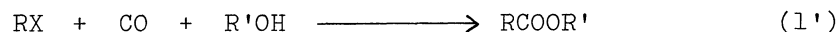
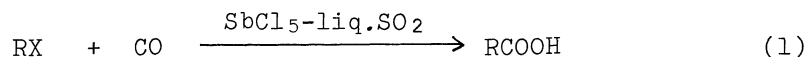


CARBONYLATION IN LIQUID SULFUR DIOXIDE.III<sup>1)</sup>  
THE ACYLATION OF VARIOUS NUCLEOPHILES WITH PIVALOYL CHLORIDE  
SbCl<sub>5</sub> COMPLEX DERIVED FROM THE REACTION OF t-BUTYL CHLORIDE  
AND CARBON MONOXIDE IN SbCl<sub>5</sub>-LIQUID SULFUR DIOXIDE SYSTEM

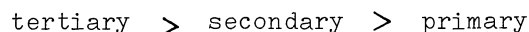
Masatomo NOJIMA, Fumiaki SHIBA, Masakatsu YOSHIMURA, and Niichiro TOKURA  
Department of Applied Chemistry, Faculty of Engineering,  
Osaka University, Suita, Osaka,

The intermediate obtained by the reaction of t-butyl chloride with carbon monoxide in the SbCl<sub>5</sub>-liq.SO<sub>2</sub> system was found to be a complex of pivaloyl chloride with SbCl<sub>5</sub> by N.M.R. spectroscopy. This intermediate was used as the acylating agent for various nucleophiles. Water, ethanol, cycloolefins and aniline reacted with the acylating agent in situ in liquid sulfur dioxide to give carboxylic acid, ester, α,β-unsaturated ketones, acid amide, respectively, in fair yields. The reaction with benzene gave only t-butylbenzene and o- and p-chloro-t-butylbenzenes.

We have recently reported a convenient carbonylation reaction of an alkyl halide with carbon monoxide in the absence or presence of an alcohol in SbCl<sub>5</sub>-liq.SO<sub>2</sub> system to prepare a carboxylic acid or an ester.<sup>1)</sup> It was found that in this reaction the



order of the reactivity of chloride or bromide is decreasing in the following order,

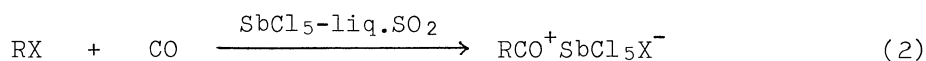


When the starting material was a vicinal dibromo compound, one being secondary and the other tertiary, only the tertiary bromide reacted with carbon monoxide to yield the corresponding acid (ester) while the secondary bromide caused halogen exchange reaction from bromine to chlorine.

Acylation reaction of nucleophilic reagents with acyl halide using a Lewis acid has been studied extensively.<sup>2)</sup> In an earlier paper, the acylation of alcohol in liquid sulfur dioxide was carried out by Tokura and Akiyama<sup>3)</sup> who established that the rate of the reaction is the fastest in liq.SO<sub>2</sub> among the eleven solvents used, since acylium ion could be developed in this solvent easily.

The existence of a t-butyl cation in SbCl<sub>5</sub>-liq.SO<sub>2</sub> system was first recognized by Olah and his collaborators<sup>4)</sup> by the NMR spectroscopy. Hogeveen and his associates<sup>5)</sup> have estimated the rate constant of t-butylcarbonylation in HF-SbF<sub>5</sub> or FHSO<sub>3</sub>-SbF<sub>5</sub> by NMR spectra, where the chemical shifts of t-butyl cation and t-butylcarbonyl cation were  $\delta=3.95$  and  $\delta=2.07$ , (TMS external standard) respectively.

A consecutive reaction system consisting of 1) the preparation of acylium ion or acyl halide complex from alkyl halide and carbon monoxide in acidic system (eq. (2)) and 2) the acylation of a variety of nucleophiles with the acylium complex in the same system (eq. (3)) has not yet been studied in spite of its importance and convenience in the preparative organic chemistry.





In this paper, the present authors wish to present the results of the acylation with a consecutive carbonylation-acylation reaction starting from t-butyl chloride in SbCl<sub>5</sub>-liq.SO<sub>2</sub> system.

