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Cryptate Chemistry. I. The Reaction of Potassium Alkanoates with Alkyl Halides in the Presence of 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane

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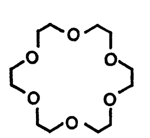
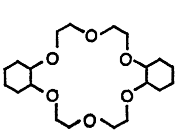
Synopsis. Potassium alkanoates reactes with organic halides in the presence of bicyclopolyether (III) in benzene to give esters in high yields.

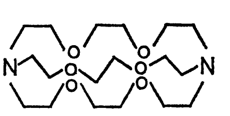
In recent years, many papers1–3) have been published reporting that such crown ethers as I and II increase the solubility of salts and the reactivity of anions in aprotic solvents. For example, Sam and Simmons4) have reported that the complexes of potassium halide and potassium hydroxide with dicyclohexyl-18-crown-6 (II) show strong nucleophilic and basic properties.



(I)



(II)



(III)

Liotta *et al.*5) have observed that potassium fluoride and the potassium acetate complex of 18-crown-6 (I), which he termed the "naked anion" in non-polar aprotic solvents, have shown unusual properties and reactivities. Dietlich *et al.*6–7) have reported the preparation and properties of a number of macrobicyclic polyethers with bridgehead nitrogens, such as 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane (III). It was shown that these compounds form stable complexes, cryptate, with alkali, alkaline earth, and other cations, and that the complexing ability of the cryptates could be correlated with the number of ligand sites, the approximate cavity size of the bicyclopolyether, and the relative cation radius in question. Our interest in the reactivities of these cryptates in aprotic solvents led us to examine the reactivities of the potassium salts of acids with some halides in the presence of III in benzene.

Nucleophilic substitution was carried out by the following method. The carboxylate complex of III was prepared by dissolving a catalytic amount of III in 7 ml of dry benzene and by then adding an appropriate amount of dry potassium salts of acids. After the heterogenious system had then been stirred for 30 min, the alkyl halide was added all at once and the mixture was stirred for a further 3 hr at 15 or 83 °C. Table 1 summarizes the results.

The data in the table clearly show that the cryptates prepared by mixing III with potassium alkanoates in benzene are sufficiently reactive to form organic esters from organic halides at an appropriate temperature. Indeed, in the absence of III, no reaction takes place under the same conditions. Benzyl bromide gives less than 2% benzyl acetate after 10 hr at room temperature when it is treated with potassium acetate in the absence of III, whereas benzyl acetate is formed quantitatively within 3 hr when III is present. The reaction of the cryptate complex from potassium propionate with 1,2-dibromoethane afforded a mixture of ethylene dipropionate and 2-bromoethyl propionate. The ratio of the two substances is dependent upon which reagent is present in excess. Another

Table 1. Reactions of the cryptate with organic halides

Organic bromide (×10^{-3} mol)	Potassium carboxylate (×10^{-3} mol)	III (×10^{-3} mol)	Reaction temp. (°C)	Yielda) (%)	Products
$PhCH_2Br$	CH_3COOK		15	99	$PhCH_2OCOCH_3$
(0.812)	(2.40)	(0.160)			
$PhCH_2Br$	CH_3CH_2COOK		15	85	$PhCH_2OCOCH_2CH_3$
(0.810)	(2.50)	(0.151)			
$PhCH_2Br$	$(CH_3)_2CHCOOK$		15	95	$PhCH_2OCOCH(CH_3)_2$
(0.304)	(0.873)	(0.093)			
$CH_3(CH_2)_6CH_2Br$	CH_3COOK		83	85	$CH_3(CH_2)_6CH_2OCOCH_3$
(0.500)	(1.60)	(0.106)			
$CH_3(CH_2)_6CH_2Br$	CH_3CH_2COOK		83	90	$CH_3(CH_2)_6CH_2OCOCH_2CH_3$
(0.301)	(0.574)	(0.154)			
$CH_3(CH_2)_6CH_2Br$	$(CH_3)_2CHCOOK$		83	99	$CH_3(CH_2)_6CH_2OCOCH(CH_3)_2$
(0.404)	(1.00)	(0.106)			
$BrCH_2CH_2Br$	CH_3CH_2COOK		83	89	$CH_3CH_2COOCH_2CH_2OCOCH_2CH_3$
(0.500)	(2.00)	(0.133)		11	$BrCH_2CH_2OCOCH_2CH_3$

a) The values are those obtained by glc. b) All products show the same retention time with authentic sample and mass spectra were consistent with the proposed structure. Reaction of *n*-octyl bromide with potassium alkanoates afforded octene in less than 0.3% yield.

feature of the reaction with the aid of the cryptate is the low degree of the formation of the olefin. *n*-Octyl bromide afforded less than 0.3% of 1-octene.

The main conclusions to be drawn from these results are as follows: 1) cryptate carboxylate can be used as an extremely valuable reagent in the preparation of alkyl esters in non-polar aprotic solvents such as benzene, and 2) cryptate carboxylate is a powerful nucleophile but a weak base.

Experimental

The gas chromatograms were obtained on a Hitachi K 23 apparatus using the following column; 10% FFAP on Chromosorb W AW/DMCS 1 m×3 mm. The mass spectra were recorded on a gas-chromatography mass spectrometer, Shimadzu LKB 9000, at an ionizing voltage of 70 eV.

Materials. Compound (III) was prepared according to the procedures described in the literature.[6] Potassium alkanoates of the Tokyo Kasei Kogyo Co., Ltd., were used without further purification. *n*-Octyl bromide and benzyl bromide of the Tokyo Kasei Kogyo Co., Ltd., were purified by distillation prior to use.

Solvent. The solvent used was purified by distillation.

General Procedure. To a solution of III in 7 ml of benzene, we added potassium alkanoate, after with the mixture was stirred for 30 min at room temperature. To the mixture we then added organic halide and continued stirring for a further 3 hr at 15 °C or 83 °C. At the end of the reaction, the organic layer was analyzed by gas chromatography and gas-chromatography mass spectrometer.

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