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LITHIUM VINYLCUPRATES. THE INFLUENCE OF SOLVENTS AND LITHIUM SALTS ON THE REACTION OF LITHIUM ALKYLCUPRATES WITH 1-ALKYNES.

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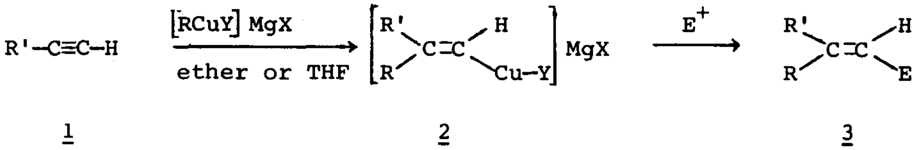
The addition of alkylcuprates [RCuY]MgX (Y=Br or R) to 1-alkynes 1 is an attractive method of obtaining stereospecifically substituted vinylcopper(I) compounds 2[1-4]. Various electrophiles are capable of converting these vinylcuprates into di- and trisubstituted alkenes 3 with retention of configuration[1,5,6]:

Scheme 1

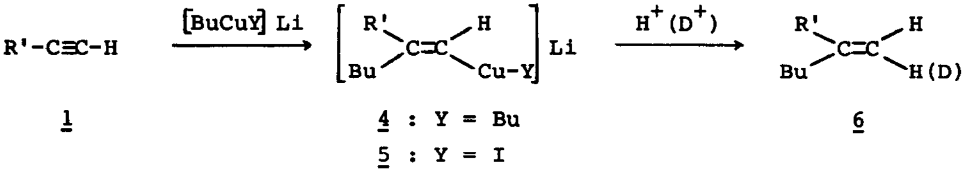


R' = Ph, H or alkyl
R = alkyl
Y = Br or R
E = Cl, Br, I, SR", $PR"_2$ or $SnR"_3$

The reaction of 1 with lithium dialkylcuprates has been studied in diethyl ether and has been described as resulting in deprotonation with formation of [R'-C≡C-Cu-R]Li[1]. In a recent report it was shown, however, that acetylene itself is an exception in this respect[7]. This alkyne appears to react with lithium dialkylcuprates as well as with lithium alkylheterocuprates with formation of vinylcopper(I) compounds in good yields.

In the course of our investigation in this field we have found that the capability of lithium alkylcuprates[8] of converting 1-alkynes into lithium vinylcuprates is not restricted to H-C≡C-H. For example, one Bu group is smoothly transferred to the 1-alkyne when 1, in which R'=Ph or n-hexyl, is treated with equivalent amounts of Bu_2CuLi in diethyl ether[9]. Protonolysis or deuterolysis of the stereospecifically formed vinylcuprates 4 leads to 6 in a yield of over 90%:

Scheme 2



1

4 : Y = Bu

5 : Y = I

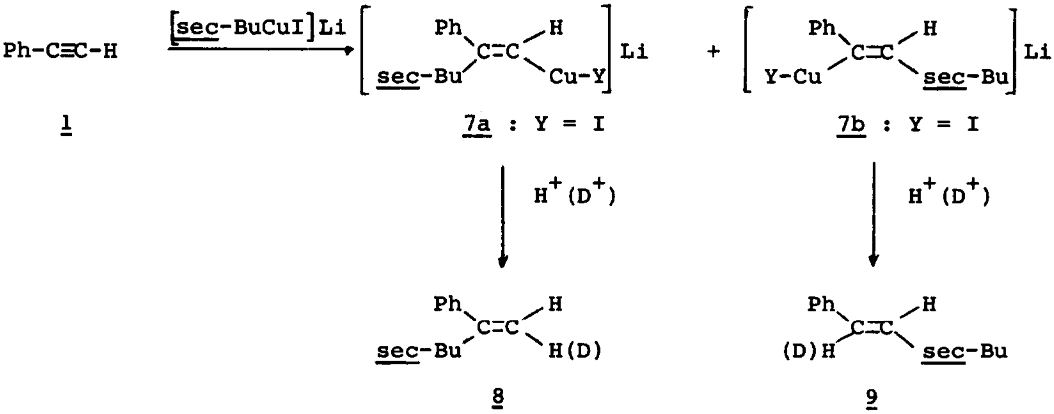
6

R'= Ph or n-hexyl

The regioselectivity of these additions is very high (95-100%). In the case of $PhC\equiv CH$, both Bu groups present in the cuprate can be used, thus producing the divinylcuprate $[Ph(Bu)C=CH]_2CuLi$. The more basic homocuprate sec-Bu_2CuLi does not convert 1 (R'= Ph or n-hexyl) into adducts under the same conditions, but abstraction of the acetylenic proton is observed.

