A Novel Synthesis of Dialkyl Carbonates from Carbon Dioxide, Alcohols, and *tert*-Amines Mediated by Acetylene

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(Received May 27, 1996)

A novel acetylene-mediated reaction of carbon dioxide with alcohols and *tert*-amines leads to effective formations of dialkyl carbonates and alkyl *N,N*-dialkylcarbamates without catalyst.

Carbonic acid diesters and carbamic acid esters are useful synthetic intermediates for pharmaceutical, agricultural, and other chemicals and are currently produced in industry using either phosgene or carbon monoxide. Since carbon dioxide, though less reactive, is also a kind of carbonyl compound abundant and less toxic, various reactions have been reported so far, in which CO_2 is reacted with alkyl halides,[1] ortho esters,[2] alkyleneoxides,[3] 2-propynol derivatives,[4] or organotin alkoxides[5] to give these esters. The author and his co-workers previously reported that *N,N*-dialkylcarbamates formed from CO_2 and *sec*-amines react with acetylene to give vinyl *N,N*-dialkyl carbamates in the presence of ruthenium complexes.[6] A similar reaction of alcohols with CO_2 and acetylene, which would give alkyl vinyl carbonates, failed even in the presence of *tert*-amines probably because of the insufficient nucleophilicity of alcohols compared with *sec*-amines.[7]

During this attempt, however, a slight formation of dialkyl carbonates was observed. Further investigation revealed that this product is formed even in the absence of ruthenium or any other transition metal complexes. Moreover, one of the alkyl groups of dialkyl carbonates was found to come from *tert*-amines, which was originally added with the intention of increasing the nucleophilicity of alcohols, while the other from alcohols. Thus, either symmetric or unsymmetric carbonic acid diesters are formed as a main product according to the alkyl groups of alcohols and *tert*-amines(eq. 1). Also formed are alkyl *N,N*-dialkylcarbamates, all the alkyl groups of which are originated from *tert*-amines.

$$R'OH + CO_2 + R_3N \xrightarrow{HC\equiv CH} R'OCO_2R + R_2NCO_2R \qquad (1)$$

In a typical experiment, acetylene(30 mmol) is introduced in a 50 mL-autoclave containing *tert*-amine(30 mmol) and alcohol (200 mmol) at -50 ℃. After CO_2 is pressurized at 5 MPa at ambient temperature, the autoclave is heated at 160 ℃ for 16 h or 40 h. The products obtained are identified by spectroscopical comparison with their authentic samples either purchased or synthesized using chloroformic acid esters and analyzed by GLC. Unreacted *tert*-amines and acetylene recovered together with CO_2 through an integrating gas-flow meter are also analyzed by GLC.

When equimolar triethylamine is used with acetylene in ethanol, diethyl carbonate and ethyl *N,N*-diethylcarbamate are formed in the yields of 32 and 11% respectively at 45% of conversion in triethylamine as shown in Table 1. The yield of diethyl carbonate and the conversion of triethylamine are increased with decrease in the amount of triethylamine introduced up to 78 and 83% respectively (entry 4). The yield of ethyl *N,N*-diethylcarbamate, on the other hand, reaches its maximum(13%) with 20 mmol of triethylamine (entry 2). Neither diethyl carbonate nor ethyl *N,N*-diethylcarbamate is formed without triethylamine(entry 5). A significant formation of diethylamine is observed in the resulting reaction solution, when triethylamine is used in smaller amounts, which may account for the formation of ethyl *N,N*-diethylcarbamate; *N,N*-diethylcarbamic acid derived from CO_2 and diethylamine formed by the preceding alkylation of monoalkyl carbonate must be alkylated in place of monoalkyl carbonate with triethylamine. It is also found that diethylamine is partially converted to triethylamine and small amounts of diethyl carbonate and ethyl *N,N*-diethylcarbamate are formed in the reaction using diethylamine instead of triethylamine(entry 6). These results, as well as the fact that the total yield(86%) of the products exceeds the conversion of triethylamine(83%) in the reaction with 5 mmol of triethylamine (entry 4), suggest that more than one ethyl group in triethylamine can be used for alkylation but most probably at the expense of higher consumption in acetylene under certain conditions. No CO_2 containing product is formed without either CO_2 or acetylene even in the presence of triethylamine.

Table 1. Reaction with ethanol and triethylamine[a]

No.	Et_3N	— Yield / %[b] —		— Conv. / % —	
	(mmol)	$EtOCO_2Et$	Et_2NCO_2Et	Et_3N	$HC\equiv CH$
1	30	32	11	45	96
2	20	42	13	56	86
3	10	65	12	77	80
4	5	78	8	83	83
5	0	-	-	-	21
6[c]	0	4	1	-9	81

[a] CO_2(5 MPa), EtOH(200 mmol), Acetylene(30 mmol), 160 ℃, 40 h. [b] based on amine. [c] Et_2NH(5 mmol).

