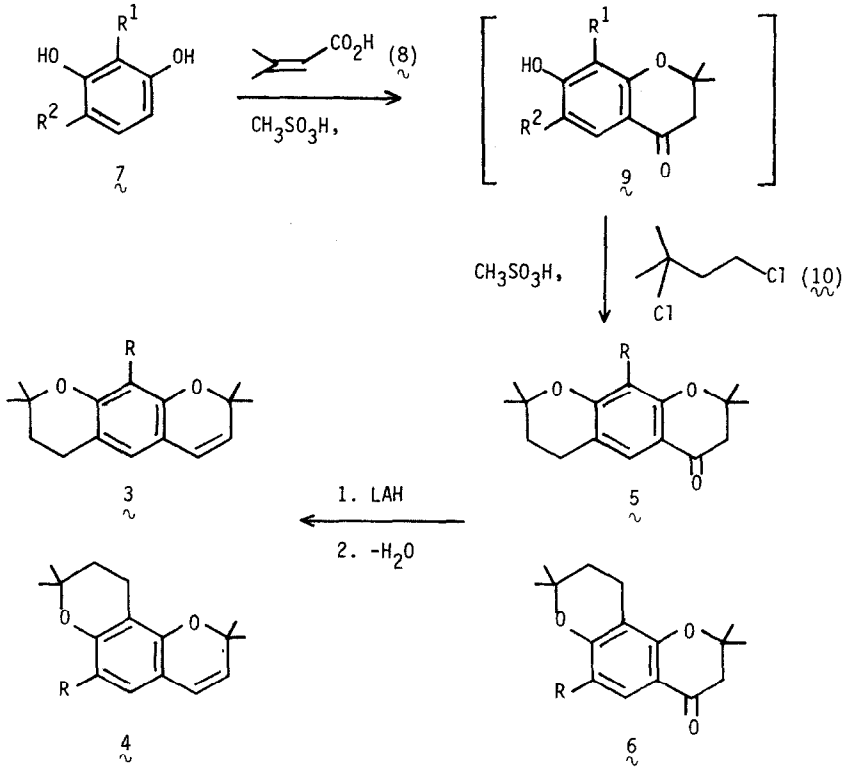
1: $R^1 = H$; $R^2 = OCH_3$

2: $R^1 = R^2 = OCH_3$

which performed a dual role as solvent and catalyst. Selection of this sequence was dictated by previous experience in which we had observed regiospecific acylation at C-6 position of resorcinols by treatment with **8**, whereas mixtures of isomeric chromans were formed in the reaction of these compounds with **10** in the presence of nickel bis(acetylacetonate) as catalyst.

A preliminary study of the above sequence was carried out with resorcinol **7a** to optimize reaction conditions. Condensation of **7a** with **8** in methanesulphonic acid for 30 min at 70° afforded an almost quantitative conversion to **9a** (GC monitoring) which, without isolation, was treated with 20% molar excess of **10** maintaining the above reaction conditions. GC monitoring of the reaction course revealed the progressive disappearance of **9a** and the simultaneous occurrence of two peaks at longer retention times. After 1 h, 20% of unreacted **9a** was recovered from the acid fraction, whereas from the neutral part, a 66% yield of a 1:4 isomeric ratio of tricyclic ketones **5a** and **6a** was isolated after separation of overalkylation products thereof. Purification of this mixture by preparative TLC on silicagel afforded pure **5a**, m.p. 86–87° and **6a**, m.p. 117–118°. Assignation of both structures was easily carried out by comparative study of the corresponding ^1H NMR spectra. Linear condensed ketone **5a** exhibited two separated singlets at δ 6.38 and 7.62 in the aromatic region, whereas angular condensed ketone **6a** showed an AB system at δ 6.38 and 7.62 with a $J = 9$ Hz. A detailed investigation of the overalkylated products was not pursued but the approximate structure of these compounds was inferred from comparison of the relative areas of prenyl and aromatic proton absorptions in the corresponding ^1H NMR spectra.

