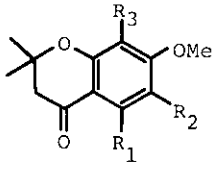
A CONVENIENT SYNTHESIS OF 2,2-DIMETHYLCHROMENES FROM 2,2-DIMETHYLCHROMANONES

Masao Tsukayama,* Tsukasa Sakamoto, Tokunaru Horie,
Mitsuo Masumura, and Mitsuru Nakayama**
Department of Applied Chemistry, Faculty of Engineering,
Tokushima University, Minamijosanjima, Tokushima 770, Japan
**Department of Chemistry, Faculty of Science, Hiroshima
University, Higashisenda-machi, Naka-ku, Hiroshima 730, Japan

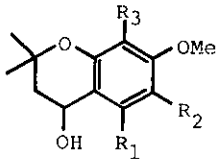
Abstract --- 2,2-Dimethylchromanones were very easily reduced to the corresponding alcohols by sodium borohydride-palladium chloride, and the alcohols were converted into the corresponding 2,2-dimethylchromenes by dehydration with potassium hydrogensulfate in high yields based on 2,2-dimethylchromanones.

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.

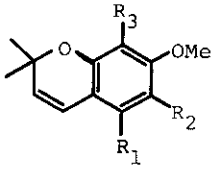
A representative procedure for reduction of 2,2-dimethylchromanones and synthesis of 2,2-dimethylchromenes is as follows: To a solution of 7-methoxy-2,2-dimethylchromanone (1) (1 mmol) in a mixture of tetrahydrofuran and water were added palladium chloride (1.5 mmol) and then gradually sodium borohydride (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) $R_1=R_2=R_3=H$



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



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

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

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

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

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

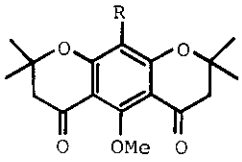
(8) $R_1=R_2=H$ $R_3=OMe$

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

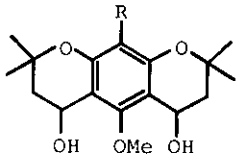
(10) $R_1=OMe$ $R_2=R_3=H$

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

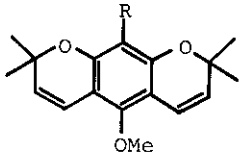
(12) $R_1=OMe$ $R_2=R_3=H$



(13) R=H



(14) R=H

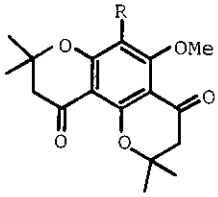


(15) R=H

(16) $R=CH_2CH_2COOMe$

(17) $R=CH_2CH_2COOMe$

(18) $R=CH_2CH_2COOMe$



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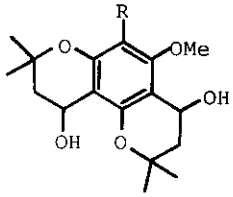

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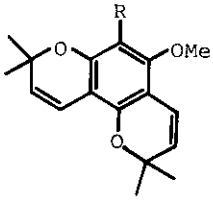
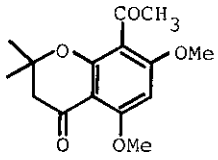


(21) R=H

(22) $R=CH_2CH_2COOMe$

(23) $R=CH_2CH_2COOMe$

(24) $R=CH_2CH_2COOMe$



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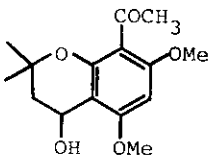

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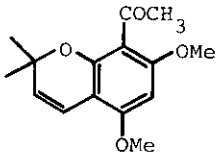

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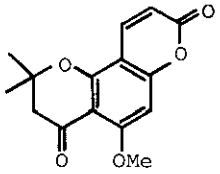

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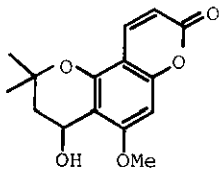

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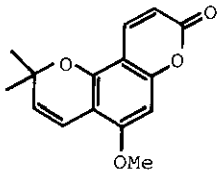

(30)

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 phlorogluci-nol-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

1. W. S. Bowers, T. Ohta, J. S. Cleere, and P. A. Marsella, Science, 1976, 193, 542.
2. T. Ohta and W. S. Bowers, Chem. Pharm. Bull., 1977, 25(9), 2788.
3. E. Rodriguez, Chem. Eng. News, 1980, Sept. 8, 42.
4. M. Nakayama, S. Hayashi, M. Tsukayama, T. Horie, and M. Masumura, Chem. Lett., 1975, 55; M. Tsukayama, Bull. Chem. Soc. Jpn., 1976, 49, 1653.
5. A. K. Ganguly, B. S. Joshi, V. N. Kamat, and A. H. Manmade, Tetrahedron, 1967, 23, 4777.
6. K. Namba, T. Satoh, and S. Suzuki, 28th National Meeting of the Chemical Society of Japan, Tokyo, April 1973, Abstr. III, 1325.
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%.
11. M. Nakayama, S. Nishimura, T. Matsui, S. Hayashi, and K. Fukui, Nippon Kagaku Zasshi, 1970, 91, 1092.

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