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Reactions of alkali metal macrocyclic complexes

XIX*. Reaction of potassium or sodium complexes with oxetane – novel route to organometallic compounds

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Abstract

Novel reactions of oxetane with K^-/K^+ and Na^-/K^+ complexes in which potassium cation is complexed by 18-crown-6 have been studied. Organometallic alkoxides formed by cleavage of an alkyl–oxygen bond in the oxetane molecule were used for one pot metallation of anisole and triphenylmethane. The reaction with carbon dioxide was also investigated. Reaction mechanisms have been studied by NMR, GLC-MS, IR techniques and chemical analysis.

Introduction

Macrocyclic complexes in etheral solvents consisting of alkali metal anions (*e.g.* Na^- or K^-) and solvated electrons and complexed by metal cations complexants were discovered many years ago [1,2]. However, only in the last decade has the nature of such systems been studied in detail [3–5] and a method developed for preparation of pure metal complexes containing very small or negligible numbers of electrons [6]. It turned out that these systems are very efficient reagents and catalysts, especially in deoxygenation of carboxylic esters or alcohols [7], reduction of hydrocarbons and their derivatives [8], and in enolisations [9,10]. β-Lactones in the presence of potassium or sodium anions undergo unusual carbon(3)–carbon(4) bond scission with formation of enolate carbanions [11,12].

We present below the results of a study of the reactions of the 4-membered cyclic ether oxetane with the K^+ complex/K^- and K^+ complex/Na^- at −20°C in THF and use of the products in metallation reactions.

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Results and discussion

Macrocyclic complexes were obtained by dissolution of potassium or sodium-potassium alloy at −20°C in THF containing the 18-crown-6. We observed that the THF reacts very slowly at −20°C with metallic reagents, but after addition of oxetane to the metal solution the blue solution became colourless and the signal of the metal anion disappeared from the ^{39}K or ^{23}Na NMR spectra (see Figs. 1 and 2). After addition of water to the decolorized mixture signals of potassium or sodium cations appeared in the spectra.

The course of the reaction may involve single electron transfer from the potassium or sodium anion to the oxetane molecule **1** to give the oxetane radical-anion **2**. After methylen–oxygen bond scission the unstable radical **3** recombines with potassium to yield the organometallic alkoxide **4**. Recombination of radical **3** with metallic potassium or sodium suggested in the proposed mechanism (Scheme 1) was observed previously by Finnegan in reactions of similar radicals [13].

The identification of both radicals **2** and **3** in ESR spectra was very difficult probably owing to their low stability, and so the final product **4** was identified by alkylation with methyl iodide and by protonation (see Experimental section). The organometallic compound **4** can be used directly as a metallation agent in reactions with anisole, triphenylmethane or in reaction with carbon dioxide.

Alkylation reactions

The outcome of direct alkylation reactions depends on the nature of the alkylation reagent. In the case of methyl iodide simple methylation occurs to yield

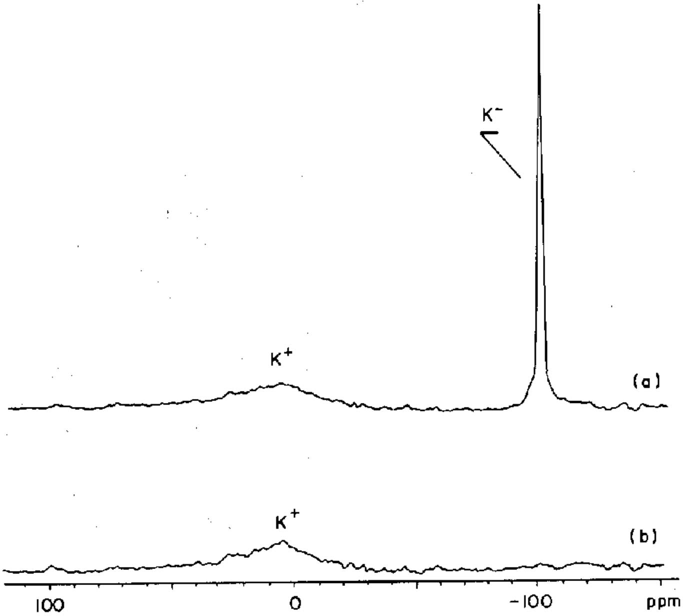


Fig. 1. The ^{39}K NMR spectra of (a) the blue solution obtained by complexation of K with 18-crown-6 in THF at −20°C, and (b) the mixture after treatment with oxetane.