The use of a larger excess of **10** or longer reaction times in the second step of the above sequence, reduced the amount of unreacted **9a**, with concomitant increase of the quantity of over-alkylation products and no substantial improvement in the yield of the desired compounds. On the other hand, replacement of **10** by 2-methylbut-3-en-2-ol as prenylating reagent gave only 40% yield of a 1:2/**5a**:**6a** isomeric ratio and no detectable amount of over-alkylated products after 24 h. To prove that a kinetically preferred over-alkylation reaction could account for the different isomeric ratios obtained with both prenylating reagents, a 1:1 mixture of **5a**:**6a** was



Scheme 1.

treated with **10** for 1 h at 70°. After this time, the original equimolecular ratio of ketones had been transformed into a 9:91 ratio (GC analysis), substantiating an overalkylation preference for linear ketone **5a**, in agreement with the previously observed results.

As shown in Table 1, only one of tetrahydrobenzodipyran-4-ones **5** or **6** was formed when 2- or 4-substituted resorcinols were used as starting materials. On the other hand, better overall yields (80–86%) could be obtained by using four fold molar excess of **10** for 2 h at 70° in the second step of the above sequence, due to the blockage of the possible sites of over-alkylation reactions in these compounds.

Ketone **6f** was obtained in only 42% yield under the standard conditions and the corresponding demethylated compound was present in the crude acid material as shown by recovery of a further 18% upon treatment of this crude with $CH_3I/Na_2CO_3/DMF$ followed by distillation of the methylated residue. Shortening of the addition time of **10** to 0.5 h improved the result of the direct isolation of **6f** to 66% (20% of the intermediate **9f** was recovered from the acid fraction in this case).

In addition, tetracyclic ketone **13** was obtained in a 73% overall yield when the same basic procedure was assayed on phloroglucinol (**11**), using longer reaction times to achieve good transformation of **11** to **12**. This is

Table 1. One-pot conversion of substituted resorcinols into tetrahydrobenzodipyran-4-ones[a]

Starting material	Products	Isolated yield (%)
7a (R^1= R^2= H)	(**5a** + **6a**) (R= H)	66 [b]
7b (R^1= CH_3; R^2= H)	**5b** (R= CH_3)	86
7c (R^1= C_2H_5; R^2= H)	**5c** (R= C_2H_5)	81
7d (R^1= OH; R^2= H)	**5d** (R= OH)	80
7e (R^1=H; R^2= C_2H_5)	**6e** (R= C_2H_5)	83
7f (R^1= H; R^2= OCH_3)	**6f** (R= OCH_3)	66

[a] See the Experimental Section for a general procedure. [b] The 1:4/**5a**:**6a** mixture isolated in this case was separated by preparative TLC (See Experimental Section).

an excellent result taking into account the formation of three new rings in a two step one-pot operation (Scheme 2).

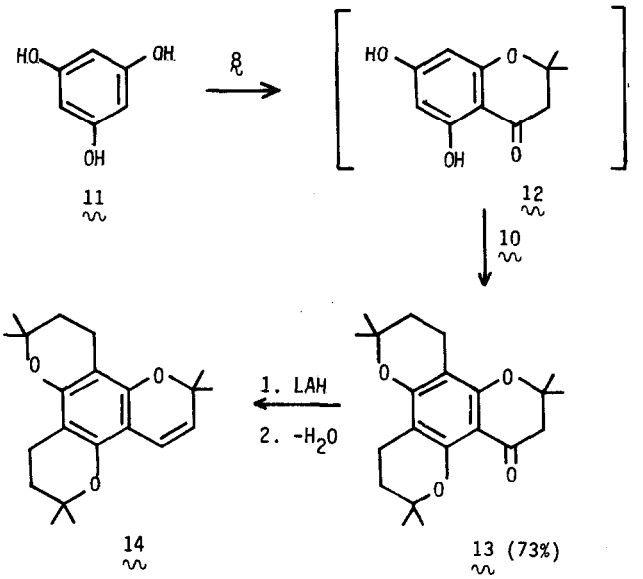
Finally, the conversion of tetrahydrobenzodipyran-4-ones to the corresponding precocene analogs was carried out with good yields by LAH reduction of the carbonyl group followed by dehydration in acid media[2i] (see Table 2). The structures of dihydrobenzodipyrans **3** and **4** were confirmed by their spectral and analytical data; an AB system in the NMR (δ 5.3–6.6 region) of **3** and **4** due to the protons of the newly formed double bond is characteristic of 2,2-dimethylchromenes. Similarly, ketone **13** afforded under the same reaction conditions the tetracyclic derivative **14** in 72% yield (Scheme 2).

