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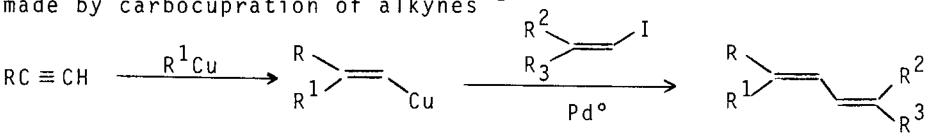
VINYL COPPER REAGENTS-16 SYNTHESIS OF CONJUGATED DIENES VIA THE ADDITION OF VINYL CUPRATES TO ACETYLENE

A Alexakis J F Normant

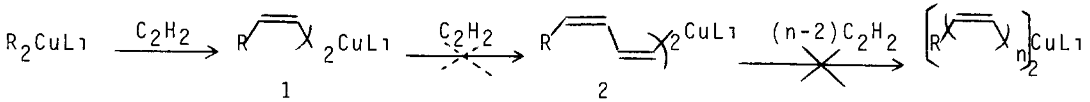
Laboratoire de Chimie des Organo-Eléments, tour 44-45
4, place Jussieu 75230 PARIS Cédex 05 France

Some alkenyl cuprates add smoothly to acetylene yielding dienyl cuprates.

The synthesis of conjugated dienes has been largely developped these last few years, particularly since sexual insect pheromones are of growing interest [1-5] We recently disclosed a stereoselective, palladium catalyzed, cross coupling reaction between 1-iodo-1-alkenes and vinyl copper reagents made by carbocupration of alkynes [1]



This letter describes a new approach to such systems, where the dienyl moiety is now metallated, and may undergo further functionnalizations The success of the carbocupration of acetylene is due to the fact that the newly formed vinylic copper reagent is unable to add further an other acetylene unit, and does not lead to polymerization



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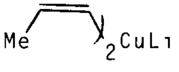
However reagents 1 add to α-acetylenic-esters [6-8] and -acetals [8-9], and to heterosubstituted acetylenes [8,10] We observed also that reagents 3,4,5 may react with acetylene to yield the corresponding



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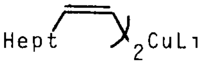

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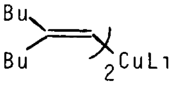

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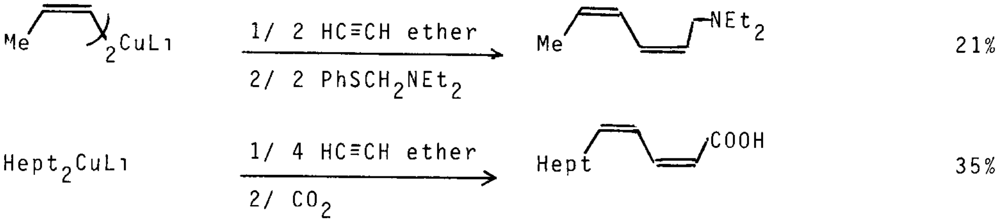
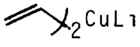
Z,Z-dienyl cuprates in varying amounts [11], the main limiting factor being the metallation of acetylene The new organometallic reagents have been characterized by their reaction with electrophiles in modest yields



On the contrary, lithium divinyl cuprate 6 or E-cuprates like 7 do not insert acetylene, but instead lead to



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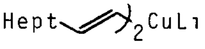

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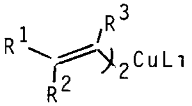

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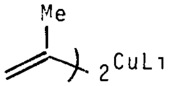
a red precipitate of copper acetylide, by metal hydrogen exchange We were thus led to study the influence of substituents R^1, R^2, R^3 in cuprates of general formula 8 on their ability to add to acetylene It turns out that only those bearing a substituent geminated to copper ($R^3 \neq H$) are prone to give satisfactory results The bis dienyl cuprates react with electrophiles under the conditions that we described for the Z dialkenylcuprates [12] Our preliminary results are concerned with the following structures



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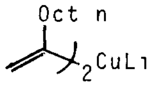

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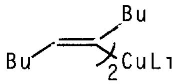

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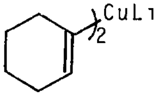