A typical procedure is as follows. To a mixture of 19.4 g (0.066 mole) of SbCl<sub>5</sub> and 50 ml of liq.SO<sub>2</sub>, a solution of 2.0 g (0.022 mole) of t-butyl chloride dissolved in 10 ml of dichloromethane was added 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 ml per minute. After the addition of t-butyl chloride 3.4 g (0.044 mole) of cyclohexene was dropped for thirty minutes. The reaction mixture was treated following the ordinary method; subsequent analysis by vpc showed the existence of t-butyl 1-cyclohexenyl ketone (2.6 g (62 %)).

The results of the similar reactions are listed in Table I. All the products obtained were isolated and characterized by NMR, infrared and mass spectroscopy.

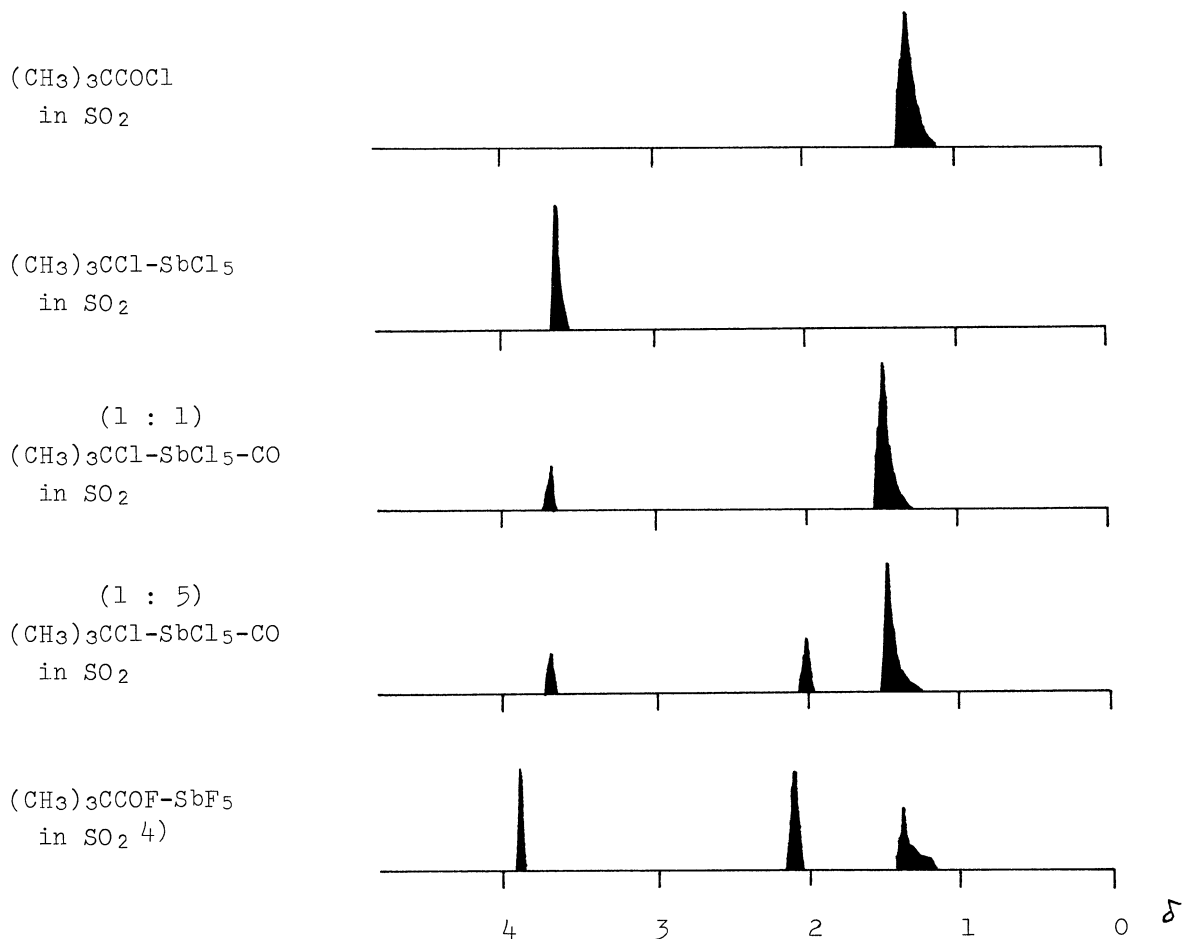
Table I. Acylation of Various Nucleophiles