Results for biological activities of these compounds will be reported elsewhere.

EXPERIMENTAL

Melting points were determined on a Kofler apparatus and are uncorrected. Boiling points refer to bulb-to-bulb distillation. Elemental analyses were performed with a Carlo Erba 1106 instrument. Proton nuclear magnetic spectra (^{1}H NMR) were recorded in a Perkin–Elmer R12B spectrometer with TMS as internal standard. IR spectra were recorded in a Perkin–Elmer 399B spectrometer. Gas chromatography–mass spectra were determined on a Hewlett–Packard 5992B apparatus using a column packed with 3% OV-101 on Chromosorb Q. Gas chromatograms were performed with a Perkin–Elmer 990 model using a glass column packed with 3% OV-101 on silanized Chromosorb W.

Commercially available methanesulphonic acid (*Fluka 98%*) and 3,3-dimethylacrylic acid (**8**) (Aldrich) were used without further purification. 1,3-dichloro-3-methylbutane (**10**) was prepared by hydrochlorination of isoprene in the presence of CuCl.[6]



Scheme 2.

Table 2. Preparation of dihydrobenzodipyrans[a]

Substrates	Products	Isolated yield (%)
(5a + 6a) (R= H) [b]	(3a + 4a)(R= H)	70
5b (R= CH_3)	3b (R= CH_3)	89
5c (R= C_2H_5)	3c (R= C_2H_5)	84
15 [c]	3d (R= OCH_3)	80
6e (R= C_2H_5)	4e (R= C_2H_5)	82
6f (R= OCH_3)	4f (R= OCH_3)	86

[a] See the Experimental Section for a general procedure. [b] A 1:4/5a:6a mixture of tetrahydrobenzodipyran-4-ones was used as starting material. The 1:4/3a:4a mixture isolated in this case was separated by preparative TLC (see Experimental Section). [c] Methylated ketone 15 instead of 5d was used as substrate (see Experimental section).

2-ethylresorcinol (**7c**) and 4-ethylresorcinol (**7e**) were obtained from the corresponding acetophenones by Clemmensen reduction.[7] 4-methoxyresorcinol (**7f**) was prepared by Baeyer–Villiger oxidation of isovanillin,[8] followed by hydrolysis with 6N HCl.

Dihydrobenzopyran-4-ones **9**. Prepared by a general procedure previously described,[4] and characterized as follows:

2,3 - Dihydro - 7 - hydroxy - 2,2,8 - trimethyl - 4H - benzopyran - 4 - one (**9b**) m.p. 179–180° (lit[9] 180°); IR (KBr) 3140, 1650, 1590 cm^{-1}; ^1H NMR (CD_3COCD_3) δ 1.20 (s, 6H), 1.85 (s, 3H), 2.40 (s, 2H), 6.30 (d, 1H, J = 9 Hz), 7.35 (d, 1H, J = 9 Hz), 8.65 (s, 1H, OH).

