A Novel Catalytic Synthesis of Vinyl Carbamates from Carbon Dioxide, Diethylamine, and Alkynes in the Presence of $Ru_3(CO)_{12}$

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The reaction of carbon dioxide, diethylamine, and hex-1-yne (**1a**) or phenylacetylene (**1b**), catalysed by $Ru_3(CO)_{12}$, gave the vinyl carbamates (**2a**), (**3a**), and (**4a**) or (**2b**) and (**3b**).

Vinyl carbamates are useful derivatives as agricultural chemicals, pesticides, intermediates for pharmaceutical products or monomers for transparent polymers or varnish.[1] General procedures are known which lead to alkyl carbamates by addition of alcohols to isocyanates or reaction of amines with chloroformates. However, these routes cannot be directly used for access to vinyl carbamates. Vinyl carbamates have previously been made *via* dehydrohalogenation of α-halogeno-[2] or β-chloro[3]-alkyl carbamates, by reaction with amines of vinyl chloroformates,[4,5] which are difficult to obtain,[6] or use toxic chemicals,[4] or by generation of alkylidenecarbenes in the presence of isocyanates.[7]

Although there have been considerable efforts recently to activate CO_2 by transition metal catalysts in order to incorporate CO_2 into organic substrates, few catalytic examples have been found, probably because of the difficulty of fixation of CO_2 onto the metal centre.[8] We now report the first example of the direct, catalytic synthesis of vinyl carbamates from alkynes, carbon dioxide, and diethylamine. This approach was tested because of (i) the existence of the equilibrium (1) between carbon dioxide and an amine, and ammonium carbamate and carbamic acid and (ii), the $Ru_3(CO)_{12}$-catalysed addition of carboxylic acids to alkynes to give vinyl esters.[9]

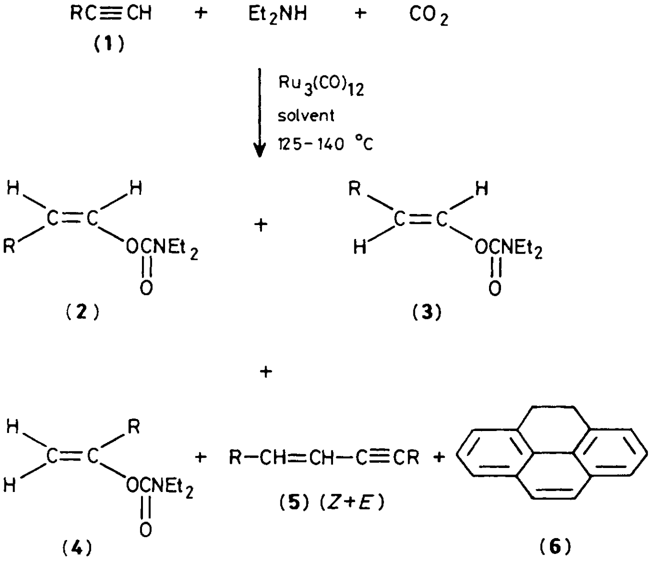
$$2R_2NH + CO_2 \leftrightharpoons R_2NCO_2^-, H_2NR_2^+ \leftrightharpoons R_2NCO_2H + HNR_2 \qquad (1)$$

Toluene (10 ml), $Ru_3(CO)_{12}$ (0.2 mmol), hex-1-yne (**1a**) (10 mmol), and diethylamine (20 mmol) were successively placed

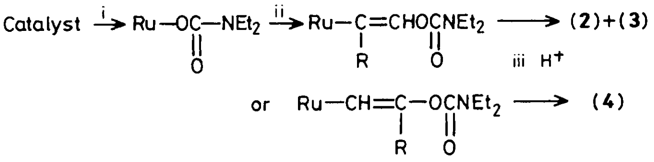
Table 1. Conversion of alkyne and yields of carbamates (**2**)—(**4**) and compounds (**5**) and (**6**).[a]

				% Yield				
Alkyne	Solvent	T/°C	% Conversion	(**2**)	(**3**)	(**4**)	(**5**)	(**6**)
(**1a**)	MeCN	140	91	11	6	1	12	—
(**1a**)	Toluene	140	91	18	15	3	16	—
(**1b**)	MeCN	140	100	6	4	—	23	8
(**1b**)	Toluene	125	92	6	11	—	11	15
(**1b**)	THF Tetrahydrofuran	125	91	6	11	—	12	14

[a] $Ru_3(CO)_{12}$ (0.2 mmol); solvent (10 ml); Et_2NH (2 ml); (50 atm), alkyne (10 mmol); 20 h.



Scheme 1. **a**; R = Bu^n
b; R = Ph



Scheme 2

in a 50 ml autoclave and stirred under carbon dioxide pressure (50 atm) at 140 °C for 20 h. (*Z*)- and (*E*)-1-(*N*,*N*-Diethylcarbamoyloxy)hex-1-ene (**2a**)[†] (18%) and (**3a**) (15%), respectively, together with the isomer (**4a**) (3%) and the (*Z*)- and (*E*)-isomers of ene–yne derivative (**5a**) (16%) were obtained (Scheme 1). The conversion of hex-1-yne was up to 91% and other products of high molecular weight were not analysed. Under similar conditions phenylacetylene (**1b**) led to the formation of (**2b**) (6%), (**3b**) (11%), and (**5b**) (11%), together with 4,5-dihydropyrene (**6**) (15%), for a total conversion of 92%. Effects of the nature of the solvent and temperature are shown in Table 1.

A possible explanation for the formation of the vinyl carbamates (**2**), (**3**), and (**4**) may be related to (i) the co-ordination of carbamate to the metal, (ii) insertion of alkyne, and (iii) protonolysis of the Ru–C bond (Scheme 2). As for the addition of acids to alkynes[10] a bimetallic catalyst may also be involved and because the reaction takes place with terminal alkynes a ruthenium–vinylidene[11] intermediate cannot be excluded.

Regardless of the precise mechanism the present reaction provides a novel catalytic reaction involving CO_2, and a simple, non-toxic access to vinyl carbamates.

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[†] Satisfactory analytical and spectroscopic data have been obtained for all new compounds.