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CARBONYLATION IN THE $SbCl_5$-LIQUID SULFUR DIOXIDE SYSTEM. THE CARBOXYLIC ACID ESTER SYNTHESIS FROM ALKYL CHLOROSULFITE AND DIALKYL SULFITE *

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A new synthesis of fatty acid esters by the carbonylation of alkyl chlorosulfite and dialkyl sulfite in $SbCl_5$-liq.SO_2 system containing ethanol has been described. The reactions of dialkyl sulfites in this medium gave esters in high yields and with lesser skeletal rearrangement.

Koch and Haaf$^{1)}$ in 1958 succeeded in the synthesis of carboxylic acid from olefin using formic acid as the source of carbon monoxide and sulfuric acid as the medium as well as the catalyst. In spite of a variety of the applicability of this method, this reaction is accompanied by a considerable extent of isomerization of the carbon skeleton, which diminishes the utility of this method for the preparative organic chemistry.

In the previous paper of this series,$^{2)}$ it was reported that the carbonylation of alkyl halide could be carried out conveniently in $SbCl_5$-liq.SO_2 system to yield the corresponding alkyl carboxylic acid or its ester, the latter being obtained in the presence of an alcohol in this system. The yields of the acids or esters from the primary halides, however, were low.

In the literature, S_Ni type reactions$^{3)}$ of alkyl$^{4)}$ and allyl chlorosulfites$^{5)}$ were examined and discussed extensively. Both alkyl chlorosulfite$^{6)}$ and dialkyl sulfite$^{7)}$ have recently been found to form carbonium ion in strong acid systems such as FSO_3H-SbF_5-SO_2, and are expected to react with carbon monoxide.

The present authors have carried out the carbonylation of alkyl chlorosulfite and dialkyl sulfite in order to prepare the carboxylic acid ester from alkyl (especially primary) derivatives efficiently with lesser skeletal rearrangement.

$$\text{R-OSOCl} \xrightarrow[\text{EtOH, CO, } -70^{\circ}]{\text{SbCl}_5\text{-liq.SO}_2} \text{RCOOEt}$$

$$\text{R-OS(O)OR'} \xrightarrow[\text{EtOH, CO, } -70^{\circ}]{\text{SbCl}_5\text{-liq.SO}_2} \text{RCOOEt} + \text{R'OH}$$

Table 1.

The Carbonylation Reaction of Alkyl Halide, Alkyl Chlorosulfite and Dialkyl Sulfite in $SbCl_5$-Liquid Sulfur Dioxide Containing Ethanol at -70°C.

Substrate	Product (yield %)
$CH_3CH_2CH_2CH_2Br$	$CH_3CH_2CH(CH_3)COOEt$ (5)
$CH_3CH_2CH_2CH_2OSOCl$	$CH_3CH_2CH(CH_3)COOEt$ (66)
$CH_3(CH_2)_3OS(O)O(CH_2)_3CH_3$	$CH_3CH_2CH_2CH_2COOEt$ (75)
$CH_3CH_2CH_2OSOCl$	$CH_3CH_2CH_2COOEt$ (65)
Cyclohexyl chloride	Ethyl Cyclohexanecarboxylate, I (8)
	Ethyl 1-Methylcyclopentanecarboxylate, II (23)
Cyclohexyl chlorosulphite	I (19) and II (37)
Dicylohexyl sulfite	I (53) and II (3)

As is shown in Table 1, the yields of the esters increased remarkably by changing the leaving group of the substrate.

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