

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

By S. M. ANAND and A. C. JAIN*

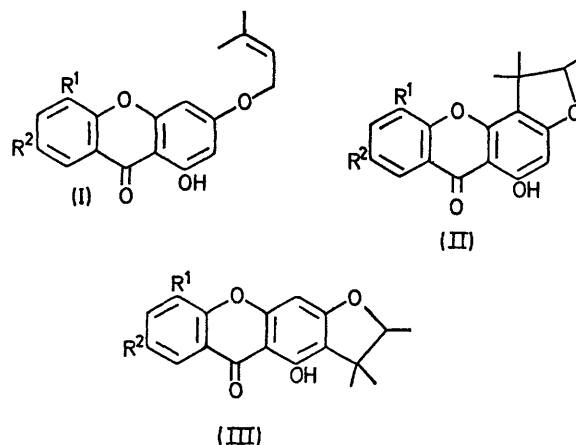
(Department of Chemistry, University of Jammu, Jammu-1, India)

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

NATURAL macluraxanthone¹ and the 1,3,6,7-tetrahydroxy-xanthone derivative of *Allanblackia floribunda* Oliver² possess $\alpha\alpha$ -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)oxyxanthenes has been studied.

The xanthone³ (Ia) (4 g), when heated *in vacuo* at 200° for 3 h gave three products: 1,3-dihydroxy-7-methoxy-xanthone⁴ (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



- a; R¹ = H, R² = OMe
b; R¹ = OMe, R² = H
c; R¹ = R² = 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 $\alpha\alpha$ -dimethylallyl derivatives followed by ring closure yielding linear and angular dihydrofuroxanthones. However, the xanthone⁶ (Ib) (5 g) yielded 1,3-dihydroxy-5-methoxyxanthone⁷ (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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