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Preliminary communication

Stereospecific synthesis of di- and tri-substituted acids by carbonation of vinylcopper reagents

J.F. NORMANT, G. CAHIEZ, C. CHUIT

Laboratoire de Chimie des Organoéléments, ERA 31, Tour 44, 4 Place Jussieu, 75230 Paris, Cedex 05 (France)

and J. VILLIERAS

Laboratoire de Synthèse Organique, ERA 31, Tour 44, 4 Place Jussieu, 75230 Paris, Cedex 05 (France)

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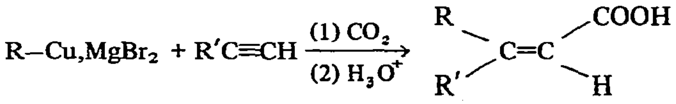
SUMMARY

Vinylcopper compounds obtained by addition of alkylcopper derivatives to terminal alkynes are converted to the corresponding α ethylenic acids stereospecifically in high yields. The influence of ligands in this insertion is emphasized.

Only recently have reports on the insertion of CO_2 into a C–Cu or C–Ag bond appeared[1–3]. Apart from its synthetic interest, this reaction can be seen as a preliminary coordination of CO_2[4] followed by an insertion which is spontaneous or is induced by a ligand.

We have prepared vinylcopper reagents[5] stereospecifically and we have tried to transform them into acrylic acids as follows:



A vinylcopper–magnesium bromide solution, in ether, does not absorb CO_2. However, in the following example we have studied the influence of various solvents or donor molecules capable of allowing the insertion of CO_2 (Table 1).

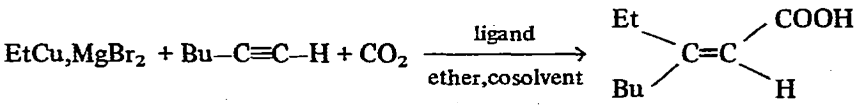


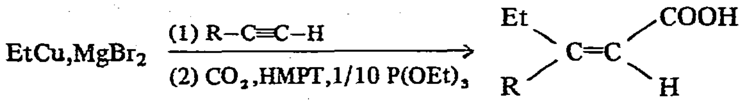
TABLE 1

INFLUENCE OF VARIOUS SOLVENTS AND DONOR MOLECULES ON THE REACTIVITY OF A VINYLCOPPER REAGENT TOWARD CO_2

Cosolvent	*Ligand*	*Acid yield (%)*
THF	2 $P(OEt)_3$	36
THF	2 $P(NMe_2)_3$	41
THF	2 PPh_3	45
N-Methylpyrrolidone		11
HMPT		48
HMPT	2 $P(NMe_2)_3$	60
HMPT	2 $P(OEt)_3$	40
HMPT	1 $P(OEt)_3$	60
HMPT	1/2 $P(OEt)_3$	69
HMPT	1/10 $P(OEt)_3$	95
	1/10 $P(OEt)_3$	0

Acetonitrile, pyridine and pyrrolidine are ineffective, and in contrast to carboxylic amides, phosphoric amide enables the reaction to take place. A practically quantitative yield of acid can be obtained with a catalytic amount of $P(OEt)_3$ present, while a greater amount is unfavourable. This seems to indicate that the vinylcopper—$2P(OEt)_3$ complex is not so suitable as vinylcopper—$1P(OEt)_3$ for coordination with a CO_2 molecule. The catalytic role of $P(OEt)_3$ could be explained by its separation after the insertion of CO_2. We are studying the mechanism of this reaction.

To make this synthesis general and to prove the stereospecificity of the insertion of CO_2, we have prepared the following acids:



(I) R = Bu (95%)
(II) R = Me (96%)
(III) R = H (62%)

The stereospecificity is proved by NMR spectroscopy and by comparison with the data from the literature (Table 2).

In acids I, II and III the ethylmethylene group shows a shift of 2.62 ppm (TMS) consistent with the *cis* structure of III. *Cis*-α-olefinic acids are usually obtained by semihydrogenation of α-acetylenic acids[8] and by Favorsky's rearrangement of dihaloketones[9,11]. The reaction described here is of synthetic value and completes the recently established preparation of *trans*-olefinic acids[5]:

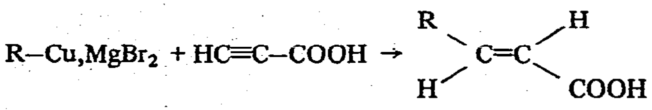
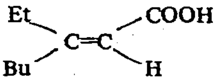
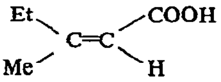
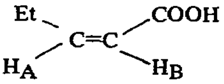


TABLE 2

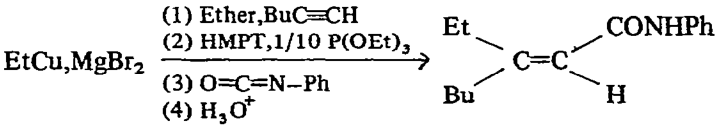
PHYSICAL CONSTANTS OF ACIDS I, II AND III

Acid	*B.p. (°C/mm) or (m.p. (°C))*	n_D^t	*NMR, δ (60 MHz (CCl$_4$−TMS))*
 (I)	134/12	1.4695 (*t* = 20)	1.05 m (6H); 1.40 m (4H) 2.18 m (2H); 2.62 q (2H) 5.57 s (1H); 12.14 s (1H)
 (II)	35.5 (36.5, lit.[6]; 22–24, lit.[7])		1.06 t (3H): 1.90 s (3H) 2.62 q (2H)[a]; 5.60 s (1H) 12.38 s (1H)
 (III)	87/13 lit.[8] 88/15 lit.[9] 39–41/0.4	1.4490 (*t* = 20) lit.[8] 1.4480 (*t* = 21) lit.[9] 1.4473 (*t* = 25)	1.06 t (3H); 2.65 m (2H) 5.69 d of t (H_B); 6.30 d of t (H_A) $J(H_A{-}H_B)$ 12 Hz; $J(CH_2{-}H_A)$ 1.5 Hz $\Delta H_A - \Delta H_B$ 0.61[b] ppm

[a] δ($CH_3{-}CH_2{-}C\equiv$) 2.56 (100 MHz, C_6D_6−TMS) as stated by ref. 7.

[b] As for *cis* crotonic acid $\Delta H_A - \Delta H_B$ (*cis*) 0.66 (ref. 10) while for *trans* crotonic acid $\Delta H_A - \Delta H_B$ (*trans*) 1.21 ppm.

Isocyanates can also be inserted into a vinylcopper reagent to obtain amides



IV (50%)

(IV): b.p. 151°/0.01 mm, m.p. 46°, NMR (100 MHz (CCl_4−TMS)) δ 1.02 m (6H); 1.28 m (4H); 2.00 m (2H); 2.66 q (2H); 5.80 s (1H); 7.04 (3H:Ph); 7.60 (2H:Ph); 9.16 (1H:NH);

Our study of the various functionalizations of vinylcopper reagents is being continued.

ACKNOWLEDGEMENTS

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