Claisen Rearrangement of 1-Hydroxy-3-(3-methylbut-2-enyl)oxyxanthones

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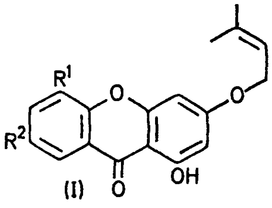
Summary Claisen rearrangement of three 1-hydroxy-3-(3-methylbut-2-enyl)oxyxanthones at 200° for 3 h yields the corresponding deprenylated xanthones and linear and angular furoxanthones, in contrast to previous results.

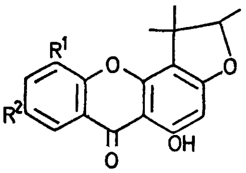
NATURAL macluraxanthone[1] and the 1,3,6,7-tetrahydroxyxanthone derivative of *Allanblackia floribunda* Oliver[2] possess αα-dimethylallyl units at the 4-position. For a synthesis of such compounds, the Claisen rearrangement of three typical 1-hydroxy-3-(3-methylbut-2-enyl)oxyxanthones has been studied.

The xanthone[3] (Ia) (4 g), when heated *in vacuo* at 200° for 3 h gave three products: 1,3-dihydroxy-7-methoxyxanthone[4] (2 g), the furoxanthone (IIa) (0·3 g), m.p. 210—212°, and its linear isomer (IIIa) (0·5 g), m.p. 146—147°. The condensed 4′,4′,5′-trimethyl-dihydrofuran portion of (IIa) and (IIIa) was established by their n.m.r. spectra. The linear and angular isomers were distinguished by Merlini's method.[5]

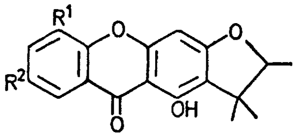
Similar results were obtained with (Ic), which afforded 1,3-dihydroxyxanthone,[4] the linear dihydrofuroxanthone



(I)



(II)



(III)

a; $R^1 = H, R^2 = OMe$
b; $R^1 = OMe, R^2 = H$
c; $R^1 = R^2 = H$

(IIIc), m.p. 179—181°, and the angular dihydrofuroxanthone (IIc), m.p. 153—155°. Obviously in the above cases normal Claisen rearrangement occurs to give the two corresponding αα-dimethylallyl derivatives followed by ring closure yielding linear and angular dihydrofuroxanthones. However, the xanthone[6] (Ib) (5 g) yielded 1,3-dihydroxy-5-methoxyxanthone[7] (1·5 g), and the normal linear xanthone (IIIb) (0·6 g) m.p. 158—159°, as in the above experiments but the third compound (0·25 g), m.p. 128—129° had the normal 4′,4′,5′-trimethyl-dihydrofuro-unit and also an extra *C*-prenyl unit as shown by its n.m.r. spectrum. Although the precise location of the prenyl and dihydrofuro-units is under investigation, the formation of the *C*-prenyl compound seems to be an intermolecular reaction.

The results with (Ia and b) are different from those recorded recently by Locksley *et al.*[8] who obtained only angular dihydrofuroxanthones (either normal or abnormal or both).

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