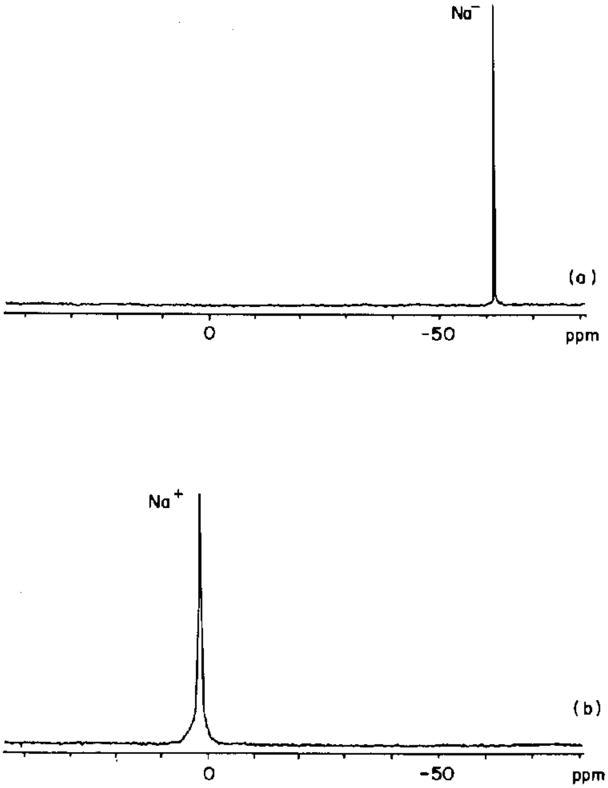
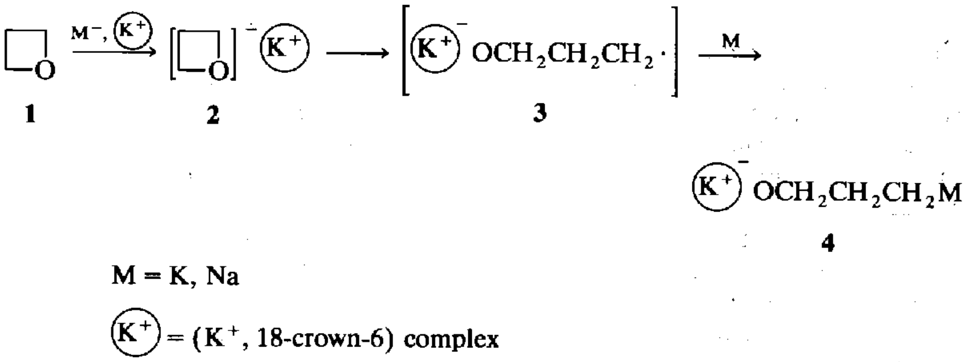
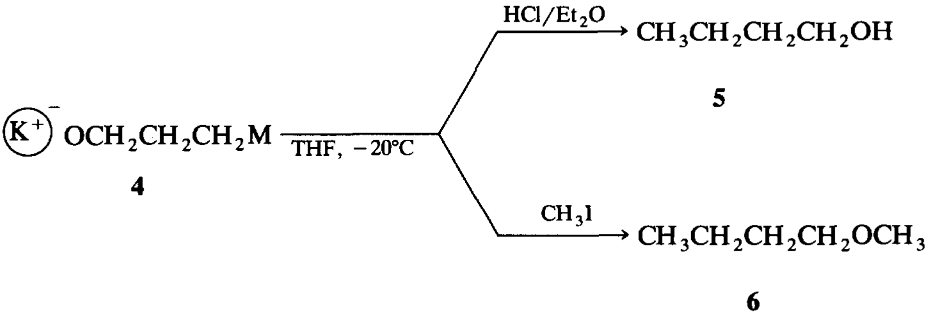


Fig. 2. The ^{23}Na NMR spectra of (a) the blue solution obtained by complexation of K/Na alloy with 18-crown-6 in THF at −20°C and (b) the mixture after treatment with oxetane.

