Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

PREPARATION OF ORGANOPOTASSIUM COMPOUNDS

L. LOCHMANN AND D. LÍM
Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague 6 (Czechoslovakia)

(Received November 18th, 1970)

SUMMARY

Some organopotassium compounds have been prepared by treatment of organolithium compounds with potassium (−)(1*R*)-menthoxide. The products are obtained in good yield and relatively pure. Treatment of n-butyllithium with potassium (−)(1*R*)-menthoxide in the presence of some aromatic hydrocarbons leads to formation of the potassium derivatives of these hydrocarbons.

The most commonly used method for preparing relatively pure organopotassium compounds involves treatment of organomercury compounds with potassium[1], but the products are contaminated with mercury metal. Factors which reduce the purity of organopotassium compounds in all methods of preparation are spontaneous decomposition, involving formation of potassium hydride and other compounds, and reaction with the solvent (aliphatic hydrocarbons)[2,3].

Preparation of high-purity organosodium compounds by treating alkyllithium compounds with sodium alkoxides has been described previously[4]. This method has now been extended to the preparation of comparatively pure organopotassium compounds. The potassium (−)(1*R*)-menthoxide can be used with advantage as the alkoxide, its solubility in hydrocarbons (more than 40g/100 ml cyclohexane or heptane) being quite satisfactory. The products, which were isolated in 55–90% yields (Table 1) contained a maximum of 0.4% Li. The slightly higher than theoretical potassium contents can be attributed to the instability of the compounds under investigation; for instance, in the case of solid butylpotassium, the alkalinity increased by 5% K during a few days at room temperature, and the originally light-brown colour of the product changed to deep-brown. The IR spectrum of butylpotassium (suspension in cyclohexane), recorded immediately after formation of the compound, differed considerably from that recorded after several days (Fig. 1). The rate of decomposition varied with different samples of the compound, probably because of the effects of trace impurities.

The new method of making organopotassium compounds has the advantages of simplicity and of giving products of higher purity than usual. tert-Butylpotassium has not yet been prepared by this method. (Attempts to make the corresponding so-

TABLE 1

PREPARATION OF ORGANOPOTASSIUM COMPOUNDS (RK) BY TREATMENT OF ALKYLLITHIUM COMPOUNDS WITH POTASSIUM (−)(1*R*)-MENTHOXIDE

R	RLi/Alkoxide (Mol. ratio)	Temp. (°C)	Reaction time (h)	Analysis of the precipitate				Yield[a] RK(%)
				Alkalinity (% K)		Metal content (%)		
				Found	Calcd.	K	Li	
C_4H_9	0.80	25	0.5	42.7	40.65	42.1	0.23	80.5[b]
C_4H_9	1	25	0.5	43.7	40.65	41.95	0.26	67
C_4H_9	1.45	25	0.5	44.6	40.65	38.7	1.07	42.7
C_4H_9	4	25	0.5	51.5		18.8	5.52[c]	90.6
C_4H_9	1	10	2	45.1	40.65	44.4	0.20	62.3
C_4H_9	1	20	2	43.6	40.65	42.6	0.22	64.0
C_4H_9	1	35	2	44.2	40.65	43.5	0.26	66.8
C_4H_9	1	20	0.2	43.1	40.65	39.9	0.22	63.1
C_4H_9	1	20	3	42.9	40.65	39.9	0.17	59.2
C_6H_{13}	1	20	2	35.9	31.46	33.4	0.30	58.0
C_8H_{17}	1	20	3	28.7	25.65	26.49	0.40	86.4
$C_{12}H_{25}$	1	20	3	19.5	18.78	18.7	0.15	60.6
$(CH_3)_3C$	1	20	0.1[d]	56.7	40.65	46.8	1.77	[e]

[a] Alkalinity of the total isolated product relative to the alkalinity of the total initial alkoxide used. [b] Related to butyllithium. [c] Complex [1.65 $C_4H_9Li \cdot C_4H_9K$]. [d] Isobutylene was evolved during the reaction. [e] Treatment with carbon dioxide did not yield pivalic acid.

dium compounds were also unsuccessful[4].) Instead, isobutylene was evolved and a product with a high potassium content was isolated; presumably the organopotassium compound was formed but then underwent decomposition.

