An Unexpected Outcome of the Reaction between β-Lactones and Dissolved Potassium

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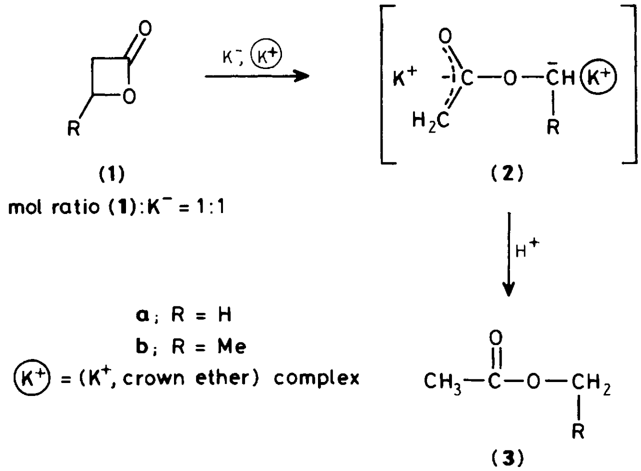
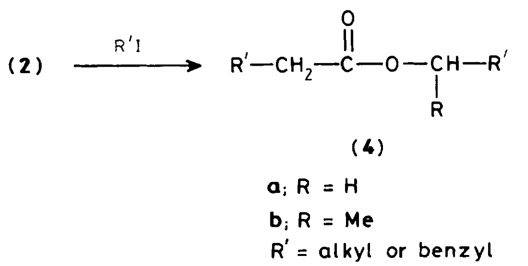
An unexpected novel reaction between β-propiolactones and a solution of potassium containing 18-crown-6, involving C–C bond scission in the β-lactone ring, provides a convenient route to enolate anions.

We have reported previously the reaction of alkali metal solutions with γ-lactones to give intermediate lactone enolates, which after alkylation or acylation yield α-substituted γ-butyrolactones.[1] We now report that the reaction of β-propiolactone with a potassium solution abounding in potassium anions proceeds in a quite different way, giving an enolate carbanion by the C–C bond cleavage in the strained four-membered β-lactone ring.

The potassium solution was obtained by contact (10 min) of a potassium mirror with a solution of 18-crown-6 in tetrahy-



Scheme 1



Scheme 2

drofuran (THF) at −20 °C, as described previously.[2] The resulting blue solution, abounding in potassium anions, when added to the β-lactone (**1a** or **b**) (molar ratio of K^- to lactone 1 : 1), became decolourised. Evidence for C–C bond scission and formation of the intermediate carbanion (**2**) (Scheme 1) was provided by protonation (*e.g.* addition of hydrochloric acid) and isolation of the product. A colourless liquid, b.p. 57 °C (uncorrected), isolated (yield 80%) from the reaction of the lactone (**1a**) was identified as methyl acetate (**3a**) by spectrometric and analytical data.†

This result clearly indicates that the first step of the reaction between potassium anions and β-propiolactone (**1**) yields the corresponding carbanion (**2**) (Scheme 1). A similar C–C bond scission occurs between aliphatic carbon atoms bearing bulky substituents and also in some dibenzyl derivatives, resulting from the action of alkali metal alloys,[3] but no such reaction seems to have been observed in heterocycles.

The present reaction affords enolate anions which can serve for many syntheses. Some alkylation reactions (Scheme 2) have been carried out: for example the carbanion (**2a**) with methyl iodide yielded ethyl propionate (**4a**) (70% yield),‡ and the carboanion (**2b**) with methyl iodide gave isopropyl propionate (**4b**) (yield 65%).§

Lehn[4] and Cram[5] have demonstrated the application of cryptands and crown ethers in many chemical processes. This paper presents crown ethers in an unusual role, bringing about ring scission in β-lactones: C–C bond scission in heterocycles has not hitherto been encountered.

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† *M/z* 74(M^+); i.r. (neat) ν 2890, 1730, 1460, 1400, 1380, 1360, 1180, 1130, and 960 cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 2.04 [s, 3H, $CH_3C(O)$] and 3.61 (s, 3H, CH_3O) Anal. (Found: C, 48.6; H, 8.1. Calc. for $C_3H_6O_2$C, 48.6; H, 8.2%); satisfactory elemental analyses were obtained.

‡ *M/z* 102 (M^+); i.r. (neat) ν 3000, 1740, 1460, 1370, 1340, 1200, 1080, and 1030 cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 0.85—1.30 [m, 6H, CH_3CH_2O and $CH_3CH_2C(O)$], 2.2 (q, 2H, CH_3CH_2O), and 4.0 [q, 2H, $CH_3CH_2(O)$]; b.p. (uncorr.) 99 °C (Found C, 58.8; H, 9.9. Calc. for $C_5H_{10}O_2$ C, 58.8; H, 9.9%); satisfactory elemental analyses were obtained.

§ *M/z* 116 (M^+); i.r. (neat) ν 3000, 1735, 1470, 1420, 1370, 1320, 1280, 1200, 1100, 1080, 1000, and 960 cm^{-1}; ^1H n.m.r., ($CDCl_3$) δ 0.85—1.20 [m, 9H, $(CH_3)_2CH$, CH_3CH_2], 2.2 (q, 2H, CH_3CH_2), and 4.7—5.1 [m, 1H, $(CH_3)_2CH$]. Satisfactory elemental analyses were obtained.