A CONVENIENT SYNTHESIS OF 2,2-DIMETHYLCHROMENES FROM 2,2-DIMETHYLCHROMANONES

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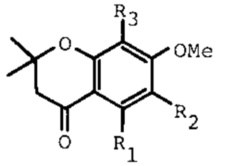
Abstract --- 2,2-Dimethylchromanones were very easily reduced to the corresponding alcohols by sodium borohydride-palladium chloride, and the alcohols were converted into the corresponding 2,2-dimethylchromenes by dehydration with potassium hydrogensulfate in high yields based on 2,2-dimethylchromanones.

2,2-Dimethylchromenes have recently been shown to possess insect antijuvenile hormone activity[1,2] or possible insecticide activity.[3] 2,2-Dimethylchromenes were synthesized by reduction and dehydration of the corresponding 2,2-dimethylchromanones by sodium borohydride or lithium aluminum hydride. However, some 2,2-dimethylchromenes were not obtained by reduction of 2,2-dimethylchromanones by sodium borohydride alone in good yields.[4,5] We wish to report reduction of 2,2-dimethylchromanones by a sodium borohydride-palladium chloride system[6] and synthesis of 2,2-dimethylchromenes.

A representative procedure for reduction of 2,2-dimethylchromanones and synthesis of 2,2-dimethylchromenes is as follows: To a solution of 7-methoxy-2,2-dimethylchromanone (1) (1 mmol) in a mixture of tetrahydrofuran and water were added palladium chloride (1.5 mmol) and then gradually sodium borohydride (11 mmol) with stirring at 0 °C. After the reaction mixture had been stirred at 0-5 °C for 3.5 h, the mixture was filtered and the filtrate was extracted with ether. The obtained alcohol (2) was dehydrated to yield 7-methoxy-2,2-dimethylchromene (3) with fused potassium hydrogensulfate in boiling toluene. All alcohols and 2,2-

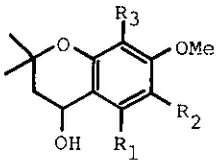


(1) $R_1=R_2=R_3=H$

(4) $R_1=R_3=H$ $R_2=OMe$

(7) $R_1=R_2=H$ $R_3=OMe$

(10) $R_1=OMe$ $R_2=R_3=H$

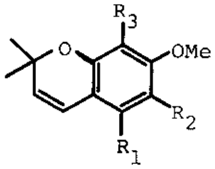


(2) $R_1=R_2=R_3=H$

(5) $R_1=R_3=H$ $R_2=OMe$

(8) $R_1=R_2=H$ $R_3=OMe$

(11) $R_1=OMe$ $R_2=R_3=H$

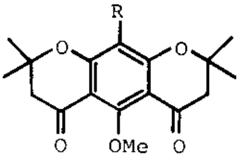


(3) $R_1=R_2=R_3=H$

(6) $R_1=R_3=H$ $R_2=OMe$

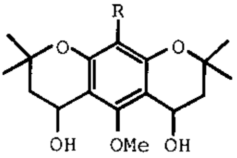
(9) $R_1=R_2=H$ $R_3=OMe$

(12) $R_1=OMe$ $R_2=R_3=H$



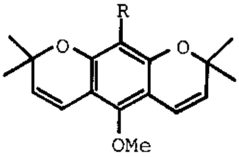
(13) R=H

(16) $R=CH_2CH_2COOMe$



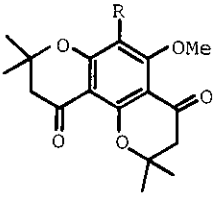
(14) R=H

(17) $R=CH_2CH_2COOMe$



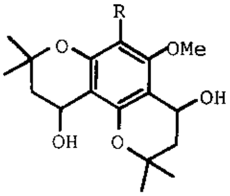
(15) R=H

(18) $R=CH_2CH_2COOMe$



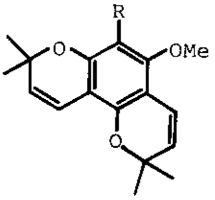
(19) R=H

(22) $R=CH_2CH_2COOMe$



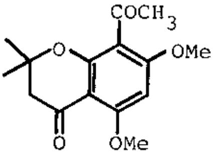
(20) R=H

(23) $R=CH_2CH_2COOMe$



(21) R=H

(24) $R=CH_2CH_2COOMe$



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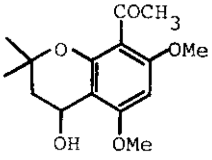

