

Reaction of Oxetane with $K^+(18\text{-crown-6})K^-$ Complex; a Convenient Route to One-pot Metallation

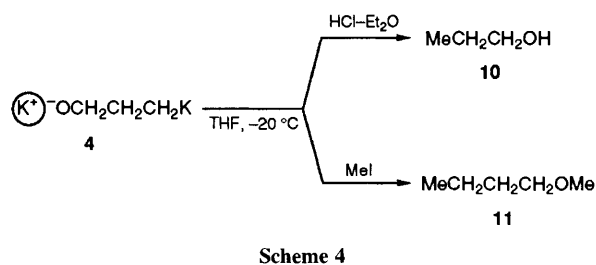
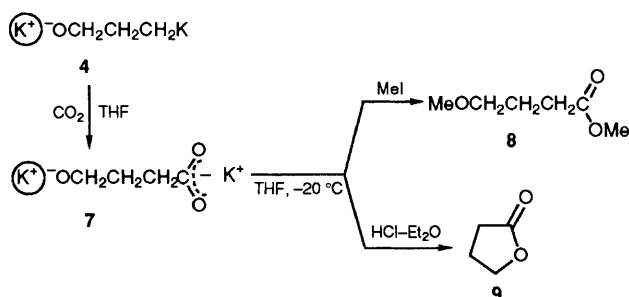
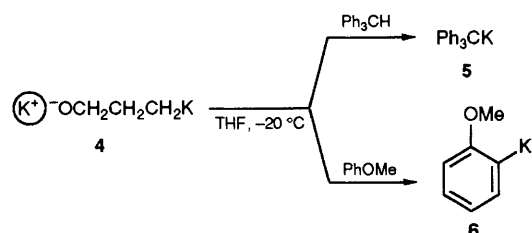
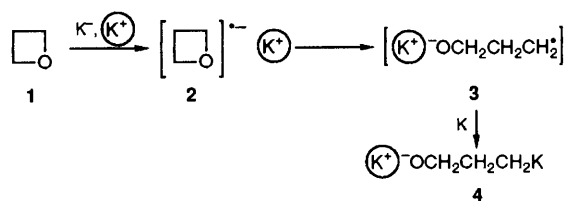
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A novel reaction of $K^+(18\text{-crown-6})K^-$ complex with oxetane yields the organometallic compound potassium γ -potassiopropoxide, a very efficient new metallating agent and a useful reagent in chemical synthesis.

In this communication we report the reaction of oxetane **1** with the potassium complex $K^+(18\text{-crown-6})K^-$ containing potassium anions and complexed by 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) potassium cations solubilised in tetrahydrofuran (THF) at -20°C . The ring cleavage of oxetane was reported previously as a result of

oxetane reduction with lithium arenides *e.g.* lithium 4,4'-*tert*-butylbiphenylide.¹ The reagent $K^+(18\text{-crown-6})K^-$ was prepared according to ref. 2. The reaction with oxetane proceeds with alkyl to oxygen bond scission (Scheme 1) yielding the potassium organometallic compound **4** (96% yield).



The experimental results suggest that at first, due to single electron transfer, an oxetane radical anion **2** and, after ring scission, potassium propoxide radical **3** are produced (see Scheme 1). The latter reacts with potassium to yield eventually the organometallic compound **4** which precipitates.

The proposed course of the reaction has been followed by ^{39}K NMR (Fig. 1) and ESR measurements (Fig. 2). The ^{39}K NMR spectra of potassium solutions in THF containing 18-crown-6 exhibit two signals: a broad signal of potassium cation complexed by 18-crown-6 and the distinct singlet which corresponds to potassium ion³⁻⁵ [Fig. 1(a)]. After addition of oxetane to the blue metal solution, both signals disappear completely [Fig. 1(b)]. The lack of cation signal in the spectrum is due to the precipitation of the insoluble compound **4** and after addition of water to the reaction mixture the very broad signal of the complexed potassium cation appears again in the ^{39}K NMR spectrum [Fig. 1(c)]. These measurements indicate that during the reaction electron transfer from the potassium anion to oxetane molecule occurs.

In the equimolar reaction of oxetane with potassium anions we did not observe any paramagnetic species in the ESR spectra. However, in the case of the reaction of an excess of

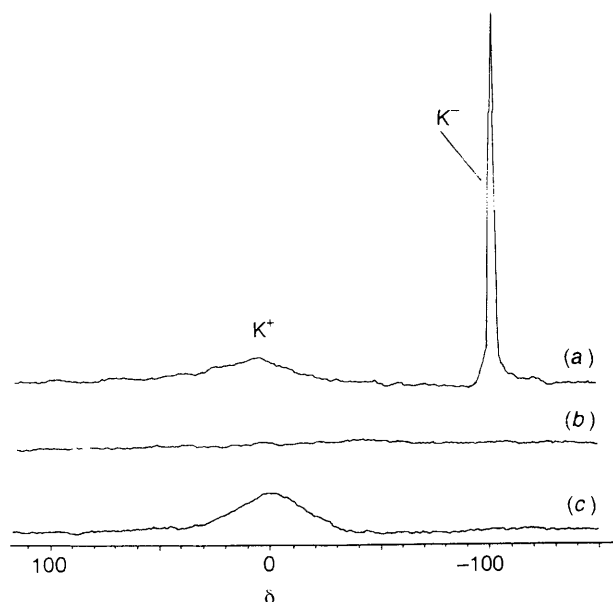


Fig. 1 ^{39}K NMR spectra of (a) potassium solution in THF containing 18-crown-6, (b) after addition of oxetane and (c) after addition of water to the solution