The n-butyllithium potassium (−)(1*R*)-menthoxide system was used to investigate the effects of experimental conditions on the preparation of n-butylpotassium (Table 1). The optimum alkyllithium/potassium alkoxide ratio is approximately equimolar. An excess of alkoxide leads to the formation of products having a stronger tendency towards spontaneous decomposition in the solid state. A small excess of

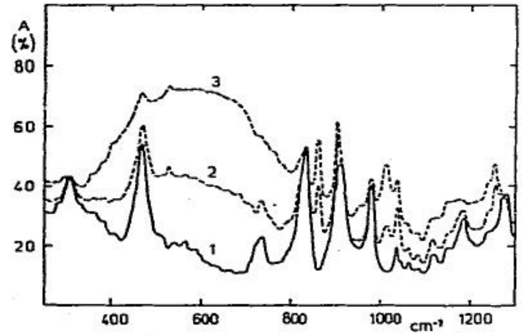

Fig. 1. Infrared spectrum of the suspension of n-butylpotassium in a mixture of cyclohexane and nujol, temperature 25°. Curve: 1 – immediately after isolation, 2 – the same mixture after 72 hours, 3 – the same mixture after 144 hours.

butyllithium (*e.g.* 1.5) lowers the yield and purity of the product. With a several-fold excess of butyllithium, complexes of butyllithium and butylpotassium of various composition such as $[1.65\ C_4H_9Li \cdot C_4H_9K]$ are formed, the IR spectrum of which bears some resemblance to the sum of spectra of the components, if frequency shifts of some bands due to the complex bond (Fig. 2) are taken into account. Change in the reaction time between 0.2 and 3 h and the temperature between 10 and 35° has little effect. At temperatures below −10°, a gel-like product is formed from butyllithium and potassium (−)(1*R*)-menthoxide in heptane, and is converted into butylpotassium at a discernible rate only above about 10°.

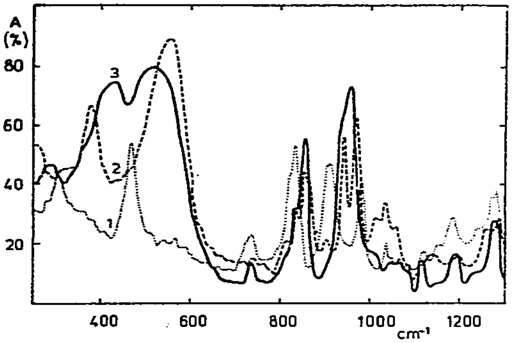

Fig. 2. Infrared spectra. Curve: 1 – n-butylpotassium (suspension in nujol), 2 – n-butyllithium (solution in cyclohexane), 3 – complex $[1.65\ C_4H_9Li \cdot C_4H_9K]$ in nujol.

As has been described previously[4,5], the metalation of reactive compounds can be carried out also by acting upon them with the system alkyllithium/potassium alkoxide. Potassium (−)(1 *R*)-menthoxide is very suitable for this purpose because it has a high solubility in hydrocarbons and because the reaction follows a smooth course (Table 2). The mechanism of the reaction has not been fully elucidated (*cf.* the assumptions made in considering the activation of organometallics)[5], but since an organopotassium compound is formed obviously at some stage there must be an exchange of the alkaline metal bound to the carbon atom.

The products of both the exchange and metalation reactions have been converted into carboxylic acids by treatment with solid carbon dioxide in pentane. Thus, a mixture of carboxylic acids was isolated from freshly prepared butylpotassium in 75% yield (based on the assumption that the product was wholly valeric acid, which constituted at least 95% of the mixture.) The complex $[1.65\ C_4H_9Li \cdot C_4H_9K]$ was transformed into an orange-yellow complex of butyllithium with benzylpotassium (Found: K, 15.6; Li, 4.25%) by shaking with toluene; an approximately equimolar mixture of valeric and phenylacetic acids was obtained from this complex by carboxylation.

EXPERIMENTAL

All operations involving the organometallic compounds and potassium alkoxide were carried out under argon containing ca. 15 ppm of oxygen. A Perkin–Elmer 900 apparatus was used in the GLC analyses.

TABLE 2

METALATION OF AROMATIC HYDROCARBONS WITH AN EQUIMOLAR BUTYLLITHIUM/POTASSIUM (–)(1*R*)-MENTHOXIDE MIXTURE

Hydrocarbon	Primary reaction product	Analysis				Yield[a]	Crude product after carboxylation[b]		
		Metal content (%)		Alkalinity (% K)		(%)	Acid	m.p. (°C)	Yield (%)
		Li	K	Calcd.	Found				
Benzene	C_6H_5K	0.37	31.2	33.65	32.9	88.6	C_6H_5COOH	117–124	74.2
Toluene	$C_6H_5CH_2K$[c]	0.19	29.1	30.04	30.4	92.7	$C_6H_5CH_2COOH$	71– 74	89.7
Cumene	$C_6H_5CK(CH_3)_2$	0.44	22.3	24.70	24.4	91.8	$C_6H_5C(CH_3)_2COOH$	65– 73	67.7

[a] Related to the starting alkoxide. [b] Reaction of the primary metalation product with solid carbon dioxide. [c] With a two-molar excess of butyllithium the product obtained (98% theor. based on potassium used) contained Li (0.71%) and K (25.6%), and on carboxylation gave phenylacetic acid in 85% yield.

