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PHOSPHINE CATALYSED SYNTHESIS OF UNSATURATED CYCLIC CARBONATES FROM CARBON DIOXIDE AND PROPARGYLIC ALCOHOLS

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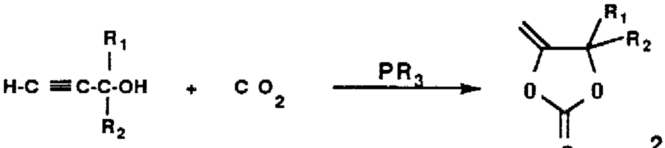
Summary - A new route to α-methylene cyclic carbonates is reported, by direct reaction of carbon dioxide with α-ethynyl alcohols in the presence of a catalytic amount of a phosphine.

Cyclic carbonates are useful intermediates for the synthesis of functional carbamates, esters or oxazolidinone compounds and their unsaturated derivatives have industrial potential for the production of transparent polymers such as varnishes or synthetic glasses[1]. Cyclic carbonates are usually obtained by insertion of CO_2 into a C-O bond of strained oxiranes in the presence of nucleophiles or Lewis acid transition metal derivatives[2,3]. α-methylene cyclic carbonates can be prepared from CO_2 and α-ethynyl alcohols by catalytic reactions involving metals such as ruthenium[4], cobalt[5], palladium[6] or copper[7] derivatives. Cyclic carbonates have also been suggested as intermediates in the ruthenium catalysed synthesis of β-oxoalkylcarbamates from α-ethynyl alcohols, amines and carbon dioxide[8,9].

We now wish to report a new route to α-methylene cyclic carbonates under mild conditions and good yields directly from CO_2, α-ethynyl alcohols and catalytic amounts of a phoshine without the presence of a metal catalyst.



1 a-d **2 a-d**

In a typical experiment, 2-methyl-3-butyn-2-ol **1a** (50 mmol) was allowed to react with tri-n-butylphosphine (4 mmol) under a 50 kg/cm^2 pressure of CO_2 at 100 °C for 8 h in a 125 mL autoclave. 4,4-dimethyl-5-methylene-2-oxo-1,3-dioxolane **2a** was isolated in 98% yield by distillation under reduced pressure. Other disubstituted α-methylene cyclic carbonates **2b-d** were obtained in a similar way without addition of solvent (Table 1).

Table 1 : Reaction of CO_2 with α-Ethynyl Alcohols [a]

Alcohol		Product	Yield(%) [b]
1a	$R_1 = R_2 = CH_3$	**2a**	98
1b	$R_1 = CH_3$, $R_2 = C_2H_5$	**2b**	92
1c	$R_1 = CH_3$, $R_2 = C_6H_5$	**2c**	32[c]
1d	R_1-R_2= $(CH_2)_5$	**2d**	58

a) alcohol (50 mmol), PBu_3 (4 mmol), CO_2 (50 kg/cm^2), 100 °C, 8 h,
b) isolated yield based on alcohol, c) 20 h.

The influence of some parameters such as reaction time, temperature and nature of the phosphine was studied (Table 2). At high temperature (140°C), the yields in cyclic carbonates were fairly good whatever the phosphine might be, but when temperature was decreased to 50°C, tributylphosphine appeared to be the only efficient catalyst. Very low yields were obtained with other phosphines such as PPh_3 or PCy_3 even at 100°C. No cyclic carbonate was formed when triethylamine was added instead of phosphine. When the reaction was carried out with propargyl alcohol itself, no cyclic carbonate formation was detected. The α-ethynyl secondary alcohols **1** (R_1= H, R_2= CH_3 or C_6H_5) also did not afford the corresponding carbonate. Consequently, the reaction appears to be limited to disubstituted alcohols.

During the reaction the phosphine was partly converted by CO_2 into phosphine oxide which was shown not to be active in the synthesis. Although the mechanism is still unknown, the formation of a linear α-ethynyl carbonate anion intermediate from **1** and CO_2 in a basic medium is likely to occur.

Table 2 : Reaction of CO_2 with 2-methyl-3-butyn-2-ol (1a) [a)]

Catalyst	Temperature (°C)	Time (h)	Yield (%)
PBu_3	140	20	86
-	100	8	98
-	50	20	97
PPh_3	140	20	78
-	100	8	7
PCy_3	140	20	97
-	100	8	8

a) alcohol 1a (50 mmol), phosphine (4 mmol), CO_2 (50 kg/cm^2)

The reaction described in this paper is a facile, one-step preparation of unsaturated cyclic carbonates directly from CO_2 and propargylic tertiary alcohols in the presence of a phosphine. It is very competitive with the patented process using a copper catalyst in the presence of amine.

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