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ADDITION OF LITHIUM DIMETHYLCUPRATE TO AN ALLENIC PHOSPHINE OXIDE

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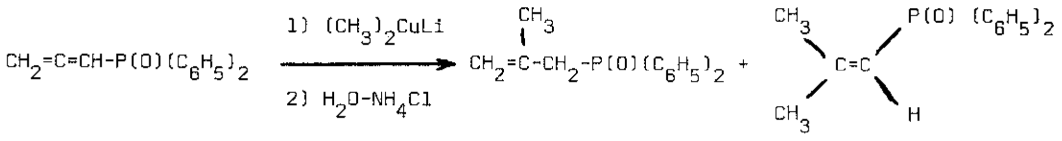
Within the past decade the addition of organocuprate reagents to α-β unsaturated carbonyl compounds has received many synthetic applications (1). Several mechanistic propositions, referring most commonly to a 1-4 addition concept, have been made (2) but the actual mechanism is not fully established.

Recently we reported (3) that the nature of the intermédiate formed by addition of dialkylcuprates to double bonds strongly depends on the activating group. We investigated this problem further using an allenic phosphine oxide and we wish to report some evidence for a 1-2 addition to the carbon-carbon double bond.

The addition of lithium dimethylcuprate to the allenic phosphine oxide 1 followed by protonation gives a mixture of two isomeric adducts 2 et 3. The compound 2 is the major product and the ratio 2/3 depends on the experimental conditions. Treatment of 2 by an equivalent amount of n-butyllithium gives, after protonation, 3 exclusively. We think that the formation of the thermodynamic product 3 arises from hydrolysis of an anionic species while the formation of 2 arises almost specifically from the hydrolysis of an organo-copper complex.



1 2 3

The addition of lithium dimetylcuprate to 1 gives an heterogenous mixture and the 2/3 ratio is very slowly influenced by the time reaction and temperature (4). To avoid this complication reactions were carried out with lithium dimethylcuprate-tributylphosphine complex (prepared from tributylphosphine iodo-copper (I) and two equivalents of methyllithium). Then the reaction mixture is homogenous and the ratio of the isomeric adducts strongly depends on time andtemperature but is independent of the hydrolysis temperature itself (compare runs 7 and 8).

REACTION OF LITHIUM DIMETHYLCUPRATE-TRI(n-BUTYL) PHOSPHINE WITH THE ALLENIC PHOSPHINE OXIDE 1

Run (a)	Temp. (°C)	Reaction time (hours)	2 (%)	3 (b)
1	- 23	0.5	80	20
2	- 23	1.5	70	30
3	- 23	3	70	30
4	- 77	0.16	93	7
5	- 77	1.5	85	15
6	- 77	3	85	15
7	- 23	1.5		
	then - 77	1.5	82	18
8	- 23	1.5		
	then - 77	(c)	73	27
9	- 23	1.5		
	(d)	1.5	82	18

a) 1(1 mmole in 10 ml of THF) was added (under argon atmosphere) to the cuprate (1 mmole in 5 ml of ester). Overall yields of isolated products 2 + 3 are 80 - 90 %.

b) 2/3ratio (average value (± 2 %) from at least two identical runs) was determined from NMR spectra of crude mixture. Purification by preparative TLC does not affect this ratio.

c) immediately hydrolysed at - 77°C.

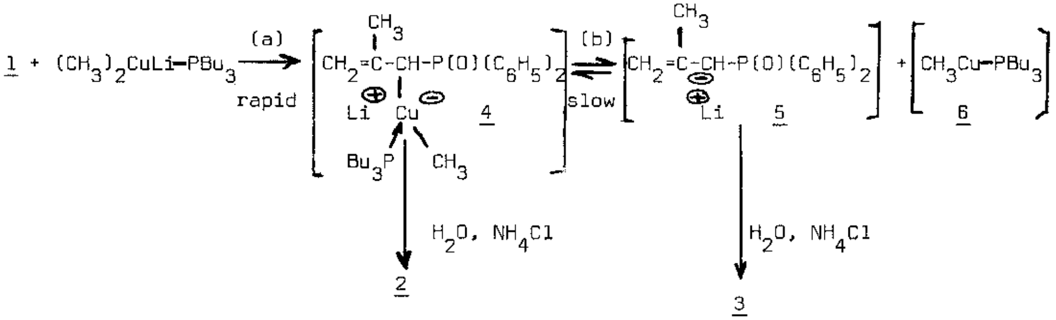
d) one equivalent of $CH_3Cu-P(nC_4H_9)_3$,ILi was added at - 23°C and the hydrolysis was made 1.5 hour later.

These results could be interpreted by a two stages reaction represented in scheme 1 :

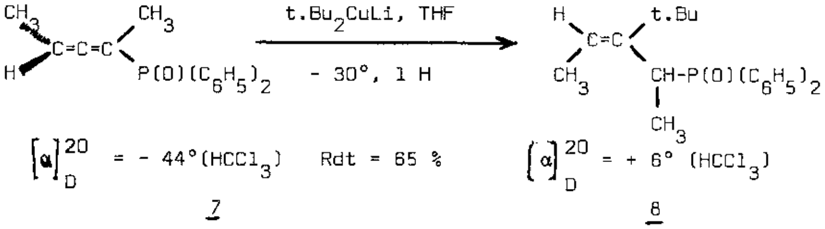
a) rapid addition of the organocuprate reagent to the carbon-carbon double bond (runs 1, 4).

b) equilibrium slowly established between two species 4 and 5 (runs 4, 5, 6). The intermediate 4 should lead to 2 while 5 leads to 3 upon hydrolysis.

Scheme 1



The 1-2 addition postulated in stage (a) is confirmed by the fact that the reaction of lithium ditertiobutylcuprate-tributylphosphine complex with an optically active allenic phosphine 7 gives an optically active adduct 8 (3b) whose formation cannot be understood via 1-4 addition (5).



The second stage (b) has been tested by the addition of one equivalent of an alkylcopper complex which should increase the amount of 2 by displacement of the equilibrium to the left. This is actually observed (run 9). Furthermore it is possible to reestablish the same equilibrium ($4 \rightleftharpoons 5$) as follows :

$$2 \xrightarrow[-50°C]{nC_4H_9Li} 5 \xrightarrow[1.5\text{ hour, }-77°C]{CH_3Cu-P(nC_4H_9)_3,ILi} \xrightarrow[-77°]{H_2O-NH_4Cl} 2 + 3\ (85 : 15)$$

The ratio 2/3 is identical to that obtained (run 5) by the direct addition of lithium dimethylcuprate to the allenic phosphine oxyde.

In conclusion a 1-4 addition can hardly explain all these phenomena. It appears that the reaction of cuprates with the allenic phosphine oxide should proceed via a 1-2 addition on the carbon-carbon double bond.

This kind of 1-2 addition mechanism has already been proposed in the case of α - β acetylenic acids, esters and sulfones(6)and α - β ethylenic ketones (2c) (7) .

Very similar results are obtained with an allenic ketone (8).

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(4) It must be noted that at - 20° hydrolysis of the preoipitate formed (25 % in wieght of the overall reaction product) affords almost exclusivelly product 2 while hydrolysis of the supernatant solution (75 % of the overall reaction product) affords a mixture 2 + 3 in a ratio 87/13.

(5) A possible allylic transposition of 4 giving a primary allylic copper seems also unlikely.

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