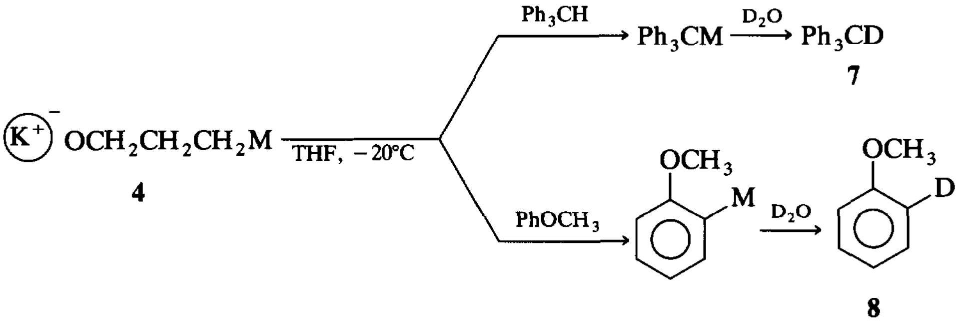
the corresponding methyl derivatives (Scheme 2). However, with higher alkyl halides, *e.g.* octyl iodide, or with benzyl chloride, side reactions involving decomposition of organometallic compounds are predominant. Such decomposition of organometallic compounds was described previously [13].



Scheme 1.



Scheme 2.



Scheme 3.

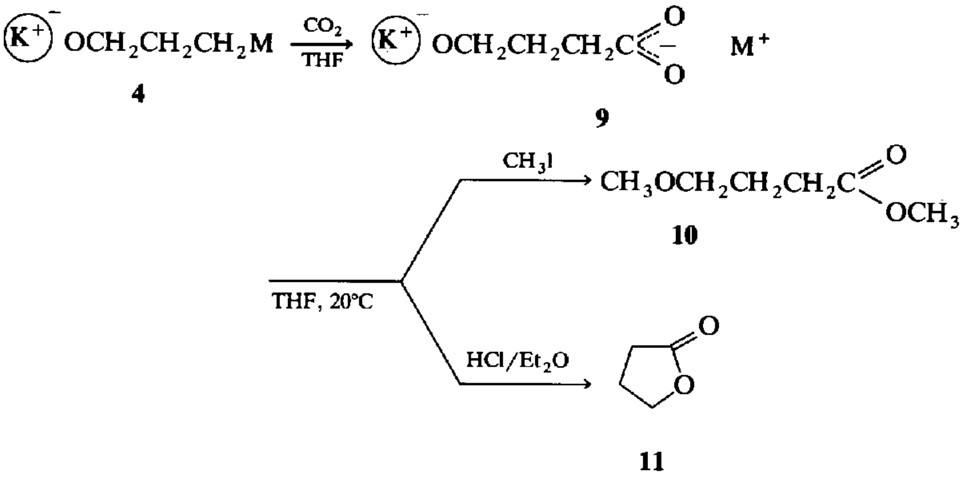
Metallation reaction of anisole and triphenylmethane

To the solution of anisole or triphenylmethane in THF at −20°C was added the organometallic compound **4** (molar ratio 1 : 1), and after 10 minutes an excess of D_2O was introduced. In the case of reaction with triphenylmethane the solution is reddish before addition of D_2O, indicating the presence of the triphenylmethane anion. The probable reaction pathway is outlined in Scheme 3. The yields of final products were 92 and 94%, respectively.