Materials used

Organometallics. Butyl-, tert-butyl-, hexyl-, octyl- and dodecyllithium were prepared from alkyl halides and lithium in a hydrocarbon solvent; tert-butyllithium was isolated in the crystalline state (alkalinity (%Li): found 10.87; calcd. 10.84)[6].

Crystalline potassium (−)(1 *R*)-menthoxide was prepared from (−)(1 *R*)-menthol (α_D^{25} −49.85°) and potassium in tetrahydrofuran[7] (alkalinity (%K): found 20.17; calcd. 20.12). A cyclohexane or heptane solution of the alkoxide was obtained either from the crystalline product or by filtering the mixture obtained from potassium metal and a 20% solution of (−)(1*R*)-menthol in hydrocarbon (1.5 g-atom K/mol of alcohol) after 15 h stirring at 70–80°. The concentration was determined titrimetrically and the solution kept below 0°.

Solvents. Cyclohexane was shaken with the nitrating acid mixture at 50°C and filtered through silica-gel. Heptane and pentane were shaken with a mixture of sulphuric acid and 15% phosphorus pentoxide. All the solvents used were rectified and dried over $LiAlH_4$.

Procedure

In a Schlenk vessel adapted for centrifuging (about 2000 rpm), a solution of lithium alkyl in cyclohexane or heptane was added dropwise during 5 min with stirring, to a solution of potassium (−)(1*R*)-menthoxide in the same solvent at a chosen temperature. The concentrations of the solutions were chosen so that after mixing there would be about 2000 ml solvent per mole of alkoxide. The mixture was stirred at the chosen temperature for the appropriate time, then the mother liquor was separated by centrifugation (filtration can also be used, but it is less favourable), the precipitate was washed 6 to 8 times by mixing with solvent and centrifugation, dried at room temperature and a pressure of 1 mm for at least five h, and kept at a temperature of approximately −50°. The alkalinity of the product was determined titrimetrically after hydrolysis. The potassium and lithium content was determined by atomic absorption spectrophotometry with a Perkin–Elmer 303 apparatus, and the potassium content was further checked by emission flame photometry on a Unicam SP 90 apparatus. The IR spectra were recorded with a Perkin–Elmer 457 apparatus, the CsI cells used being provided with special cocks permitting filling and measurement in an inert atmosphere[8].

In the metalations a solution of butyllithium in heptane was added dropwise to a solution of an equimolar amount of (−)(1*R*)-menthoxide potassium in the aromatic hydrocarbon (3000 ml/mol alkoxide) at 25°; the mixture was then shaken at room temperature for 8 h and treated as described above.

In the identification of products by carboxylation, the precipitate obtained was suspended in pentane and treated with solid carbon dioxide. The melting points of the isolated carboxylic acids and the GLC retention times of their methyl esters (after treatment with diazomethane) were compared with those for authentic compounds.

ACKNOWLEDGEMENT

The authors are indebted to Miss E. Šrámková for technical assistance, to Mr. M. Mikšovský and Mrs. O. Kinterová from the Central Institute of Geology for photometric determinations of the alkaline metals, and to Mrs. E. Plachetková (Institute of

Macromolecular Chemistry of the Czechoslovak Academy of Sciences) for the gas chromatographic analyses.

REFERENCES

1 M. Schlosser, *Angew. Chem.*, 76 (1964) 124, 258; M. Schlosser, *Neuere Methoden der präparativen organischen Chemie*, Vol. 5, Verlag Chemie, Weinheim, 1967, p. 210.
2 R. A. Finnegan, *Tetrahedron Lett.*, (1962) 1303; *ibid.*, (1963) 429, 851; *Trans. N.Y. Acad. Sci.*, 27 (1965) 730.
3 M. Mergard and F. Korte, *Monatsh. Chem.*, 98 (1967) 763.
4 L. Lochmann, J. Pospíšil and D. Lím, *Tetrahedron Lett.*, (1966) 256.
5 M. Schlosser, *J. Organometal. Chem.*, 8 (1967) 9.
6 L. Lochmann, J. Pospíšil, J. Vodňanský, J. Trekoval and D. Lím, *Collect. Czech. Chem. Commun.*, 30 (1965) 2187.
7 L. Lochmann, J. Čoupek and D. Lím, *Collect. Czech. Chem. Commun.*, 35 (1970) 733.
8 P. Schmidt and L. Lochmann, *Chem. Listy*, 63 (1969) 609.