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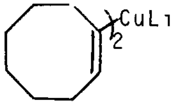

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and are quoted in table I

Particularly interesting are the cycloalkenyl cuprates, which may further lead to cyclizations , for example acid 14 by heating gives the deconjugated lactone 15

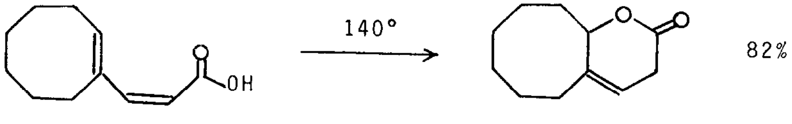

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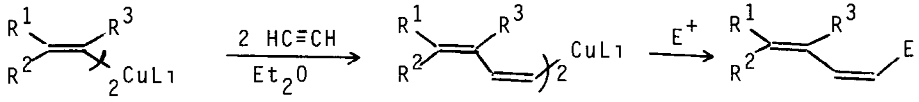
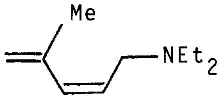
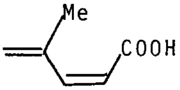
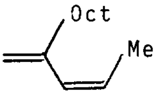
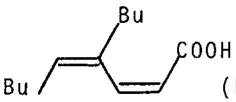
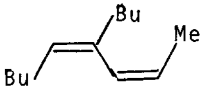
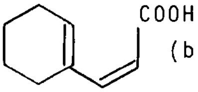
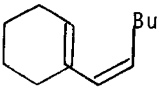
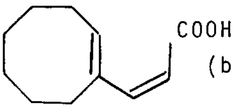
Table I

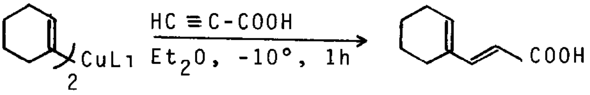


Cuprate 8	T°C(time min)	Electrophile	Products[a]	Isolated yield %
9	+15 (20)	$PhS\text{-}CH_2NEt_2$		67
9	+15 (20)	CO_2		81
10	+15 (20)	MeI		50
11	+20 (15)	CO_2	 (b)	58
11	+20 (15)	MeI		81
12	+20 (30)	CO_2	 (b,c)	57
12	+20 (30)	BuI		71
13	+15 (30)	CO_2	 (b)	83

(a) all spectroscopic data NMR ^1H, ^{13}C , I R. agree with the proposed structures

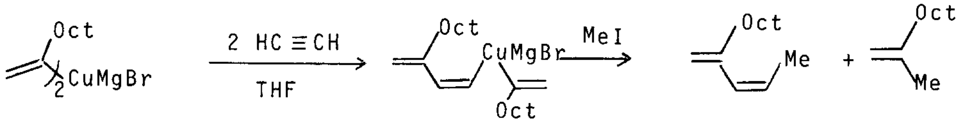
(b) acids are purified by sequential acidic, basic, then acidic work up

(c) we compared this acid with its E isomer prepared according to



86%

Magnesium vinylic cuprates also add acetylene in THF, but only one insertion occurs, and further trapping by methyl iodide gives a mixture of the two methylated moieties



so that such cuprates cannot be exploited for synthetic purposes

It is important to note that the temperature threshold is relatively high with regard to the thermal stability of the vinylic cuprates, so that the temperature range is to be checked accurately

The scope of this reaction is actively studied, with acetylene and its homologs Synthesis of natural products by this approach are under way.

Experimental

The vinylic cuprates are prepared by addition of the corresponding lithium reagents (30 mmol)~1N in ether to 3.3 g (16 mmol) of the complex CuBr,Me_2S in 50 ml ether at -30° (or by carbocupration [12] reagent 4) The temperature of the solution is raised to 0° and 0 8 l of acetylene (35 mmol) are bubbled (a total or partial absorption is observed according to the cases) The temperature is then fixed to the value given in the table (time also quoted) and the dark brown solution is treated at -20°C by the electrophilic reagent according to ref 12

Aknowledgements

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11 Cuprates 4 reacted in 65% (G L C yield)whereas 5 reacted to an extent of only 15%
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