8-Ethyl - 2,3 - dihydro - 7 - hydroxy - 2,2 - dimethyl - 4H - benzopyran - 4 - one (**9c**) m.p. 163–164° (hexane–acetone); IR (KBr) 3200, 1640, 1580 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10 (t, 3H, J = 8 Hz), 1.45 (s, 6H), 2.65 (s, 2H), 2.70 (q, 2H, J = 8 Hz), 6.50 (s, 1H), 7.35 (s, 1H, OH), 7.65 (s, 1H). Calc. for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 71.02; H, 7.38%.

2,3 - Dihydro - 7,8 - dihydroxy - 2,2 - dimethyl - 4H - benzopyran - 4 - one (**9d**) m.p. 139–140° (lit[10] 142–143°); IR (neat) 3300, 1655, 1600 cm^{-1}; ^1H NMR (CD_3COCD_3) δ 1.50 (s, 6H), 2.65 (s, 2H), 6.65 (d, 1H, J = 9 Hz), 7.35 (d, 1H, J = 9 Hz), 7.70 (s, 1H, OH), 8.25 (s, 1H, OH).

6 - Ethyl - 2,3 - dihydro - 7 - hydroxy - 2,2 - dimethyl - 4H - benzopyran - 4 - one (**9e**), m.p. 170–171° (lit[11] 175–176°); IR (CCl_4) 3560, 3350, 1675, 1615 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20 (t, 3H, J = 8 Hz), 1.41 (s, 6H), 2.55 (q, 2H, J = 8 Hz), 2.67 (s, 2H), 6.40 (s, 1H), 7.68 (s, 1H), 7.6–8.4 (br, 1H, OH).

2,3 - Dihydro - 7 - hydroxy - 6 - methoxy - 2,2 - dimethyl - 4H - benzopyran - 4 - one (**9f**).[4]

2,3-Dihydro - 5,7 - dihydroxy - 2,2 - dimethyl - 4H - benzopyran - 4 - one (**12**), m.p. 192–193° (lit[12] 198°); IR (KBr) 3150, 1650, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.40 (s, 6H), 2.55 (s, 2H), 5.85 (s, 2H), 9.1 (br, 1H, OH), 12.0 (s, 1H, OH).

General procedure for the preparation of tetrahydrobenzodipyran-4-ones 5–6. The resorcinol **7** (10 mmol) and 3,3-dimethylacrylic acid (**8**, 10 mmol) were added simultaneously with vigorous stirring to methanesulphonic acid (20 ml), at 70°, and the reaction mixture was stirred for 30 min. Then, 1,3-dichloro-3-methylbutane (**10**, 40 mmol) was added dropwise for 2 h at 70°; after addition was completed, the crude reaction mixture was stirred for 30 min at the same temperature, cooled, poured into ice-water (100 g) and extracted with Et_2O (3 × 50 ml). The combined organic fractions were washed with 1N NaOH (2 × 50 ml), H_2O, brine and dried ($MgSO_4$). The residue obtained after solvent removal was purified by flash column chromatography[13] to afford the corresponding tetrahydrobenzodipyran-4-ones **5–6**. The results are summarized in Table 1.

2,3,6,7 - Tetrahydro - 2,2,8,8 - tetramethyl - 4H,8H - benzo[1,2-b:5,4-b']dipyran - 4 - one (**5a**) and 2,3,9,10 - tetrahydro - 2,2,8,8 - tetramethyl - 4H, 8H - benzo[1,2-b:3,4-b']dipyran - 4 - one (**6a**). Reaction with resorcinol (**7a**) using only 20% molar excess of **10** afforded a **5a**:**6a** isomeric mixture (1:4j 66% overall yield), which was separated by preparative TLC (silicagel; EtOAc:hexane = 1:6). Compound **5a** crystallized on standing: m.p. 86–87° (hexane–acetone); IR (CCl_4) 1675, 1610, 1565 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.32 (s, 6H), 1.42 (s, 6H), 1.80 (t, 2H, J = 7 Hz), 2.5–3.0 (4H), 6.38 (s, 1H), 7.62 (s, 1H); mass spectrum *m/e* (relative intensity) 260 (M^+, 20), 245 (27), 205 (77), 189 (20), 149 (100). Calc. for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.77; H, 7.92%. Compound **6a**[14] crystallized on standing, m.p. 117–118° (hexane–acetone); IR (CCl_4) 1675, 1600, 1580 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.32 (s, 6H), 1.42 (s, 6H), 1.78 (t, 2H, J = 7 Hz), 2.4–2.9 (4H), 6.38 (d, 1H, J = 9 Hz), 7.62 (d, 1H, J = 9 Hz); mass spectrum *m/e* (relative intensity) 260 (M^+, 38), 245 (40), 205 (64), 204 (32), 149 (100). Calc. for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.73; H, 8.03%.