Reaction with carbon dioxide

Organoalkali metal compounds are known to react with carbon dioxide to yield carboxylate salts. In the reaction of the organopotassium compound **4** the carboxylate anion **9** is formed (Scheme 4). Methylation or protonation of the latter yields the methyl ester of 4-methoxy-butyric acid **10** (82%) or γ-butyrolactone **11**, respectively (88%).

The novel reactions of the potassium or sodium macrocyclic complexes with oxetane yields reactive organometallic compounds that are useful reagents for many organic syntheses. The value of this compound, especially in one pot metallation is noteworthy. Along with the recently reported reactions of related lithium organometallic compounds [14], these novel reactions of potassium and sodium complexes with oxetane open up new synthetic possibilities.



Scheme 4.

Experimental

General methods

Boiling and melting temperatures were uncorrected. The GLC analyses were performed with a Varian 2800 gas chromatograph which was also equipped with preparative facilities. The analyses were carried out on a glass column packed with OV-17, 15% on Chromosorb W DMSC, 80–100 mesh. Preparative separations were run on a column packed with OV-17, 20% on Chromosorb W DMSC, 45–60 mesh. Products were identified from their IR, ^{1}H NMR, ^{13}C NMR and mass spectra. IR spectra were determined by means of a Specord M80 instrument. ^{1}H NMR spectra were recorded at 300 MHz and ^{13}C NMR spectra at 75 MHz on a Varian VXL-300 spectrometer. Spectra were obtained for $CDCl_3$ solutions with TMS as internal standard. The GLC-MS analyses were carried out with a 30 m long DB-1701 fused silica capillary column in Varian 3300 gas chromatograph linked to a Finnigan MAT 800 AT ion trap detector.

^{39}K and ^{23}Na NMR measurements

^{39}K and ^{23}Na NMR spectra were recorded on a Varian VXR-300 multinuclear spectrometer of 14 MHz for 39 K and 79.35 MHz for 23 Na. Spectra were recorded at 253 K with 85 μs $\pi/2$ ^{39}K and ^{23}Na pulse width and 0.2 s delay between pulses. The alkali metal solutions and reagents were introduced into a 10 mm diameter NMR tube. The initial concentrations of potassium and oxetane in THF were both 0.2 mol/l.

Materials

Oxetane (Aldrich) was dried over molecular sieves 4A and distilled under dry argon; the fraction of b.p. 48°C was collected (99.9% by GLC). Anisole (POCh) was dried over molecular sieves 4 Å and distilled under dry argon; the fraction of b.p. 154°C was collected (99.8% by GLC). Triphenylmethane (Aldrich) was recrystallized from dry ethanol and the crystals dried for 48 h under vacuum at 69°C in an Abderhalden drying apparatus in the presence of P_2O_5 (m.p. 93°C). Methyl iodide (Aldrich) was dried over calcium chloride and distilled under dry argon; the fraction of b.p. 42°C was collected (99.6% by GLC). Deuterium oxide (IBJ-Swierk; isotopic purity 99.7%) and methyl-d_3 alcohol-*d* (IBJ Swierk; isotopic purity 99.6%) were used as received. The solution of HCl in diethyl ether (2.6 mol/l) was obtained by saturation of dry diethyl ether (FLUKA) (purified and dried as previously described [15]) with dry hydrogen chloride gas. The 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) (FLUKA) was purified by precipitation of its complex with acetonitrile, removal of the acetonitrile under high vacuum, and drying of the crown ether under vacuum at 50°C for 48 h. THF (POCh) was purified by the standard method [16] and dried over a sodium-potassium alloy under dry argon.

Reaction of potassium complex with oxetane

The preparation of the potassium complex solution and the reaction of the potassium anions with oxetane was performed under dry argon in the apparatus previously described [17]. The potassium solution was obtained by a contact of potassium mirror with a solution of 18-crown-6 in THF (0.2 mol/l) at −20°C; after exactly 15 min the blue solution was filtered through a coarse frit into the reactor and equimolar amount of oxetane (solution in THF 0.5 mol/l) was added dropwise until the colour of the potassium solution disappeared. The reaction mixture was immediately protonated, or alkylated with the relevant alkyl halides, or treated with triphenylmethane, anisole, or carbon dioxide.