The results of the reactions with several alcohols and *tert*-amines are summarized in Table 2. When propanol is used instead of ethanol, ethyl propyl carbonate is formed in the yield of 22% together with ethyl *N,N*-diethylcarbamate(7%) and di-propyl carbonate(1%). This result clearly shows that one of the ethyl group of diethyl carbonate formed in the reaction with ethanol mostly comes from triethylamine. The slight formation of dipropyl carbonate, however, suggests that the ester exchange reaction of dialkyl carbonate occurs to some extent in excess

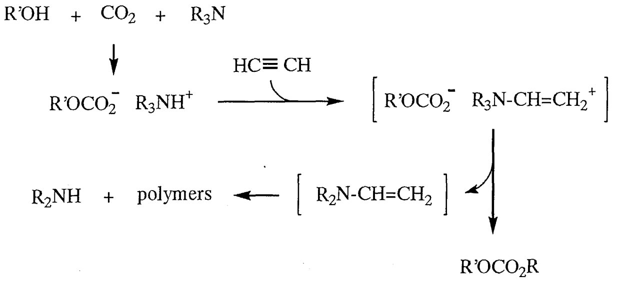
Table 2. Reaction with various alcohols and *tert*-amines[a]

R_3N	R'OH	Yield / %[b]			Conv. / %	
		$R'OCO_2R$	$R'OCO_2R'$	R_2NCO_2R	R_3N	$HC\equiv CH$
Et_3N	EtOH	30	-	9	41	74
Et_3N	*n*-PrOH	22	1	7	35	68
Et_3N	$CH_2=CHCH_2OH$	19	8	14	42	89
n-Pr_3N	EtOH	17	3	2	26	46
n-Pr_3N	*n*-PrOH	12	-	1	16	38
n-Pr_3N	$CH_2=CHCH_2OH$	21	6	4	32	56

[a] R_3N(*ca.* 30 mmol), R'OH(200 mmol), acetylene(30 mmol), CO_2(5 MPa), 160 °C, 16 h.
[b] based on amine.

alcohols. This reaction becomes rather significant when allyl alcohol is used; 19% of ethyl allyl carbonate is formed together with diallyl carbonate(8%) and ethyl *N, N*-diethylcarbamate(14%). It is not yet clear why the carbamate is obtained in such a high yield in this reaction compared with the other saturated alcohols. Tripropylamine can be also used in place of triethylamine for the reactions of these alcohols, although it shows a little lower reactivity; 12-21% yields of the corresponding propyl carbonates are formed together with small amounts of symmetric carbonates and propyl *N,N*-di-propyl-carbamate. All the reaction solutions are homogeneous but colored in brown when the reaction has proceeded, while the use of either methanol or trimethylamine results in the formation of polymers probably because of their excessive reactivity toward acetylene.

The reaction mechanism may include the insertion of acetylene to the N-H bond of trialkylammonium monoalkyl carbonate, $R'_3NH^+\ ROCO_2^-$, giving trialkylvinylammonium monoalkyl carbonate, $R'_3N\text{-}CH=CH_2^+\ ROCO_2^-$, followed by its thermal decomposition to dialkyl carbonate and dialkylvinylamine as shown in Scheme 1. Although dialkylvinylamine itself has not yet been detected by GLC analysis probably because of its instability under the reaction conditions, its temporary formation is likely because some polymeric materials are observed after the distillation of reaction solutions. These polymers and diethylamine are supposed to originate from dialkylvinylamine. The first step of the proposed mechanism is analogous to the insertion of triethylammonium chloride[8] to acetylene giving triethylvinylammonium chloride, $Et_3N\text{-}CH=CH_2^+\ Cl^-$. The second step, the reaction of monoalkyl carbonate with quaternary ammonium, is similar to the esterification of carboxylic acids with large steric hindrances by forming tetramethylammonium salts and their thermal decomposition.[9] To verify this step, the direct reaction of alcohol, CO_2, and tetraethylammonium bromide was performed in the presence of tri-propylamine, which led to considerable formations of diethyl carbonate and triethylamine(eq. 2).



Scheme 1. Estimated reaction mechanism.

$$\underset{(200\ \text{mmol})}{\text{EtOH}} + \underset{(5\ \text{MPa})}{CO_2} + \underset{(30\ \text{mmol})}{Et_4N^+Br^-} \xrightarrow[n\text{-}Pr_3N]{160\ ^\circ C,\ 16\ h} \underset{(3.3\ \text{mmol})}{EtOCO_2Et} + \underset{(6.4\ \text{mmol})}{Et_3N} \qquad (2)$$

References and Notes

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