2,3,6,7 - *Tetrahydro* - 2,2,8,8,10 - *pentamethyl* - 4*H*,8*H* - *benzo*[1,2-*b*:5.4-*b'*]*dipyran* - 4 - *one* (**5b**). From 2-methylresorcinol (**7b**) it was isolated as a crystalline solid in 86% yield, m.p. 128° (hexane–acetone); IR (KBr) 1690, 1615, 1570 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.32 (s, 6H), 1.42 (s, 6H), 1.80 (t, 2H, J = 8 Hz), 2.02 (s, 3H), 2.5–3.0 (4H), 7.50 (s, 1H); mass spectrum *m/e* (relative intensity) 274 (M^+, 16), 259 (25), 219 (80), 203 (17), 163 (100). Calc. for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.50; H, 8.14%.

10 - *Ethyl* - 2,3,6,7 - *tetrahydro* - 2,2,8,8 - *tetramethyl* - 4*H*,8*H* - *benzo*[1,2-*b*:5,4-*b'*]*dipyran* - 4 - *one* (**5c**). From 2-ethylresorcinol (**7c**) it was isolated as a crystalline solid in 81% yield, m.p. 89–90° (hexane–acetone); IR (KBr) 1670, 1600, 1565 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10 (t, 3H, J = 7 Hz), 1.32 (s, 6H), 1.42 (s, 6H), 1.80 (t, 2H, J = 8 Hz), 2.4–3.0 (6H), 7.55 (s, 1H); mass spectrum *m/e* (relative intensity) 288 (M^+, 23), 173 (36), 233 (100), 217 (25), 177 (80). Calc. for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39. Found: C, 74.96; H, 8.58%.

2,3,6,7 - *Tetrahydro* - 10 - *hydroxy* - 2,2,8,8 - *tetramethyl* - 4*H*,8*H* - *benzo*[1,2-*b*:5,4-*b'*]*dipyran* - 4 - *one* (**5d**). It was obtained from pyrogallol (**7d**) (but without the 1N NaOH wash) and isolated as a crystalline solid in 80% yield, m.p. 200–201° (hexane–acetone); IR (KBr) 3480, 1680, 1620, 1580 cm^{-1}; ^1H NMR (CD_3COCD_3) δ 1.40 (s, 6H), 1.50 (s, 6H), 1.80 (t, 2H, J = 7 Hz), 2.5–3.0 (4H), 5.42 (s, 1H, OH), 7.25 (s, 1H); mass spectrum *m/e* (relative intensity) 261 (M^+ − 15, 26), 221 (67), 219 (26), 205 (33), 165 (100). Calc. for $C_{16}H_{20}O_4$: C, 69.55; H, 7.30. Found: C, 69.85; H, 7.41%.

