Synthesis of o-Isopentenylphenols from 2,2-Dimethylchromans by Cleavage with Boron Trichloride

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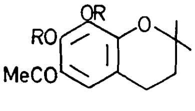
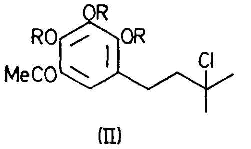
Summary Cleavage of 2,2-dimethylchromans with boron trichloride yields chloroisopentyl phenols which can be dehydrochlorinated to the isopentenylphenols.

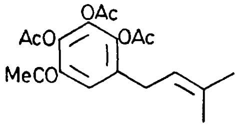
Although 2,2-dimethylchromans can be readily synthesized,[1] cleavage of the heterocyclic ring to yield the *o*-isopentenylphenol grouping, common to many natural products, is difficult.[2]



(I)



(II)



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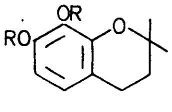
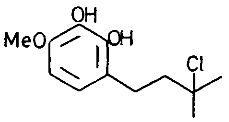


(IV)



(V)

a; R = H
b; R = Me
c; R = MeCO

During an attempt to demethylate[3] the 7-methoxy group of 6-acetyl-7,8-dimethoxy-2,2-dimethylchroman (Ib), using excess BCl_3 in CH_2Cl_2 at 0° for 1 h, a white crystalline solid, m.p. 137—40° (decomp.) (92%) was obtained which analysed for $C_{13}H_{17}ClO_4$, gave a deep blue colour with alcoholic $FeCl_3$ solution indicative of a pyrogallol nucleus, and had a 100 MHz n.m.r. spectrum [($CDCl_3$) δ 1·67 (6H,s, CMe_2), 1·94—2·11 and 2·73—2·90 (each 2H, A_2B_2, CH_2), 2·58 (3H, s, CH_3CO), and 5·14 (1H, s, ArH)] which showed no methoxy groups. Acetylation with Ac_2O–pyridine gave a triacetate, m.p. 98—99°. On the basis of this evidence the reaction product must be the tertiary chloride (IIa), formed by cleavage of the chroman ring with concomitant demethylation.

Reaction of 6-acetyl-7,8-dihydroxy-2,2-dimethylchroman (Ia) with BCl_3 under identical conditions gave the same product (IIa) (87%). The chloride (IIa), decomposed after 1·5 h at 150° with evolution of HCl to give a brown oil from which (Ia) was recovered (69%). Treatment of the triacetyl derivative (IIc) with LiCl in DMF at 100° for 3 h under argon gave 2,3,4-triacetoxy-5-isopentenyl-acetophenone (III); [m.p. 96—97°; 100 MHz n.m.r. ($CDCl_3$) δ 1·69 and 1·76 (each 3H, s, vinyl Me), 2·27 (3H, s, OAc), 2·28 (6H, s, 2 OAc), 2·51(3H, s, CH_3CO), 3·17 (2H, d, *J* 7 Hz, CH_2), 5·12 (1H, t, olefinic H) and 7·58 (1H, s, ArH).]

Similar treatment of 7,8-dimethoxy-2,2-dimethylchroman (IVb) with BCl_3 resulted in cleavage of the heterocyclic ring to give the chloride (V), which gave a green colour with alcoholic $FeCl_3$ solution, characteristic of a catechol grouping; [m.p. 96—97°; 100 MHz n.m.r. ($CDCl_3$) δ 1·64 (6H, s, $CMe)_2$, 1·93—2·10 and 2·70—2·87 (each 2H, A_2B_2, CH_2), 3·84 (3H, s, OMe), 5·28 and 5·50 (each 1H, s, OH), 6·40 and 6·64 (each 1H, d, *J* 8 Hz, *o*-coupled ArH)]. In contrast, the corresponding 7,8-dihydroxy-2,2-dimethyl-chroman (IVa) was recovered completely unchanged even on prolonged treatment with a large excess of BCl_3.

The products obtained with BCl_3 suggest that cleavage of the chroman ring results from nucleophilic attack of the chloride ion at the 2-position of the chroman ring to yield an intermediate phenoxydichloroborane which can then react further to give an *o*-phenylene chloroboronate, hydrolyzed during work-up. Demethylation of the methoxy group *ortho* to the acetyl substituent is unexceptional.[3] The lack of reaction of 6,7-dihydroxy-2,2-dimethylchroman (IVa) is probably due to direct formation of an *o*-phenylene chloroboronate with the catechol group,[4] thus preventing attack at the heterocyclic ring.

Although cleavage of simple cyclic ethers such as ethylene oxide, tetrahydrofuran and tetrahydropyran with BCl_3 has been reported as a method for preparation of alkoxyhaloboranes,[5] the corresponding reaction of 2,2-dimethylchromans has not been described previously. Cleavage of the latter to yield 3-chloroisopentylphenols appears to be a general method for preparation of naturally occurring isopentenylphenols from the more accessible 2,2-dimethylchromans.

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[1] R. J. Molyneux and L. Jurd, *Tetrahedron*, 1970, **26**, 4743.

[2] A. J. Birch, M. Maung, and A. Pelter, *Austral. J. Chem.*, 1969, **22**, 1923.

[3] F. M. Dean, J. Goodchild, L. E. Houghton, J. A. Martin, R. B. Morton, B. Parton, A. W. Price, and N. Somvichien, *Tetrahedron Letters*, 1966, 4153.

[4] W. Gerrard, M. F. Lappert, and B. A. Mountfield, *J. Chem. Soc.*, 1959, 1529.

[5] H. Steinberg in 'Organoboron Chemistry,' vol. 1, Interscience, New York, chap. 12.