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# Formation of Radical Anions and Not Deprotonation Starts the Reaction of γ-Butyrolactone with Potassium Anions

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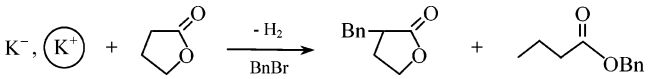


A mechanism is proposed for the reaction of γ-butyrolactone with the potassium anion as a two-electron-transfer reagent. Potassium hydride and potassium 4-potassiobutyrate are formed in this process as intermediates. These compounds deprotonate γ-butyrolactone. Potassium lactone enolate, potassium butyrate, and hydrogen are the final reaction products.

Lactones form enolates very easily in the presence of strong bases. Potassium *tert*-butoxide,[1,2] potassium naphthalenide,[3] and potassium hydride[4] transform β-lactones to appropriate enolates. The latter are, however, unstable and rapidly rearrange to salts of unsaturated acids.[4]

On the other hand, enolates obtained from γ- or δ-lactones in the reaction with potassium naphthalenide are stable.[5] It is assumed that this reagent behaves as a base and abstracts α-proton from the lactone molecule. It results in an appropriate enolate and a mixture of 1,2- and 1,4-dihydronaphthalene (in a molar ratio equal to 1:4). The reaction mechanism is similar to that proposed previously, for example, for water.[6,7] It shows that potassium naphthalenide does not act as an electron-transfer reagent in the mention systems.

Several α-substituted derivatives of lactones can be obtained by the treatment of enolates with alkyl or acyl halides.[8,9] For example, enolates formed in the reaction of γ-lactones with lithium dialkylamides,[10] i.e., diisopropylamide or isopropylcyclohexylamide, give α-methyl-γ-lactones after treatment with methyl iodide. The process occurs by deprotonation of the lactone.

Jedliński[11] used alkalide $K^-$, $K^+$(18-crown-6) in tetrahydrofuran solution to generate several γ-lactone enolates. That procedure constituted a novel route to α-alkyl- or α-acyl-γ-lactones. It was suggested that this reaction proceeded by deprotonation of the lactone by $K^-$. The reaction mechanism was not proposed. However, data concerning the reagent selected in that work allowed us to conclude that the deprotonation of γ-butyrolactone by $K^-$ could not occur.

The potassium anion has been known as an electron-transfer reagent. It transfers two electrons to the acceptor molecule in two steps, giving finally the potassium cation as it was proved in the excellent work of Perrin[12] and accepted in other papers.[13−16] Therefore, $K^-$ cannot behave as a nucleophile and, consequently, cannot be able to deprotonate γ-lactone. Furthermore, alkalide $K^-$, $K^+$-(18-crown-6) already decomposes autocatalytically to a large extent during its preparation at room temperature.[17] It results in a mixture of various dipotassium glycoxides, and their influence on the formation of enolates is not known.

Therefore, we decided to reinvestigate the study described in the work.[11] γ-Butyrolactone and alkalide $K^-$, $K^+$(15-crown-5)$_2$ **1** in tetrahydrofuran solution were selected as suitable model reagents for that purpose. That alkalide has been found to be much more stable than $K^-$, $K^+$(18-crown-6) and free from decomposition products even 1 h after preparation.[18]

Hydrogen (0.7 mmol, 70% yield) was found to evolve during the reaction of γ-butyrolactone with **1**. GC−MS analysis of the reaction mixture treated with benzyl bromide revealed two benzylated derivatives, i.e., α-benzyl-γ-butyrolactone (1.7 mmol, 85% yield) and benzyl butyrate (0.24 mmol, 12% yield). It means that potassium lactone enolate, potassium butyrate, and hydrogen were the real reaction products. The last two were identified for the first time in this work. Yields of reaction products indicated that the amount of hydrogen evolved is connected rather with the formation of enolate than with potassium butyrate.