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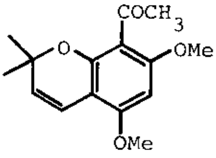

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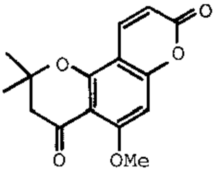

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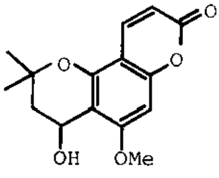

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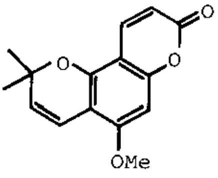

(30)

dimethylchromenes obtained by this procedure were purified by silica gel column-chromatography with chloroform as eluent. The 2,2-dimethylchromenes were identified by mp, IR and NMR spectra. The results are shown in Table 1.

Table 1. Conversion of 2,2-dimethylchromanones into 2,2-dimethylchromenes by sodium borohydride-palladium chloride

2,2-Dimethyl-chromanone	2,2-Dimethylchromene[a] Yield (%)	mp (°C)
(1)	(3) 74	liquid[2,b]
(4)	(6) 90	liquid[2,c]
(7)	(9) 89	liquid[7]
(10)	(12) 80	liquid[8]
(13)	(15) 85	liquid[9]
(16)	(18) 97	96-97[4]
(19)	(21) 93	83-84[10]
(22)	(24) 94	liquid[4]
(25)	(27) 76	105-106[11]
(28)	(30) 56	114-115[5]

a) Structures were confirmed by means of IR and NMR spectral data. b) Precocene I. c) Precocene II.

The present reduction of 2,2-dimethylchromanones was found to possess the following characteristics: 1) 2,2-dimethylchromanones of resorcinol- and phloroglucinol-type are very easily reduced to the corresponding alcohols, and then the alcohols are converted into the corresponding 2,2-dimethylchromenes by dehydration in high yields based on 2,2-dimethylchromanones. 2) In the compounds (13, 16, 19, 22), both carbonyl groups are simultaneously reduced to the corresponding alcohols. 3) Esters are not affected. 4) In acetyl-2,2-dimethylchromanone (25), the carbonyl group of the dihydro-γ-pyrone is reduced more easily than the acetyl one. From the above results, the sodium borohydride-palladium chloride system is more useful than sodium borohydride alone as a reducing agent for conversion of 2,2-dimethylchromanones into 2,2-dimethylchromenes. Further application for the reduction of some useful compounds is in progress.

References and Notes

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7. New compound (9): NMR ($CDCl_3$) δ 1.41 (6H, s, CH_3 x 2), 3.82 and 3.85 (each 3H, s, OCH_3), 5.45 and 6.22 (each 1H, d, J=10 Hz, CH=), 6.35 and 6.63 (each 1H, d, J=9 Hz, Arom. H).
8. J. Hlubucek, E. Ritchie, and W. C. Taylor, Tetrahedron Lett., 1969, 1369.
9. New compound (15): NMR ($CDCl_3$) δ 1.41 (12H, s, CH_3 x 4), 3.76 (3H, s, OCH_3), 5.48 and 6.48 (each 2H, d, J=10 Hz, CH=CH x 2), 6.10 (1H, s, Arom. H). Found: C, 74.68; H, 7.58%. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40%.
10. New compound (21): NMR ($CDCl_3$) δ 1.41 (12H, s, CH_3 x 4), 3.73 (3H, s, OCH_3), 5.37 (2H, d, J=10 Hz, CH= x 2), 5.92 (1H, s, Arom. H), 6.54 and 6.56 (each 1H, d, J=10 Hz, CH=). Found: C, 75.04; H, 7.65%. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40%.
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