Enolate Anions. 2. Reaction between Potassium Solutions Containing Crown Ethers and β-Lactones

Z. Jedliński,* A. Misiołek, and P. Kurcok

Institute of Polymer Chemistry, Polish Academy of Sciences, 41-800 Zabrze, Poland

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A novel fission of the α carbon to β carbon by the treatment of β-lactones with potassium solutions containing crown ether is reported. The enolate carbanion formed, upon subsequent treatment with HCl or methyl iodide, yielded respective esters.

In our previously reported work[1] we demonstrated that alkali-metal solutions containing 18-crown-6 and γ-butyrolactones yielded an enolate anion that upon subsequent treatment yielded straightforward α-alkylation and α-acylation products. We report here that β-lactones in contrast to γ-lactones undergo unusual scission of the α carbon to β carbon bond and upon subsequent treatment yield open-chain esters (Scheme I). β-Lactones are well known to undergo not only acyl-oxygen cleavage as do most esters but also the alkyl-oxygen cleavage[2] presumably facilitated by the release in strain by the opening of the four-membered ring. However, the C–C cleavage at the α to β position, which also releases strain by the ring opening, seems to be very unique.

Results and Discussion

The hydrolysis, aminolysis, or polymerization of β-lactones is believed to proceed either due to acyl–oxygen or alkyl–oxygen bond scission.[3]

It has been revealed in this work that under certain conditions quite different cleavage of four-membered lactones can occur and C–C bonds are cleaved. The unexpected reaction of a β-lactone and potassium solution containing 18-crown-6 proceeds due to the action of a loose ion pair or "naked" potassium anion, the potassium cations being complexed with a crown ether. Such complexation consequently shifts the equilibrium to the right

$$\underset{\text{contact pair}}{K^+/K^-} \rightleftarrows \underset{\text{solvated pair}}{K^+/S/K^-} \xrightleftharpoons{\text{crown ether}} \underset{\text{loose pair}}{\enclose{circle}{K^+},K^-} \qquad (1)$$

where K^+ = cation, K^- = anion, $\enclose{circle}{K^+}$ = cation complexed by a crown ether

It is known that some crown ethers are able to dissolve alkali metals due to the complexation of metal cations. This process can be described briefly by the following equations:[4,5]

$$\text{K metal in contact with THF} \rightleftarrows K^0 \text{ (in solution)} \qquad (2)$$

$$K^0 \rightleftarrows K^+ + e_s^- \qquad (3)$$

$$K^+ + \text{crown ether} \rightleftarrows \enclose{circle}{K^+} \quad \text{or} \qquad (4)$$

$$\text{K metal in contact with adsorbed crown ether} \rightleftarrows \enclose{circle}{K^+} + e_s^- \qquad (5)$$

$$\enclose{circle}{K^+} + e_s^- \rightleftarrows \enclose{circle}{K^+}\ e_s^- \qquad (6)$$

$$K^0 + e_s^- \rightleftarrows K^- \qquad (7)$$

where $\enclose{circle}{K^+}$ = cation complexed by crown ether,
e_s^- = solvated electron, K^- = anion

We have recently revealed that these equilibria can be kept under control and a THF solution with a high concentration of potassium anions can be obtained.[6] When a β-lactone is added into such solution the blue color, observed due to the presence of potassium anions,[7] disappears and the high electric conductivity of the original solution drops down dramatically. After introduction of hydrochloric acid into the reaction mixture, carboxylic acid esters are the main products isolated from the reaction mixture (yield about 80%) (Scheme Ia). When an alkylating agent, e.g., methyl iodide, is added instead of HCl, the respective alkylation products are obtained as shown in Scheme Ib.

The yields of the alkylation are usually smaller (65–70%) than those of the protonation reaction and depend on the substrate employed and reaction conditions, e.g., temperature. It is due to side reactions involving possibly Claisen reaction. This assumption was confirmed by the fact that in the case of the α,α-disubstituted β-lactones having no hydrogen at the α carbon atom, the yields of both protonation and alkylation are very high, almost quantitative.