Protonation of reaction mixture obtained from the potassium complex and oxetane. To the reaction mixture obtained from 58 mg (1 mmol) of oxetane and 15 ml potassium solution under argon was immediately added 2.35 ml of the solution of HCl in Et_2O (2.6 mol/l). After 5 min at −20°C the potassium chloride formed was filtered off, the crude product was evaporated off under reduced pressure together with the THF, and the final product then isolated by preparative gas chromatography and shown to be 1-Propanol (**5**) (yield 82% by GLC, based on starting oxetane); *m/e* 60 (M^+, 3%), 59 (8, $C_3H_7O^+$), 42 (6, $C_3H_6^{+\cdot}$), 31 (100, CH_2OH^+); IR (neat), $\nu = 3340$, 2964, 2940, 2884, 1456, 1346, 1236, 1052, 1016, 968, 888, 860 cm^{-1}; ^1H NMR ($CDCl_3$), $\delta = 0.92$ (t, 3H), 1.57 (m, 2H), 3.06 (s, 1H), 3.56 (t, 2H).

Reaction with methyl iodide of the reagent obtained from the potassium complex and oxetane. Methyl iodide (0.86 g, 6 mmol) was added immediately to the mixture obtained from 58 mg (1 mmol) of oxetane and 15 ml of the potassium solution under argon. After 60 min at −20°C the potassium iodide was filtered off and the solution washed three times with saturated aqueous NaCl then dried over anhydrous $MgSO_4$. The crude product was distilled out under reduced pressure together with THF and the product was then isolated by preparative gas chromatography and shown to be butyl methyl ether (**6**) (yield, 80% GLC, based on starting oxetane); *m/e* 88 (M^+, 1%), 87 (2, $CH_3OC_4H_8^{+\cdot}$), 57 (4, $C_4H_9^+$), 56 (7, $C_4H_8^{+\cdot}$), 45 (100, $CH_3OCH_2^+$), 41 (12, $C_3H_5^+$); IR (neat), $\nu = 2970$, 2942, 2870, 2840, 1460, 1388, 1232, 1200, 1120, 1064, 960, 940, 828 cm^{-1}; ^1H NMR ($CDCl_3$), $\delta = 0.92$ (t, 3H), 1.37 (m, 2H), 1.55 (m, 2H), 3.32 (s, 3H), 3.37 (t, 2H).

Metallation of triphenylmethane with organopotassium compound 4. A solution of triphenylmethane in THF (1 ml of 1 mol l^{-1}) was added to the mixture obtained from 58 mg (1 mmol) of oxetane and 15 ml of the potassium solution under the argon. A red colour developed. After 60 min at -20°C deuterium oxide (0.29) was added to stirred mixture and the red colour disappeared. The THF was evaporated under reduced pressure and the residue recrystallized from methyl-d_3 alcohol-d, and dried under vacuum, and shown to be triphenylmethane-d (**7**) (234 mg, 96%); m/e 245 (M^+, 84%), 168 (53, $C_{13}H_{10}D^+$), 166 (100, $C_{13}H_8D^+$), 153 (22, $C_{12}H_7D^+$), 77 (13, $C_6H_5^+$); IR (CCl_4), $\nu = 3090$, 3064, 3028, 2120, 1948, 1872, 1808, 1750, 1596, 1492, 1448, 1080, 1032, 1004, 988, 908 cm^{-1}; ^1H NMR ($CDCl_3$), $\delta = 7.05$–7.15 (m, 6H), 7.16–7.34 (m, 9H); ^{13}C NMR ($CDCl_3$), $\delta = 56.45$ (t, tertiary C, J(C–D) = 19.2), 126.28 (s, C-4), 128.29 (s, C-2), 129.43 (s, C-3), 143.87 (s, C-1).

