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REACTION OF THALLIC ACETATE, PIPERIDINE AND CARBON MONOXIDE IN METHANOL

Takeo Saegusa, Tetsuo Tsuda and Katsuhiko Isayama

Department of Synthetic Chemistry, Faculty of Engineering,

Kyoto University, Kyoto, Japan

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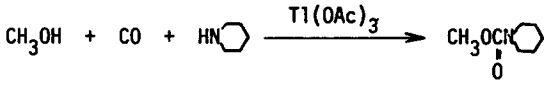
It has been known that a methanolic solution of mercuric acetate absorbs carbon monoxide to form carbomethoxymercuric acetate[1]. Recently,[2] the reaction of carbomethoxymercuric acetate with primary and secondary amines was reported, in which the corresponding urethane was formed.

Thallium (III) is isoelectronic with mercury (II) and thallic salt exhibits chemical property similar to that of mercuric salt in the oxymetallation reaction.[3] These facts prompted us to examine the reaction of thallic acetate, amine and carbon monoxide in methanol. Now we found that this reaction yielded urethane as expected. As the amine component, piperidine was used and methyl 1-piperidinecarboxylate was produced.



To a 100 ml stainless steel autoclave, 10 g (0.026 mole) of thallic acetate[4] and 40 ml of methanol were added, to which carbon monoxide was compressed up to 80 kg/cm^2. The reaction mixture was stirred for 30 hrs. at room temperature. After the absorption of carbon monoxide ceased, the resultant homogeneous solution was filtered and utilized in the second reaction with piperidine. In the second reaction, 5 ml of this solution containing 3.3 mmoles of thallic salt and 2.5 g (33 mmoles) of piperidine was heated at the desired temperature in a 50 ml stainless steel tube with or without the addition of compressed carbon monoxide gas. The reaction mixture was then distilled to isolate volatile materials at temperature up to 150°C under reduced pressure to 2 mm Hg. The distillate was subjected to gas chromatography analysis. Urethane (Methyl 1-piperidinecarboxylate) and N-formylpiperidine were obtained as the reaction products, which were identified by the comparison of the retention times of gas chromatography with the authentic

samples. The results are shown in Table I. In the last two runs, the one step procedure instead of the two step procedure was adopted, i.e., thallic acetate, piperidine, methanol and carbon monoxide were reacted simultaneously.

TABLE I. Reaction of Thallic Acetate, Piperidine, Methanol and Carbon Monoxide

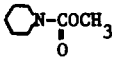
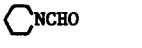
$Tl(OAc)_3$ (mole)	 (mole)	CH_3OH (ml)	CO (kg/cm^2)	Time (hr.)	Temp. (°C)	Yields of Products (%)[a] 	
Two Step Procedure							
0.0033	0.033	5	—	68	room temp.	3	—
〃	〃	〃	—	30	120	1	—
〃	〃	〃	80	54	room temp.	8	trace
〃	〃	〃	〃	54	50	8	5
One Step Procedure							
0.008	0.08	8.5	80	49	room temp.	12	trace
〃	〃	〃	〃	64	50	14	5

a) The yields of products are based on thallic salt.

It is clearly shown that urethane was formed, although the yield itself is not high, by the reaction of piperidine with a methanolic solution prepared beforehand from thallic acetate, carbon monoxide and methanol. Better result was obtained, however, in the one step procedure at 50°C. Besides urethane, N-formylpiperidine was formed in a small amount and 1-acetylpiperidine was produced as the reaction temperature was increased.

For the urethane formation from amine and carbon monoxide, there have been reported two reactions, i.e., the copper catalyzed reaction of amine, methanol and carbon monoxide-oxygen mixture[5] and the reaction of the isolated carbomethoxymercuric acetate with amine.[2] In Table II, the thallic acetate procedure of the present study is compared with the reactions of other metal acetates under similar reaction conditions in the one step procedure.

TABLE II. Reaction of Metallic Acetate, Piperidine, Methanol and Carbon Monoxide[a)]

Metallic acetates	Reaction time (hr.)	Yields of Products (%)[b)]	
			
$Hg(OAc)_2$	44	28	trace
$Tl(OAc)_3$[c)]	49	12	trace
$Cu(OAc)_2$	43	9	2
AgOAc	54	trace	55
$Cd(OAc)_2$	98	trace	18
$Zn(OAc)_2$	97	trace	2

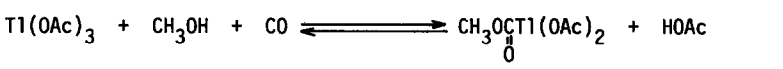
a) To a mixture of 0.01 mole of metallic acetate, 0.06 mole of piperidine (0.03 mole of piperidine in the case of silver acetate) and 0.5 mole of methanol in a 50 ml stainless steel tube, carbon monoxide was compressed up to 80 kg/cm^2. The reaction tube was closed and reacted at the room temperature.

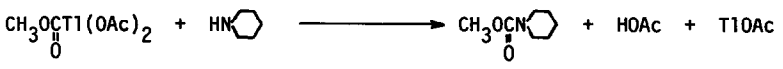
b) The yields of products are based on metallic acetate.

c) See Table I.

Thallic acetate exhibited the reactivity similar to the reactivities of mercuric and cupric acetates, yielding urethane in preference to formamide. The fact that urethane formation was negligible in the reactions of silver and cadmium acetates agrees with an early report that the attempt to prepare the carbomethoxy compounds of silver and cadmium by the reaction of corresponding acetates with carbon monoxide in methanol was unsuccessful.[6)]

From the result of the urethane formation in the reaction of thallic acetate, piperidine and carbon monoxide in methanol as well as the similarity of chemical nature between thallic and mercuric acetates, for example, in the oxymetallation reaction, the following scheme of reaction including carbomethoxythallic acetate as an essential intermediate may possibly be postulated.





Attempts to isolate and characterize the carbomethoxythallic acetate is being made now.

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