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NEW PREPARATION OF ALKYL IODIDES FROM THE CORRESPONDING ALCOHOLS

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Abstract : It is shown that alkyl iodides can be obtained from the corresponding alkyl α-chloroethyl carbonate and NaI or by direct reaction between the alcohol, α-chloroethyl chloroformate and NaI.

Continuing our studies on the use of α-chloroethyl chloroformates[1] we describe two new methods allowing the transformation of alcohols into the corresponding alkyl iodides. Thus, when alkyl α-chloroethyl carbonates[2] were submitted under proper conditions to the action of NaI the corresponding alkyl iodides were formed in fair to good yields (Table, method A) :

$$\mathrm{ROCOOCHClCH_3 + NaI \xrightarrow[\text{2) Toluene, }\Delta]{\text{1) Acetone, }\Delta} R\text{-}I}$$

During the reaction we observed the transient back formation of a large amount of the corresponding free alcohol ROH. This rather unexpected observation led us to think that the reaction could be realized one-pot, directly from the alcohol and chloroethyl chloroformate (method B) :

$$\mathrm{ROH + ClCOOCHClCH_3 + NaI \xrightarrow[\text{2) Toluene, }\Delta]{\text{1) Acetone, }\Delta} R\text{-}I}$$

The Table shows that method B must be generally preferred to method A as far as yields and reaction time are concerned. However HCl formation may constitute a drawback with acid sensitive substrates. Method A does not present this disadvantage. Other chloroformates (such as n-BuCH(Cl)OCOCl, 2-$\mathrm{ClC_6H_4CH(Cl)}$-OCOCl) may be used instead of $\mathrm{CH_3}$-CH(Cl)OCOCl. Comparison of NaI with LiI, KI or $\mathrm{MgI_2}$ showed that sodium iodide was the best reagent. The mechanisms of these reactions are still rather obscure. However alkyl α-iodoethyl carbonates could be proposed as intermediates. Indeed we were able to show that n-octyl α-iodoethyl carbonate (obtained from n-octyl α-bromoethyl carbonate and NaI) decomposes rapidly under the conditions used in method A or B to lead to n-octyl iodide. Work is continued in order to improve the yields and to clarify the mechanisms of these reactions.

General procedures. The reactions were monitored by GC analysis of small syringed aliquots on either GIRDEL 3000 or SPECTRA PHYSICS 7100 apparatus (flame ionization detectors) equipped with SE 30 capillary column.

Method A. A mixture of the alkyl α-chloroethyl carbonate (40 mmol) and NaI (44 mmol) in acetone (40 ml) was stirred at the temperatures and for the times indicated in the Table.

Toluene (40 ml) was then added, acetone distilled from the flask under atmospheric pressure and the mixture stirred at the temperatures and for the times indicated in the Table. The cooled mixture was then hydrolyzed and extracted with diethylether. The organic phase was washed with 5 % sodium thiosulfate solution then with water, and dried over $CaCl_2$. The alkyl iodide was obtained either by distillation or by column chromatography over silica gel.

Method B. α-Chloroethyl chloroformate (44 mmol) was slowly added to a stirred mixture of the alcohol (40 mmol) and NaI (44 mmol) in acetone (40 ml). After warming at the temperatures and during the times indicated in the Table, toluene (40 ml) was added and the reaction was continued as described in method A.

TABLE

$$[ROCOOCHClCH_3]\text{ or }[ROH + ClCOOCHClCH_3] + NaI \xrightarrow[\text{then Toluene, }\Delta]{\text{Acetone, }\Delta} R\text{-}I$$

R-	Method	Reaction conditions Acetone °C	t (h)	then toluene °C	t (h)	R-I$^{a)}$ %
n.C_4H_9-	A	56	5	then 75	30	65$^{b)}$
n.C_5H_{11}-	B	56	5	105	10	52$^{c)}$
n.C_8H_{17}-	A	56	5	95	24	83$^{c)}$
	B	56	5	105	4	91$^{b)}$
n.$C_{12}H_{25}$-	B	56	5	105	10	81$^{c)}$
C_6H_5-$(CH_2)_2$-	B	56	5	105	10	81$^{c)}$
C_6H_5-CH_2-	A	56	5	105	25	67$^{b)}$
	B	56	5	d)		65$^{c)}$
Cl-$(CH_2)_3$-	B	56	5	105	10	50$^{c)}$
-$(CH_2)_4$-	B	56	5	105	10	66$^{e)}$
s.C_8H_{17}-	A	56	64	75	42	57$^{c)}$
	B	56	5	105	10	55$^{c)}$
c.C_6H_{11}-	A	56	10	100	35	65$^{c)}$
	B	56	5	105	10	56$^{c)}$
1-Adamantyl	A	56	5	80	113	51$^{c)}$
	B	56	5	105	10	76$^{c)}$

a) Alkyl iodides were identified either by direct comparison (IR, NMR) with authentic samples or by comparison of their spectroscopic properties (IR, NMR) with those reported in the literature ; b) Determined by GLC analysis with internal standards ; c) Yield of isolated product ; d) Warming in acetone was sufficient to perform the reaction ; e) 1,4-Diodobutane.

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