Novel Dehydrogenation of a Chromanone to a Chromone during a Grignard Reaction

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Summary A novel dehydrogenation of a chromanone to a chromone, to the extent of 12%, occurred when the former was treated with vinylmagnesium bromide under the usual Grignard reaction conditions.

WITH a view to synthesizing 6-oxa-7-methylequilenin by the method reported[1] for the synthesis of oestrone, 7-methoxy-2-methylchroman-4-one (I) was treated with vinylmagnesium bromide under the well-known Normant[2] reaction conditions to afford the desired 4-hydroxy-7-methoxy-2-methyl-4-vinylchroman (II). The expected vinylcarbinol (II) was isolated as a viscous brown oil in 50% yield. Surprisingly, however, a pale yellow solid (III) in *ca.* 12% yield was also isolated as ether-insoluble solid during the usual work-up of the vinylcarbinol (II). Recrystallization of (III) from alcohol afforded an analytically pure sample, m.p. 112—113°. That this was not the starting ketone (I) was proved by the observed depression in the mixed m.p. and by the non-identity of the i.r. ($CHCl_3$) and u.v. spectra.

The by-product (III) was shown to be the known 7-methoxy-2-methylchromone[3] from the chemical and spectral data: u.v.[4] λ_{max} (EtOH) 240, 294, and 320 nm (ϵ 12,140; 12,900; and 18,290); i.r. ν_{max} ($CHCl_3$) 1645 (conjugated C=O, characteristic of chromones[5]), 1618 and 842 cm^{-1} (trisubstituted C=C); n.m.r. τ ($CDCl_3$) 2·4—3·73 (4H, m, aromatic and olefinic), 6·24(3H,S,OMe), and 8·05 (3H, d, *J* 5·5 Hz, CH_3). Satisfactory elemental-analysis results were obtained.

The compound (III) absorbed one mole of hydrogen on hydrogenation over 15% palladium-on-carbon[6] affording the starting chromanone (I). The i.r. spectrum ($CHCl_3$) of (III) was superimposable on that of authentic 7-methoxy-2-methylchromone[3] synthesized by the methods reported by Bloch and Kostanecki[7] and Mehta and his colleagues.[8]

The occurrence of such a dehydrogenation of a chromanone to a chromone (even to the extent of 12%) in the course of a Grignard reaction is quite unusual.

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