6 - *Ethyl* - 2,3,9,10 - *tetrahydro* - 2,2,8,8 - *tetramethyl* - 4*H*,8*H* - *benzo*[1,2-*b*:3,4-*b'*]*dipyran* - 4 - *one* (**6e**). From 4-ethylresorcinol (**7e**) it was isolated as a crystalline solid in 83% yield, m.p. 130–131°; IR (CCl_4) 1670, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.12 (t, 3H, J = 7 Hz), 1.32 (s, 6H), 1.42 (s, 6H), 1.67 (t, 2H, J = 8 Hz), 2.3–2.9 (6H), 7.55 (s, 1H); mass spectrum *m/e* (relative intensity) 288 (M^+, 21), 273 (34), 233 (48), 217 (51), 177 (100). Calc. for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39. Found: C, 74.68; H, 8.39%.

2,3,9,10 - *Tetrahydro* - 6 - *methoxy* - 2,2,8,8 - *tetramethyl* - 4*H*,8*H* - *benzo*[1,2-*b*:3,4-*b'*]*dipyran* - 4 - *one* (**6f**). Obtained from 4-methoxyresorcinol (**7f**) following the general procedure but treatment with **10** was reduced to 1 h to avoid demethylation at C-6. Compound **6f** was isolated as a crystalline solid in 66% yield, m.p. 162–163° (hexane–acetone); IR (KBr) 1660, 1590 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.38 (s, 6H), 1.43 (s, 6H), 1.78 (t, 2H, J = 8 Hz), 2.4–2.8 (4H), 3.81 (s, 3H), 7.15 (s, 1H); mass spectrum *m/e* (relative intensity) 290 (M^+, 37), 275 (30), 235 (40), 234 (27), 179 (100). Calc. for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 70.05; H, 7.61%.

2,3,7,8,11,12 - *Hexahydro* - 2,2,6,6,10,10 - *hexamethyl* - 4*H*,6*H*,10*H* - *benzo*[1,2-*b*:3,4-*b'*:5,6-*b''*]*tripyran* - 4 - *one* (**13**). From phloroglucinol (**11**) (reaction time with **8** was 2 h and a twofold ratio of **10**, 80 mmol, was used), it was isolated as a crystalline solid in 73% overall yield, m.p. 127–128° (hexane–acetone); IR (KBr) 1670, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.32 (s, 6H), 1.37 (s, 6H), 1.42 (s, 6H), 1.75 (t, 2H, J = 8 Hz), 2.3–2.8 (6H); mass spectrum *m/e* (relative intensity) 344 (M^+, 22), 289 (26), 288 (30), 233 (58), 177 (100). Calc. for $C_{21}H_{28}O_4$: C, 73.23; H, 8.19. Found: C, 73.19; H, 8.46%.

Preparation of 2,3,6,7 - *tetrahydro* - 10 - *methoxy* - 2,2,8,8 - *tetramethyl* - 4*H*,8*H* - *benzo*[1,2-*b*:5,4-*b'*]*dipyran* - 4 - *one* (**15**). Compound **5d** (1.24 g, 4.5 mmol) was treated with Na_2CO_3 (1.24 g, 11.8 mmol) and CH_3I (6 ml, 57 mmol) in DMF (15 ml) and the mixture was stirred for 18 h at room temperature. When the reaction was completed (GC monitoring), the crude reaction mixture was poured into 6N HCl (100 ml) and extracted with benzene (3 × 50 ml). The combined organic fractions were washed with H_2O, brine and dried ($MgSO_4$). The residue obtained after solvent removal was purified by flash column chromatography[13] to afford **15** as a crystalline solid in 88% yield: m.p. 76–77° (hexane–acetone); IR (KBr) 1690, 1615, 1570 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.40 (s, 6H), 1.50 (s, 6H), 1.85 (t, 2H, J = 8 Hz), 2.6–3.0 (4H), 3.81 (s, 3H), 7.43 (s, 1H); mass spectrum *m/e* (relative intensity) 290 (M^+, 18), 275 (18), 234 (59), 219 (24), 179 (100). Calc. for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 70.38; H, 7.65%.