The reaction mechanism is proposed on the basis of these results and known behavior of potassium anions. At first, one electron is transferred from $K^-$ of **1** to the LUMO orbital of the lactone (Scheme 1). This orbital is

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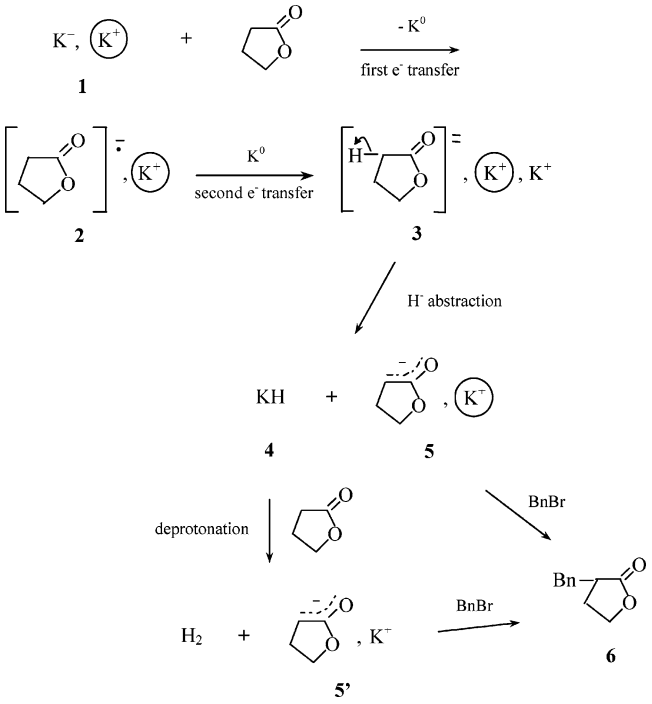
**SCHEME 1**[a]




[a] Circled $K^+$ denotes $K^+$(15-crown-5); the second crown molecule was omitted.

localized mainly on the carbonyl group. The resulting radical anion **2** can receive the second electron from $K^0$ giving dianion **3**. It decomposes with the abstraction of the hydride anion to produce potassium hydride **4** and potassium enolate **5**. Next, **4** reacts with another $\gamma$-butyrolactone molecule causing its deprotonation and giving hydrogen and potassium enolate without crown ether **5′**.

A similar reaction mediated by KH in the presence of 18-crown-6 was previously described in ref 5.

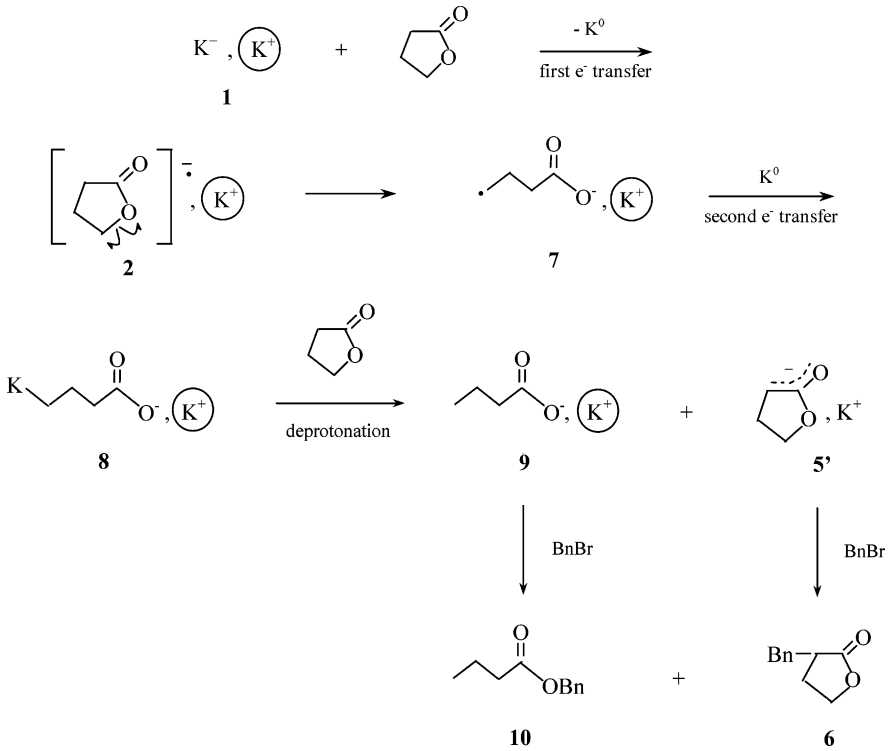
Radical anion **2** can also decompose by the alkyl–oxygen bond opening (homolytic cleavage) giving radical anion **7** (Scheme 2). Such a phenomenon was already found in the reaction of $K^-$ with linear aliphatic esters.[19,20] Organopotassium salt **8** was formed after the second electron transfer from $K^0$ to **7**. This salt and not $K^-$ deprotonates $\gamma$-butyrolactone. It results in lactone enolate **5′** and potassium butyrate **9**. Their benzylated products **6** and **10**, respectively, were found in the reaction mixture treated with benzyl bromide. It is worth noting that for this kind of experiments the stoichiometry fits the expected ([**6**] − [**10**]) ≈ 2[$H_2$].

