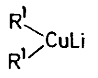
Controlled Formation of Allenes with Organocuprates

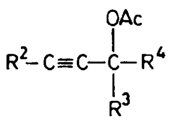
By Pierre Crabbé,* Eliezer Barreiro, Jean-Marie Dollat, and Jean-Louis Luche
(*Laboratoire de Chimie Organique, C.E.R.M.O., Université Scientifique et Médicale,* 38041 *Grenoble, France*)

Summary Precise conditions, that allow the preparation from prop-2-ynylic acetates of either non-alkylated allenes or alkylated allenes in good yields using organocuprate reagents, are reported.

The potential utility of the propadiene unit in organic synthesis and its unusual reactivity,[1] make it desirable to develop efficient procedures for preparation of compounds containing this unit.

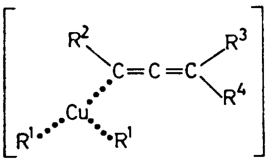


(1)



$R^2{-}C{\equiv}C{-}C(OAc)(R^3){-}R^4$

(2)



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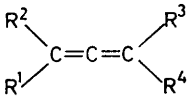

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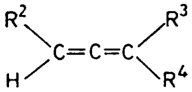

(5)

a; $R^1 = Me$, $R^2 = R^3 = H$, $R^4 = C_5H_{11}$
b; $R^1 = R^2 = Me$, $R^3 = H$, $R^4 = C_5H_{11}$
c; $R^1 = Me$, $R^2 = H$, $R^3R^4 = -[CH_2]_5-$
d; $R^1 = Me$, $R^2 = H$, $R^3R^4 = -[CH_2]_4-$

In the past, we reported the preparation of alkylated (**4**) and non-alkylated (**5**) allenes by the reaction of lithium dialkylcopper reagents (**1**) with acetylenic acetates (**2**).[2,3] A mechanism was proposed later[4] which may explain the formation of (**4**) and (**5**). An important practical problem was to find out the appropriate methodology giving rise *at will* to one or the other allenic compound. We report now our results in this field.

Based on the proposed reaction mechanism involving an organometallic intermediate of type (**3**),† it was expected that conditions favouring the transfer of an alkyl group from the copper to the carbon atom would furnish the alkylated allene (**4**). Conversely, inhibition of such a transfer followed by the addition of a quenching reagent should lead to the non-alkylated allene (**5**).

Table

	Reaction times/h		Allenes (**4**) and (**5**)	
Ester	$R^1{}_2CuLi$	$LiAlH_4$[a]	Total yield (%)	Ratio (**4**):(**5**)
(**2a**)	1[b]	1·5	90	23:77
(**2a**)	2[a]	1·5	95	5:95
(**2b**)	3[a]	2	75	10:90
(**2c**)	2[a]	2	80	25:75
(**2d**)	1[a]	2	80	28:72

[a] At −75 °C. [b] At −40 °C.

Treatment of prop-2-ynylic acetates with lithium dialkylcopper (1·2 equiv.) for 2 h (see below) at *ca.* −10 °C in ether gave the alkylated propadienes (**4**) in high yield. The ratio of compounds (**4**):(**5**) was *ca.* 95:5 with the exception of the ester (**2a**), for which the ratio was only 3:1. When the reactions were carried out at room temperature, the percentage of compounds (**4**) was always 95%. In contrast, lowering the temperature slowed down the rearrangement process sufficiently to permit hydrolysis of the intermediates (**3**), thus giving access to the non-alkylated allenes (**5**). For instance, addition of the prop-2-ynylic ester (**2a**) to lithium dimethylcopper (**1**, R = Me; 2 equiv.) at −50 °C, stirring for 1 h, and addition of 1 N HCl in MeOH at −75 °C, afforded mainly the non-alkylated allene (**5a**) (68%) and only 32% of (**4a**). Unfortunately, the reaction mixture contained unidentified compounds and the total yield of the allenes was rather low (*ca.* 37%). The process for the

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† Formula (**3**) representing the organometallic intermediate should be considered as a 'working hypothesis' and not necessarily a true physical entity involving copper with a formal oxidation state of +3. Representation by an ion-pair, such as a dialkylcopper anion and an allylic cation, was ruled out because of stereochemical considerations, since optically active allenes have been obtained with this reagent (see ref. 4).

formation of non-alkylated allenes (**5**) has been improved as follows. Esters (**2**) are added to lithium dimethylcopper (2 equiv.) in ether at −75 °C, and stirred at this temperature for 1—3 h (see Table). This is followed by treatment with $LiAlH_4$ (8 equiv.) in tetrahydrofuran. The colour of the reaction mixture changes from orange to dark-brown after stirring for an additional 2 h at −75 °C. The usual work-up affords the allenes (**5**). Typical results, by g.l.c. analysis, are listed in the Table.

The above observations, supporting the intervention of an organometallic intermediate of type (**3**),[4,5] can probably be extrapolated to organocuprate reactions with entities different from prop-2-ynylic acetates.

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[1] See: T. F. Rutledge, 'Acetylene and Allenes,' Reinhold, New York, 1969.

[2] P. Rona and P. Crabbé, *J. Amer. Chem. Soc.*, 1969, **91**, 3289.

[3] P. Crabbé and H. Carpio, *J.C.S. Chem. Comm.*, 1972, 904.

[4] J. L. Luche, E. Barreiro, J. M. Dollat, and P. Crabbé, *Tetrahedron Letters*, 1975, 4615.

[5] See also: J. K. Crandall, P. Battioni, J. T. Wehlacz, and R. Bindra, *J. Amer. Chem. Soc.*, 1975, **97**, 7171.