General procedure for the preparation of dihydrobenzodipyrans **3–4**. A soln of the appropriate tetrahydrobenzodipyran-4-one **5** and/or **6**[15] (5 mmol) in anhydrous Et_2O (40 ml) was treated with LAH (5 mmol) and stirred for 1 h at room temperature. After the careful addition of H_2O, the mixture was filtered; the filtrate, containing the 4-chromanol was vigorously stirred with 6N HCl

for 1 h at room temperature. The organic fraction was washed ($NaHCO_3$, brine), and dried ($MgSO_4$). After solvent removal, the residue was distilled bulb-to-bulb to afford the corresponding dihydrobenzodipyrans **3–4**. The yields are summarized in Table 2.

6,7 - *Dihydro* - 2,2,8,8 - *tetramethyl* - 2*H*,8*H* - *benzo*[1,2-*b*:5,4-*b'*]*dipyran* (**3a**) *and* 9,10 - *dihydro* - 2,2,8,8 - *tetramethyl* - 2*H*,8*H* - *benzo*[1,2-*b*:3,4-*b'*]*dipyran* (**4a**). From **5a**:**6a** mixture (1:4; GC analysis), the procedure above described afforded chromenes **3a** and **4a** in the same isomeric ratio in 70% yield, which were separated by preparative TLC (Silicagel, hexane:CH_2Cl_2/2:1). Compound **3a** crystallized on standing: m.p. 55–56°; IR (CCl_4) 1630, 1615 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (s, 6H), 1.38 (s, 6H), 1.72 (t, 2H, J = 7 Hz), 2.62 (t, 2H, J = 7 Hz), 5.40 (d, 1H, J = 10 Hz), 6.22 (d, 1H, J = 10 Hz), 6.22 (s, 1H), 6.60 (s, 1H); mass spectrum *m/e* (relative intensity) 224 (M^+, 16), 230 (16), 229 (100), 173 (24). Calc. for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.48; H, 8.50%. Compound **4a**, b.p. 125–130° (0.5 mm); IR (CCl_4) 1630, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (s, 6H), 1.40 (s, 6H), 1.72 (t, 2H, J = 7 Hz), 2.62 (t, 2H, J = 7 Hz), 5.37 (d, 1H, J = 10 Hz), 6.20 (d, 1H, J = 10 Hz), 6.22 (d, 1H, J = 9 Hz), 6.70 (d, 1H, J = 9 Hz); mass spectrum *m/e* (relative intensity) 244 (M^+, 21), 229 (100), 174 (15), 173 (97). Calc. for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.39; H, 8.54%.

6,7 - *Dihydro* - 2,2,8,8,10 - *pentamethyl* - 2*H*,8*H* - *benzo*[1,2-*b*:5,4-*b'*]*dipyran* (**3b**). From compound **5b** it was isolated as a pale yellow oil in 89% yield, b.p. 121–124° (0.35 mm); IR (CCl_4) 1645, 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (s, 6H), 1.40 (s, 6H), 1.72 (t, 2H, J = 7 Hz), 2.03 (s, 3H), 2.65 (t, 2H, J = 7 Hz), 5.42 (d, 1H, J = 10 Hz), 6.18 (d, 1H, J = 10 Hz), 6.50 (s, 1H); mass spectrum *m/e* (relative intensity) 258 (M^+, 18), 244 (19), 243 (100), 187 (28). Calc. for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 79.25; H, 8.78%.

10 - *Ethyl* - 6,7 - *dihydro* - 2,2,8,8 - *tetramethyl* - 2*H*,8*H* - *benzo*[1,2-*b*:5,4-*b'*]*dipyran* (**3c**). From compound **5c** it was isolated as a pale yellow oil in 84% yield: b.p. 105–107° (0.3 mm); IR (CCl_4) 1620, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05 (t, 3H, J = 7 Hz), 1.30 (s, 6H), 1.40 (s, 6H), 1.72 (t, 2H, J = 7 Hz), 2.3–2.9 (4H), 5.40 (d, 1H, J = 10 Hz), 6.18 (d, 1H, J = 10 Hz), 6.60 (s, 1H); mass spectrum *m/e* (relative intensity) 272 (M^+, 13), 258 (18), 257 (100), 201 (21). Calc. for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.45; H, 8.84%.

