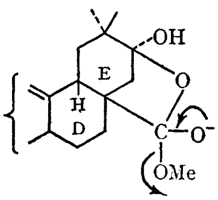
Intramolecular Participation by a Neighbouring Ketone Group in Ester Hydrolysis

By U. R. GHATAK and J. CHAKRAVARTY

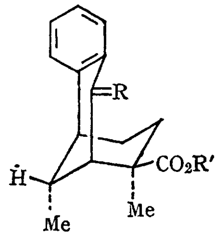
(*Department of Organic Chemistry, Indian Association for the Cultivation of Science, Calcutta* 32, *India*)

INTRAMOLECULAR participation by a ketone group in ester hydrolysis was noted by Djerassi and Lippman,[1] in the easy saponification (refluxing with 5% methanolic potassium hydroxide) of the highly hindered tertiary ester group of methyl machaerate (methyl 21-oxo-oleanolate), where the activating influence of the γ-ketone group was explained by its involvement through intermediate hemiacetal formation such as (I). In this Communication we report a remarkable example of ketone group participation in a simple hydrolysis of the tertiary keto-ester (II),[2] which has a conformationally rigid benzobicyclo[3,3,1]nonene system.

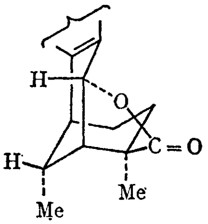
The keto-ester (II) was completely hydrolyzed to the corresponding keto-acid (III), m.p. 175—176° by heating under reflux for 15 min. with 1% methanolic KOH; $\nu_{\max}$ (CHCl$_3$) 1680 and 1725 cm.$^{-1}$; $\lambda_{\max}$ (EtOH) 255 mμ (log ϵ, 4·20) and 294 mμ (log ϵ, 3·24). Similarly, on refluxing for 2—4 hr. with excess of 0·13% methanolic sodium methoxide the keto-ester (II) yielded the corresponding keto-acid in 80% yield along with a neutral product, m.p. 112—113°; $\nu_{\max}$ (CHCl$_3$) 1765 cm.$^{-1}$ (γ-lactone), $\lambda_{\max}$ (EtOH) 258 mμ (log ϵ, 3·4) in variable yields (8—13%), which was assigned as the γ-lactone (IV) from its elemental analysis and spectral properties. The γ-lactone evidently arises from the corresponding hydroxy-acid, formed through sodium methoxide-induced reduction of the carbonyl group, analogous to a recently reported[3] example. The ester (V) and the isomeric keto-ester (VI)[2] have been recovered unchanged under the above hydrolysis conditions or comparatively drastic conditions (*e.g.*, prolonged refluxing with 5% methanolic potassium hydroxide).



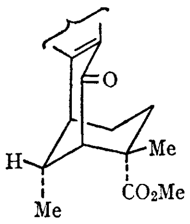
(I)



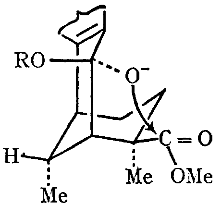
(II) $R = O$, $R' = Me$
(III) $R = O$, $R' = H$
(V) $R = H_2$, $R' = Me$



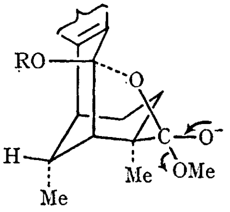
(IV)



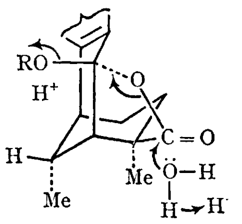
(VI)



(VII)



(VIII)



(IX)

The easy hydrolysis of the keto-ester (II) is envisaged as proceeding through the operation of proximity effect of the ketone group with the suitably oriented ester group (examined from Drieding models) following the route (VII) → (VIII) → (IX) ($R = H$ and Me) through final cleavage of hemiacetal (IX) during isolation.

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[1] C. Djerassi and A. E. Lippman, *J. Amer. Chem. Soc.*, 1955, **77**, 1825; see also B. Belleau and S. McLean in "Technique of Organic Chemistry," ed. A. Weissberger, Interscience Publishers, 1963, Part II, p. 1005.

[2] U. R. Ghatak and J. Chakravarty, unpublished work.

[3] G. L. Buchanan, A. McKillop, and R. A. Raphael, *J. Chem. Soc.*, 1965, 833.