The Carbonylation of Alkyl Halide with Carbon Monoxide in the $SbCl_5$-Liquid Sulfur Dioxide System

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The synthesis of several carboxylic acids or esters from olefins and alkyl halides with carbon monoxide, and water or alcohol catalyzed by acid catalysts has been studied by many investigators.[1a)] Simon and Warner have reported the reaction in hydrogen fluoride with water, which gave isobutyric acid from isopropyl chloride.[1b)]

Considerable success in this synthesis has been won by Koch and Haaf using formic acid as the source of carbon monoxide and sulfuric acid as the catalyst.[2)] In spite of the applicability of the Koch method to a great variety of compounds, this reaction is accompanied by the considerable isomerization of the double bond and the carbon skeleton, which diminishes the utility of this method from the point of view of preparation.

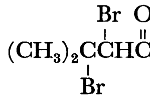
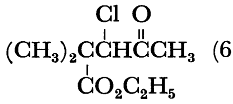
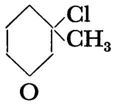
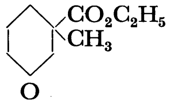
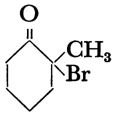
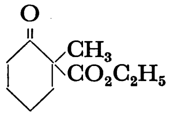
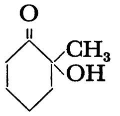
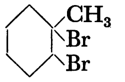
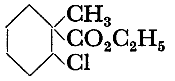
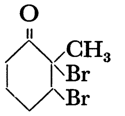
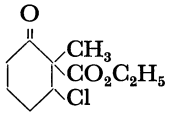
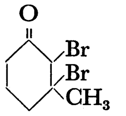
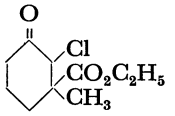
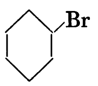
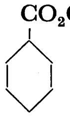
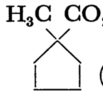
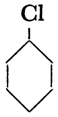
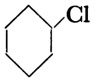
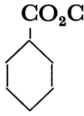
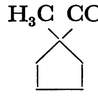
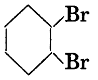
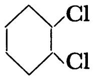
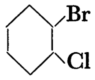
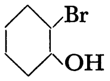
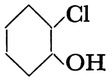
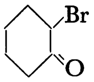
To carry out the carbonylation under milder conditions, the present authors attempted the carbonylation of alkyl halides in the $SbCl_5$-liquid SO_2 system at $-70°C$ under atmospheric pressure. The selectivity of the reaction and the skeletal rearrangement of the substrate are also examined using mono- and dihalogeno-substituted cyclohexane derivatives. The reaction scheme is as follows:

$$RX + CO + ROH \xrightarrow[SbCl_5+SO_2]{1\,atm\ -70°} RCOOR + HX \qquad (1)$$

A typical procedure is as follows. To a mixture of 20 g (0.07 mol) of $SbCl_5$ and 50 m*l* (about 0.5 mol) of liquid SO_2, a solution of 4.6 g (0.05 mol) of *t*-butyl chloride and 3.7 g (0.08 mol) of ethanol, dissolved in 20 m*l* of dichloromethane, was dropped at $-70°C$ over a thirty-minute period while a current of carbon monoxide gas was bubbled into the flask at a velocity of 70 m*l* per minute, after which the reaction was continued for thirty additional minutes. The reaction mixture was treated following the ordinary method; subsequent analysis by vpc showed the existence of only one product, the pivalic acid ethyl ester (4.2 g (66%)). All the products obtained were characterized by NMR, infrared, and mass spectroscopy.

The results obtained are summarized in Table 1. When a tertiary alkyl halide was used as the substrate the ester corresponding to the starting material was obtained in a fair yield without the isomerization of the carbon skeleton. A control experiment without liquid SO_2 gave no carbonylated product. The secondary halide reacted upon isomerization, and the yield of the corresponding ester was depressed as a result of the skeletal transformation. Moreover, the following facts are worth noting.

Table I. Reactions of alkyl halide with carbon monoxide

Halide	Product, (Yield %)[a)]
$(CH_3)_3CCl$	$(CH_3)_3CCO_2C_2H_5$ (66)
 $(CH_3)_2\underset{Br}{\overset{}{C}}\overset{Br}{C}H\overset{O}{C}CH_3$	 $(CH_3)_2\overset{Cl}{C}\underset{CO_2C_2H_5}{C}H\overset{O}{C}CH_3$ (63)
	 (51)
	 (4)  (20)
	 (59)
	 (35)
	 (50)
	 (10)  (43)  (39)
	 (8)  (23)
	 (25)  (10)
	 (29)
	No Reaction

a) The products were analyzed by gas-liquid partition chromatography and characterized by NMR, IR, and mass spectra.

(1): The compound with vicinal dibromo substituents, one a tertiary, and the other, a secondary, bromide, reacts only with the tertiary bromide to yield the corresponding ester, while the secondary bromide exchanges its bromine with the chlorine atom by the reaction with antimony chloride.

(2): The reactivity of the tertiary and the secondary bromides in the neighborhood of a substituent such as a carbonyl group is greatly diminished in the carbonylation reaction.

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[1] a) G. A. Olah, "Friedel Crafts and Related Reactions," Vol. III, Part II, ed. by G. A. Olah, Interscience Publishers, New York (1964), p. 1257; b) J. H. Simons and A. C. Werner, *J. Amer. Chem. Soc.*, **64**, 1356 (1942).

[2] H. Koch and W. Haaf, *Ann. Chem.*, **618**, 251 (1958).