6,7 - *Dihydro* - 10 - *methoxy* - 2,2,8,8 - *tetramethyl* - 2*H*,8*H*-*benzo*[1,2-*b*:5,4-*b'*]*dipyran* (**3d**). From compound **15** it was isolated as a colourless oil (b.p. 115–120° at 0.4 mm) which crystallized on standing (80% yield), m.p. 66–67°; IR (CCl_4) 1640, 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (s, 6H), 1.45 (s, 6H), 1.78 (t, 2H, J = 7 Hz), 2.68 (t, 2H, J = 7 Hz), 3.81 (s, 3H), 5.48 (d, 1H, J = 10 Hz), 6.23 (d, 1H, J = 10 Hz), 6.45 (s, 1H); mass spectrum *m/e* (relative intensity) 274 (M^+, 15), 260 (18), 259 (100), 203 (28). Calc. for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.35; H, 8.37%.

6 - *Ethyl* - 9,10 - *dihydro* - 2,2,8,8 - *tetramethyl* - 2*H*,8*H* - *benzo*[1,2-*b*:3,4-*b'*]*dipyran* (**4e**). From compound **6e** it was isolated as a pale yellow oil in 82% yield: b.p. 110–112° (0.35 mm); IR (CCl_4) 1640, 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.15 (t, 3H, J = 7 Hz), 1.30 (s, 6H), 1.40 (s, 6H), 1.75 (t, 2H, J = 7 Hz), 2.3–2.9 (4H), 5.40 (d, 1H, J = 10 Hz), 6.23 (d, 1H, J = 10 Hz), 6.61 (s, 1H); mass spectrum *m/e* (relative intensity) 272 (M^+, 21), 258 (19), 257 (100), 201 (80). Calc. for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.42; H, 9.12%.

9,10 - *Dihydro* - 6 - *methoxy* - 2,2,8,8 - *tetramethyl* - 2*H*,8*H* - *benzo*[1,2-*b*:3,4-*b'*]*dipyran* (**4f**). From compound **6f** it was isolated as a pale yellow oil in 86% yield: b.p. 130–132° (0.4 mm); IR (CCl_4) 1640, 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (s, 6H), 1.45 (s, 6H), 1.81 (t, 2H, J = 7 Hz), 2.71 (t, 2H, J = 7 Hz), 3.71 (s, 3H), 5.48 (d, 1H, J = 10 Hz), 6.28 (d, 1H, J = 10 Hz), 6.47 (s, 1H); mass spectrum *m/e* (relative intensity) 274 (M^+, 17), 259 (66), 204 (14), 203 (100). Calc. for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.55; H, 8.35%.

7,8,11,12 - *Tetrahydro* - 2,2,6,6,10,10 - *hexamethyl* - 2*H*,6*H*,10*H*-*benzo*[1,2-*b*:3,4-*b'*:5,6-*b''*]*tripyran* (**14**). From ketone **13** it was isolated as a pale yellow oil (b.p. 135–138° at 0.4 mm), which crystallized on standing (72% yield), m.p. 90–91° (hexane); IR (CCl_4) 1620, 1590 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1,30 (s, 12H), 1.40 (s, 6H), 1.71 (t, 2H, J = 7 Hz), 2.4–2.7 (4H), 5.32 (d, 1H, J = 10 Hz), 6.56 (d, 1H, J = 10 Hz); mass spectrum *m/e* (relative intensity) 329 (M^+, 9), 313 (48), 257 (37), 217 (18), 201 (100). Calc. for $C_{21}H_{28}O_3$: C, 76.79; H, 8.59. Found: C, 76.57; H, 8.71%.

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