The described unexpected reaction of β-lactones provides a unique example of C–C bond cleavage in heterocycles due to the action of potassium anions. The crown ether enables the dissolution of an alkali metal and after addition of a lactone facilitates the formation and stabilization of the intermediate enolate anion **2** formed (Scheme I). It should be noted that similar scission of the C–C bond in hydrocarbons bearing bulky substituents by cesium–potassium–sodium alloys has been reported in the literature.[8]

Experimental Section

Boiling points were not corrected. Gas chromatographic analyses were performed on a Varian 2800 gas chromatograph

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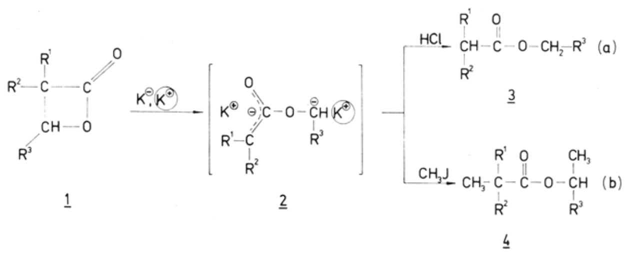
Scheme I



1,2,3,4	R^1	R^2	R^3
a	H	H	H
b	CH_3	C_2H_5	H
c	H	H	CH_3

$K^{\oplus}$ = ($K^{\oplus}$, 18-crown-6) complex

equipped with a preparative unit. GC analyses were carried out on a glass column packed with OV-17, 15% on Chromosorb W DMCS, 80–100 mesh. Preparative separations were run on a column packed with OV-17, 20% on Chromosorb W, 45–60 mesh. IR spectra were recorded on a Specord M80 spectrophotometer. ^{1}H NMR spectra were recorded on a Varian VXR-300 spectrometer, using TMS as an internal standard. GC-MS data were obtained on a Varian MAT 711 mass spectrometer at 70 eV, with an ion source temperature of 200 °C.

Materials. β-Propiolactone (**1a**) (Fluka) was distilled twice over a sodium mirror in an atmosphere of dry argon. The fraction boiling at 51 °C (10 mmHg) was collected (99.7% GC). α,α-Methyl, ethyl-β-propiolactone **1b** was obtained as described in the literature[9] and distilled twice over a sodium mirror in an atmosphere of dry argon. The fraction boiling at 66 °C (16 mmHg) was collected (99.6% GC). β-Butyrolactone **1c** (Fluka) was dried in a similar manner. The fraction boiling at 47 °C (6 mmHg) was collected (99.8% GC). Methyl iodide (Fluka) was dried over calcium chloride and distilled in an atmosphere of dry argon. The fraction boiling at 42 °C was collected. An HCl solution in diethyl ether (2.6 mol/L) was obtained by saturation of diethyl ether (Fluka), purified, and dried as described in ref 10a, with dry hydrogen chloride gas. 18-Crown-6 (Fluka) was purified by precipitation of its complex with acetonitrile. Acetonitrile was then removed under high vacuum and the crown ether was dried under vacuum at a temperature of 50 °C during 48 h. THF (POCh) was purified according to ref 10b and then was dried over a sodium–potassium alloy in an atmosphere of dry argon.

Preparation of Potassium Solutions and Syntheses of Enolates 2. Preparation of the potassium solutions and syntheses of lactone enolates **2** were performed in the apparatus depicted in Figure 1 and described in ref 1. The potassium solution was obtained by contact of the potassium mirror (A) with a solution of 18-crown-6 in THF (0.2 mol/L) at −20 °C. After exactly 15 min the resulting blue solution was filtered through a coarse frit (B) to the reactor (C) and an equimolar amount of lactone **1** was added into the reactor containing the blue potassium solution ($[K^-]$ = 0.2 mol/L); $[K^-]:[1]$ = 1:1.