| Nucleophiles        | Products (Yield %)  |
|---------------------|---|
| H <sub>2</sub> O    | (CH <sub>3</sub> ) <sub>3</sub> CCOOH (42)  |
| EtOH                | (CH <sub>3</sub> ) <sub>3</sub> CCOOEt (49)   |
| Cyclohexene         | (CH <sub>3</sub> ) <sub>3</sub> CCO-  (69) |
| 1-Methylcyclohexene | (CH <sub>3</sub> ) <sub>3</sub> CCO-  (40) |
| Aniline             | (CH <sub>3</sub> ) <sub>3</sub> CCONHC <sub>6</sub> H <sub>5</sub> (22)   |

At -70°C the reaction with benzene did not take place under these reaction conditions. However, at 20°C the reaction gave a mixture of t-butylbenzene (18 %), p-chloro-t-butylbenzene (33 %) and o-chloro-t-butylbenzene (19 %). This will be due to the dissociation of acylium complex into t-butyl cation by the loss of carbon monoxide at this temperature.<sup>4,5)</sup>

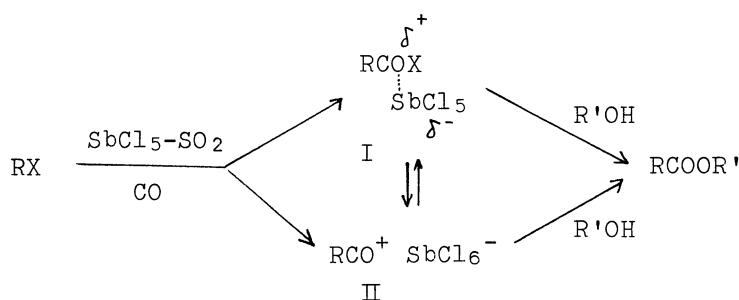
The NMR spectra of the intermediates: the NMR spectra of intermediates formed by the reaction of t-butyl chloride in this system are illustrated in Fig. 1.

Fig. 1. NMR SPECTRA OF REACTION INTERMEDIATES



Into the mixture of t-butyl chloride and antimony pentachloride in liquid sulfur dioxide, carbon monoxide was bubbled at  $-70^{\circ}\text{C}$  for two minute and the reaction mixture was analyzed by NMR spectrometer. When the molar ratio of t-butyl chloride and  $\text{SbCl}_5$  was one to one, the spectrum of the solution showed explicitly the formation of the polar coordination complex of pivaloyl chloride and  $\text{SbCl}_5$  (I),  $\delta=1.45$  ppm, accompanied with the formation of a small amount of t-butyl cation,  $\delta=3.70$ ,<sup>4,5)</sup> and when the ration was changed to one to five, a small amount of acylium ion (II),  $\delta=2.0$ , about 5 % was found with I.

Scheme 1



These results suggest that the intermediate in the reaction is probably the polar coordination complex (I) from pivaloyl chloride and  $\text{SbCl}_5$ , and not the ion pair (II). The selective carbonylation exhibited in this reaction system<sup>1)</sup> is perhaps due to the rapid ion pair formation of acyl cation formed transiently during the reaction with antimony chloride ion which prevents the isomerization and other side reactions.<sup>6)</sup>

## References

- 1) a) Part I, M. Nojima, K. Tatsumi, and N. Tokura, Bull. Chem. Soc., Japan, 44, 2001 (1971).  
b) Part II, M. Nojima, M. Yoshimura, and N. Tokura, *ibid*, in contribution.
- 2) a) G. A. Olah, "Friedel-Crafts and Related Reaction", Vol. III, Part II, Interscience, New York (1964).  
b) J. Falbe, "Synthesen mit Kohlenmonoxyde" Springer, Berlin, 1967.
- 3) N. Tokura and F. Akiyama, Bull. Chem. Soc., Japan, 37, 1723 (1964).
- 4) G. A. Olah, W. S. Tolgyesi, S. J. Kuhn, M. E. Moffatt, I. J. Bastien, and E. B. Baker, J. Amer. Chem. Soc., 85, 1328 (1963).
- 5) H. Hogeveen, F. Baardham, and C. F. Roobeek, Rec. Trav. Chim., 89, 227 (1970).
- 6) K. Hinoue, M. Nojima, and N. Tokura, Bull. Chem. Soc. Japan, 44, 3096 (1971).

( Received September 12, 1972 )