Metallation of anisole by organopotassium compound 4. To the reagent obtained from 58 mg (1 mmol) of oxetane and 15 ml of the potassium solution under argon was added 1 ml of a solution of anisole in THF (1 mol/l). After 3 h at -20°C the stirred mixture was treated with the 0.2 g of deuterium oxide. The crude product was distilled out under reduced pressure together with THF and then the product isolated by distillation in a Hickman apparatus or by preparative gas chromatography and shown to be 2-deuteroanisole (**8**): (99 mg, 92%); m/e 109 (M^+, 100%), 94 (4, $C_6H_4DO^+$), 79 (52, $C_6H_6D^+$), 78 (20, $C_6H_5D^+$), 66 (70, $C_5H_4D^+$), 52 (16, $C_4H_2D^+$), 40 (38, $C_3H_2D^+$); IR (neat), $\nu = 3068$, 3004, 2956, 2944, 2836, 1908, 1800, 1700, 1592, 1480, 1436, 1308, 1284, 1248, 1180, 1160, 1124, 1116, 1052, 1032, 980, 944, 866, 844, 764 cm^{-1}; ^1H NMR ($CDCl_3$), $\delta = 3.88$ (s, 3H), 6.99–7.09 (m, 2H), 7.35–7.44 (m, 2H); ^{13}C NMR ($CDCl_3$), $\delta = 55.32$ (s, CH_3), 113.92 (t, C-2, J(C–D) = 24.7), 114.26 (s, C-6), 120.92 (s, C-4), 129.61, 129.71 (s, s, C-3, C-5), 159.90 (s, C-1).

Reaction of the organopotassium reagent 4 with carbon dioxide. The mixture obtained from 58 mg (1 mmol) of oxetane and 15 ml potassium solution under argon was treated immediately with 4.4 g (0.1 mol) of solid carbon dioxide. When the carbon dioxide had all disappeared the mixture was treated with MeI or protonated.

Methylation proceeded as follows. To the reaction mixture was added the 0.86 g (6 mmol) of methyl iodide. After 24 h at room temperature the potassium iodide formed was filtered off and the solution mixture washed three times with saturated aqueous NaCl (10 ml) then dried over anhydrous $MgSO_4$. The crude product was distilled out under reduced pressure together with THF and then the pure product isolated by distillation in a Hickman apparatus or by preparative gas chromatography and shown to be 4-methoxybutyric acid methyl ester (**10**) (108 mg, 82%); m/e 132 (M^+, 2%), 101 (18, $C_5H_9O_2^+$), 74 (11, $CH_3CO_2CH_3^+$), 69 (21, $C_3H_5CO^+$), 59 (92, $CO_2CH_3^+$), 45 (100, $CH_3OCH_2^+$), 31 (12, CH_3O^+); IR (neat), $\nu = 2980$, 2936, 2880, 2830, 1740, 1456, 1376, 1260, 1180, 1120, 1024, 992, 916, 872 cm^{-1}; ^1H NMR ($CDCl_3$), $\delta = 1.89$ (quint, 2H), 2.40 (t, 2H), 3.33 (s, 3H), 3.41 (t, 2H), 3.68 (s, 3H).

Protonation proceeded as follows. An HCl solution in Et_2O (2.35 ml of 2.6 mol/l) was added to the reaction mixture. After 60 min at room temperature the potassium chloride was filtered off and the crude product was distilled out under reduced pressure together with the THF. The product was isolated by distillation in a Hickman apparatus or by preparative gas chromatography and shown to be γ-butyrolactone (**11**) (76 mg, 88%); m/e 86 (M^+, 40%), 56 (12, $C_2H_4CO^+$), 42 (100, $C_3H_6^+$), 41 (96, $C_3H_5^+$), 39 (40, $C_3H_3^+$); IR (neat), $\nu = 2996$, 2920, 1772, 1460, 1420, 1376, 1280, 1168, 1084, 1036, 988, 932, 872 cm^{-1}; ^{1}H NMR ($CDCl_3$), $\delta = 2.28$ (quint, 2H), 2.50 (t, 2H), 4.36 (t, 2H).