Unexpectedly, **8** did not react with 15-crown-5. The benzylated product of the crown ring opening, i.e., tetraethylene glycol benzyl vinyl ether, was not identified in the reaction mixture, although it was observed in several processes with the participation of organopotassium compounds.[13−16,21]

In the second series of experiments, the $\gamma$-butyrolactone solution was dropped into blue alkalide solution at the same molar ratio of reagents as in the first experiments. At that dosage, $K^-$ was still in excess in relation to $\gamma$-butyrolactone except for the end of the reaction when discoloration of the solution occurred. Then, an enhanced amount of hydrogen was produced (0.9 mmol, 90% yield) as well as α-benzyl-$\gamma$-butyrolactone **6** (1.9 mmol, 95%). Only traces of benzyl butyrate **10** were found in that system. Thus, dianion **3** was almost exclusively formed at those conditions, which well confirmed the proposed reaction mechanism. The stoichiometry fitted in that case the equation [**6**] ≈ 2[$H_2$] because [**10**] ≈ 0.

In summary, $\gamma$-butyrolactone does not undergo deprotonation by $K^-$ but it receives one or two electrons from

**SCHEME 2**



the metal anion. The deprotonation occurs really with intermediate reaction products, i.e., potassium hydride **4** and potassium 4-potassiobutyrate **8**. It should be emphasized that the genuine evidence for the mechanism involving electron transfer and radical anions is the formation of benzyl butyrate **10** after benzylation of the reaction mixture.

## Experimental Section

**Materials.** Tetrahydrofuran (POCH) was purified as in the earlier work.[17] $\gamma$-Butyrolactone was distilled over $CaH_2$; the fraction boiling at 80 °C (11 mmHg) was collected. 15-Crown-5 was dried under vacuum at 50 °C for several hours. $K^-$, $K^+(15\text{-crown-}5)_2$ (0.1 M) dark blue solution was prepared by dissolution of metallic potassium in 0.2 M 15-crown-5 tetrahydrofuran solution at 20 °C. The contact time was equal to 25 min. The details have been described elsewhere.[18]

**General Procedure.** The reaction was conducted at 20 °C in a reactor described in ref 21. Tetrahydrofuran solution (10 mL) of $K^-$, $K^+(15\text{-crown-}5)_2$ (1 mmol) was dropped into $\gamma$-butyrolactone (2 mmol) dissolved in tetrahydrofuran (10 mL). The molar ratio of the reagents allowed us the complete conversion of $\gamma$-butyrolactone. After mixing of the reagents, discoloration of the system was observed indicating the decay of potassium anions. Hydrogen (16 mL) was found to evolve. Then, the reaction mixture was treated with benzyl bromide to identify nonvolatile reaction products. The solvent was evaporated, and the benzylated products were identified without separation. Their mass spectra and NMR spectra were similar to those reported already in the literature for α-benzyl-$\gamma$-butyrolactone[11,22,23] and benzyl butyrate.[24]

In the second version of experiments, the reagents were dosed conversely; i.e., $\gamma$-butyrolactone tetrahydrofuran solution was introduced to the alkalide solution. The enhanced volume of hydrogen (20 mL) was produced in that case.

**Measurements.** Analysis of hydrogen was conducted by GC technique on a 2.4 m long stainless steel column packed with $Al_2O_3$ (0.02−0.03 mm) and deactivated with 5% $K_2CO_3$ using a gas chromatograph with flame ionization detector. GC−MS analyses of benzylated products were performed on a 30 m long fused silica capillary column DB-1701 using a gas chromatograph equipped with an ion-trap detector. Diethylene glycol dimethyl ether was used as an internal standard for the yield determination. NMR spectra were recorded at 20 °C on a multinuclear spectrometer at the $^1H$ resonance frequency of 300 MHz and $^{13}C$ resonance frequency of 75 MHz. $CDCl_3$ was used as the solvent. Chemical shifts were referenced to tetramethylsilane (TMS) serving as an internal standard.

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