Reactions of Enolates 2. Protonation (Scheme Ia). A 4.65-mL diethyl ether solution of HCl (2.6 mol/L) was added slowly under a dry argon atmosphere into a reactor containing a solution of enolate **2a** obtained from 430 mg (6 mmol) of lactone **1a**. The reaction was conducted for 30 min at room temperature. The potassium chloride formed was filtered. Then the reaction mixture was washed with a saturated aqueous solution of NaCl (three times, 10 mL) and dried over anhydrous $MgSO_4$. The crude product was evaporated together with THF and then the final product was isolated from THF solution by distillation using a Hickman apparatus (bp 57 °C) or by preparative gas chromatography (to give 355 mg (yield 80%)) of methyl acetate **3a**: MS, *m/e* 74 (M^+); IR (neat) ν 2890, 1730, 1460, 1400, 1380, 1360, 1180, 1130, 960 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.04 (s, 3 H, $CH_3C(O)$), 3.61 (s, 3 H, CH_3O). Anal. Calcd for $C_3H_6O_2$: C, 48.61; H, 8.16. Found: C, 48.61; H, 8.10.

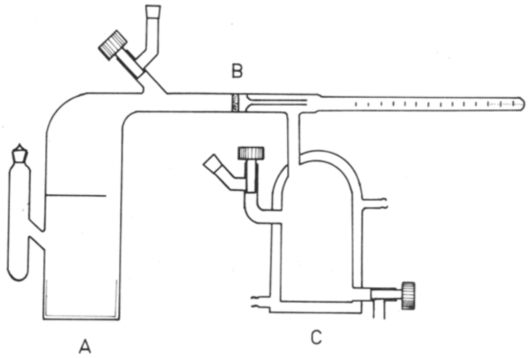


Figure 1. Apparatus used for the preparation of potassium solution.

The following compounds were silimarly obtained.

Methyl ester of 2-methylbutyric acid (3b) (obtained from the enolate **2b**): yield, 590 mg (85%); bp 116 °C; MS, *m/e* 116 (M^+); IR (neat) ν 2970, 2880, 1740, 1460, 1440, 1380, 1260, 1200, 1160, 1090, 1020, 980, 870 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90 (t, 3 H, CH_3CH_2), 1.15 (d, 3 H, CH_3CH), 1.48, 1.67 (m, m, 2 H, CH_3CH_2), 2.37 (m, 1 H, $CHC(O)$), 3.67 (s, 3 H, CH_3O). Anal. Calcd for $C_6H_{12}O_2$: C, 62.04; H, 10.41. Found: C, 62.02; H, 10.40.

Ethyl acetate (3c) (obtained from the enolate **2c**): yield, 370 mg (70%); bp 77 °C; MS, *m/e* 88 (M^+); IR (neat) ν 2980, 1745, 1480, 1460, 1370, 1360, 1300, 1240, 1100, 1050, 940 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.26 (t, 3 H, CH_3CH_2), 2.04 (s, 3 H, $CH_3C(O)$), 4.12 (q, 2 H, CH_3CH_2). Anal. Calcd for $C_4H_8O_2$: C, 54.53; H, 9.15. Found: C, 54.52; H, 9.10.

Methylation (Scheme Ib). The methylation reactions were performed by addition of methyl iodide to solutions of enolate **2**. The products 4 were isolated from washed and dried reaction mixture by evaporation with THF. Then the final products were isolated from THF solution by distillation using a Hickman apparatus.

The data of obtained products 4 were as follows.

Ethyl propionate (4a) (obtained from the enolate **2a**): yield, 430 mg (70%); bp 99 °C; MS, *m/e* 102 (M^+); IR (neat) ν 2980, 1735, 1460, 1420, 1370, 1340, 1190, 1030 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.85–1.30 (m, 6 H, CH_3CH_2O, $CH_3CH_2C(O)$), 2.20 (q, 2 H, $CH_3CH_2C(O)$), 4.00 (q, 2 H, CH_3CH_2O). Anal. Calcd for $C_5H_{10}O_2$: C, 58.80, H, 9.87. Found: C, 58.82; H, 9.87.

Isopropyl propionate (4c) (obtained from the enolate **2c**): yield, 455 mg (65%); bp 110 °C; MS, *m/e* 116 (M^+); IR (neat) ν 2990, 1735, 1470, 1420, 1370, 1330, 1280, 1200, 1110, 1080, 1000, 930 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.85–1.20 (m, 9 H, $(CH_3)_2CH$, CH_3CH_2), 2.20 (q, 2 H, CH_3CH_2), 4.70–5.10 (m, 1 H, CH_3CH). Anal. *Calcd* for $C_6H_{12}O_2$: C, 62.05; H, 10.41. Found: C, 62.09; H, 10.39.

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