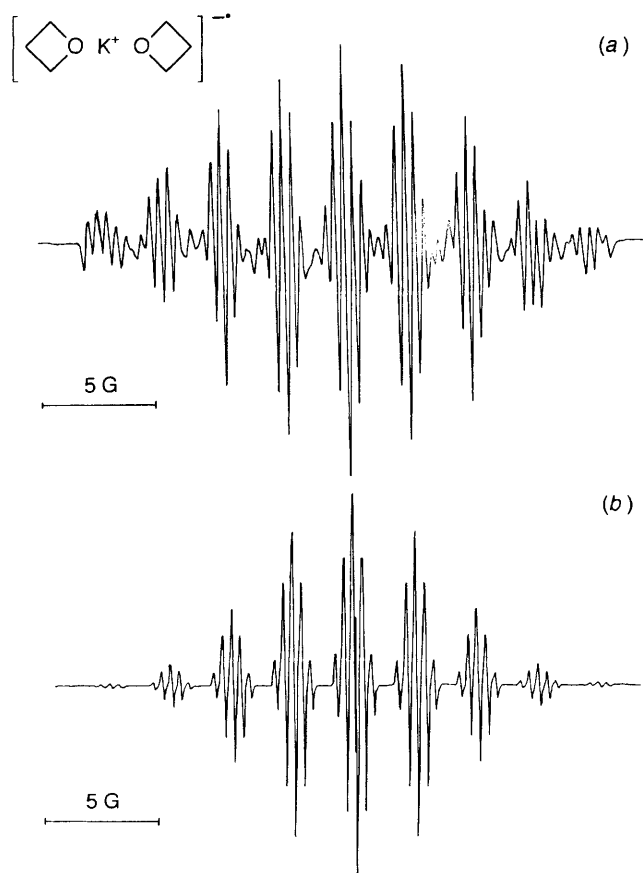


Fig. 2 ESR spectra of the reaction between an excess of oxetane and potassium anions under (a) experimental and (b) simulated conditions

oxetane in relation to potassium anions (molar ratio 4 : 1), a broad splitting multiplet (total width of 24 G) centred at $g = 2.008$ appears in the ESR spectrum, indicating that an oxetane radical anion consisting of two oxetane entities is formed [Fig. 2(a)]. The multiplet consists of 45 lines of $\Delta H_{pp}^{\circ} = 0.21$ G (nine quintets). The determined splitting constants $a^{H_{2,4}} = 0.39$ G, $a^{H_3} = 2.66$ G can be assigned to interaction of eight α -

and four β -ring protons of the two molecules of oxetane. The experimental spectrum [Fig. 2(a)] is in good agreement with the simulated one [Fig. 2(b) using a Bruker simulation program] obtained by using experimental hyperfine constants and confirms formation of the intermediate oxetane radical anion **2** (Scheme 1).

The final product, **4**, seems to be comparatively stable, however, it is very efficient in metallation reactions with triphenylmethane and anisole (Scheme 2). The yield of metallation is high (above 90%) and reaction conditions milder than used for metallation with traditional reagents like *n*-butyllithium with potassium *tert*-butoxide^{6,7}.

In the reaction of compound **4** with carbon dioxide compound **7** is formed. Methylation or protonation of compound **7** yields methyl 4-methoxybutanoate **8**, (yield 82%) or γ -butyrolactone **9**, (yield 88%) (see Scheme 3).

The protonation and methylation reactions of compound **4** yield *n*-propyl alcohol **10** or butyl methyl ether **11**, respectively (yields above 80%) (Scheme 4). Satisfactory spectroscopic data was obtained for the products shown in Schemes 2–4.

The experiments described reveal the usefulness of this complex containing potassium anions and crowned cations in the reaction with oxetane to yield a new metallating agent. The process of metallation as shown in the reactions

with anisole or triphenylmethane is surprisingly free of side reactions, proceeds with good yield and 2–3 times faster than that with traditional reagents like *n*-butyllithium or *tert*-butyllithium.

The described functionalised organometallic compound **4** can be also employed as a useful reagent in carboxylation, alkylation and protonation reactions.

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References

- 1 B. Mudryk and T. Cohen, *J. Org. Chem.*, 1989, **54**, 5657.
- 2 Z. Jedliński, A. Misiołek and P. Kurcok, *J. Org. Chem.*, 1989, **54**, 1500.
- 3 J. L. Dye, C. W. Andrews and J. M. Ceraso, *J. Phys. Chem.*, 1975, **79**, 3076.
- 4 P. P. Edwards, A. S. Ellaboudy, and D. M. Holton, *Nature (London)*, 1985, **317**, 242.
- 5 M. Sokół, J. Grobelny and Z. Jedliński, *Magn. Res. Chem.*, 1990, **28**, 934.
- 6 M. Schlosser and J. Hartmann, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 508.
- 7 M. Schlosser and S. Strunk, *Tetrahedron Lett.*, 1984, 741.