Reaction of sodium-potassium complex with oxetane

The preparation of the sodium-potassium solutions and the reaction of sodium anions with oxetane were carried out in a dry flask under dry argon. The sodium-potassium solution was obtained by a contact of sodium-potassium alloy 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 into the reactor and an equimolar amount of oxetane (solution in THF 0.5 mol/l) was added dropwise until the colour of the sodium-potassium solution disappeared. The mixture was immediately protonated or treated with an alkyl halide, triphenylmethane, anisole or carbon dioxide.

Protonation of reagent obtained from sodium-potassium complex and oxetane. To the reaction mixture obtained from 58 mg (1 mmol) of oxetane and 15 ml sodium-potassium solution 2.35 ml of a solution of HCl in Et_2O (2.6 mol/l) was immediately added under argon. After 5 min at −20°C the potassium and sodium chloride were filtered off and the crude product was distilled out under reduced pressure together with THF and the pure product isolated by preparative gas chromatography and shown to be 1-propanol (**5**) yield (86% by GLC based on starting oxetane); the analytical data were identical with those for the product from the reaction with potassium anions.

Alkylation of reagent obtained from sodium-potassium complex and oxetane by methyl iodide. To the mixture obtained from 58 mg (1 mmol) of oxetane and 15 ml of the sodium-potassium solution 0.86 g (6 mmol) of methyl iodide was added immediately under argon. After 60 min at −20°C the potassium and sodium iodide were filtered off and the solution washed three times with saturated aqueous NaCl (three times, 10 ml) then dried over anhydrous $MgSO_4$. The crude product was distilled out under reduced pressure together with THF and the pure product isolated by preparative gas chromatography and shown to be butyl methyl ether (**6**); yield (83% by GLC) (based on starting oxetane); analytical data were identical with that of reaction with potassium anions.

Metallation of triphenylmethane by organosodium compound 4. To the reaction mixture obtained from 58 mg (1 mmol) of oxetane and 15 ml of the sodium-potassium solution 1 ml of a solution of triphenylmethane in THF (1 mol/l) was added under argon a red colour developed. After 60 min at −20°C 0.2 g of deuterium oxide was added with stirring and the red colour disappeared. The THF was evaporated off under reduced pressure and the residue recrystallized from methyl-d_3 alcohol-*d*, dried under vacuum and shown to be triphenylmethane-*d* (**7**) (236 mg, 97%.

Metallation of anisole by organosodium compound 4. To the reagent obtained from 58 mg (1 mmol) of oxetane and 15 ml of the sodium-potassium solution 1 ml of a solution of anisole in THF (1 mol/l) was added under argon. After 3 h at −20°C the stirred mixture was treated with 0.2 g of deuterium oxide. The crude product was distilled off under reduced pressure together with THF and then the pure produced isolated by distillation in a Hickman apparatus or by preparative gas chromatography and shown to be 2-deuteroanisole (**8**) (101 mg, 94%).

Reaction of organosodium compound 4 with carbon dioxide

To the reagent obtained from 58 mg (1 mmol) of oxetane and 15 ml of the sodium-potassium solution under argon were added 4.4 g (0.1 mol) of solid carbon dioxide. When the carbon dioxide had disappeared the mixture was methylated or protonated.

Methylation: To the mixture was added 0.86 g (6 mmol) of methyl iodide. After 24 h at room temperature the potassium and sodium iodide were filtered off and the solution washed three times with saturated aqueous NaCl (three times, 10 ml) then dried over anhydrous $MgSO_4$. The crude product was distilled under reduced pressure together with THF and the pure product isolated by distillation in a Hickman apparatus or by preparative gas chromatography and shown to be 4-methoxybutyric acid methyl ester (**10**) (109 mg, 83%).

Protonation: The reaction mixture was treated with 2.35 ml of HCl solution in Et_2O (2, 6 mol/l). After 60 min at room temperature the potassium and sodium chloride were filtered off and the crude product was distilled under reduced pressure together with THF and the pure product isolated by distillation in a Hickman apparatus or by preparative gas chromatography and shown to be γ-butyrolactone (**11**) (78 mg, 90%).

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