In a similar study we have investigated the reactivity of lithium alkylheterocuprates [RCuI]Li (R= Bu or sec-Bu) towards 1 in the same solvent. Both heterocuprates convert 1-octyne into traces of addition products only. Phenyl acetylene is much more reactive, and an almost quantitative formation of adduct 5 can be realized by adding this 1-alkyne to equimolar amounts of [BuCuI]Li. With [sec-Bu--CuI]Li two adducts, viz. 7a and 7b, are formed in a ratio of 50:50 (yield: 40%; the yield is increased to 75% if two mole equivalents of the cuprate are used). Loss of regioselectivity also occurs when organocuprates, derived from RMgX in which R is a branched alkyl group, interact with some 1-alkynes(cf[3,4]). It is most likely that steric hindrance between R' in 1 and the bulky alkyl group in the cuprate is responsible for this phenomenon.

Scheme 3



1

7a : Y = I

7b : Y = I

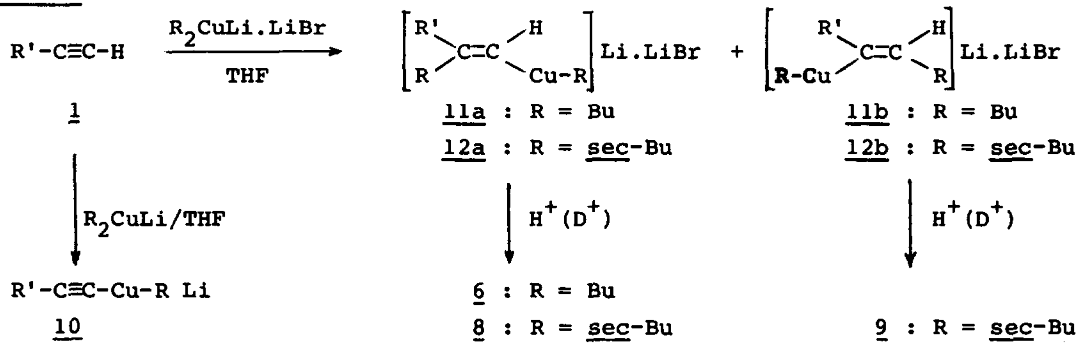
8

9

In two recent papers[3,4] we reported on an efficient synthesis of vinylcuprates from 1-alkynes and [RCuY]MgX (Y= Br or R) in the more polar ether tetrahydrofuran (THF). This prompted us to carry out a similar investigation with the corresponding lithium organocuprates.

In THF the lithium dialkylcuprates R_2CuLi (R = Bu or *sec*-Bu) appear to cause a quantitative metal-hydrogen exchange in 1 (R' = Ph or n-hexyl). However, a remarkable effect of lithium bromide on the course of the reaction is observed. In the presence of this salt the deprotonation reaction is suppressed in all cases, while the desired adducts are formed in high yields (80-95%)[10]:

Scheme 4



R' = Ph or n-hexyl

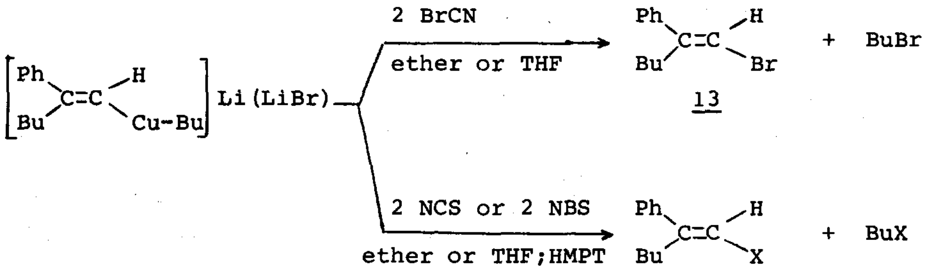
Adduct 11a is formed almost exclusively (relative amount $\geqslant$ 95%)[11] from both 1-alkynes. No regioselectivity is observed when PhC≡CH is converted by *sec*-$Bu_2CuLi.LiBr$ (ratio 12a:12b $\approx$ 50:50), but in the case of 1-octyne 12a is formed preferentially (ratio 12a:12b $\approx$ 90:10).

The heterocuprates [BuCuI]Li and [*sec*-BuCuI]Li are likewise capable of reacting with PhC≡CH in THF (amounts of addition products: 80% and 75% respectively). The possible addition products are formed in the same ratio as that found with $R_2CuLi.LiBr$ in THF. Although the use of the complex [RCuI]Li.LiBr is favourable when R = *sec*-Bu (the percentage conversion of PhC≡CH into the adducts is raised to 95), this is not the case when R = Bu. With [BuCuI]Li.LiBr the amount of the adduct is even much lower (45%). A similar influence of LiBr on the reactivity of the cuprates [RCuBr]MgX, in which R is a primary or a secondary alkyl group, was observed previously[3]. The less reactive 1-octyne only yields traces of addition products upon reaction with [BuCuI]Li or with [BuCuI]Li.LiBr. On the other hand, 1-octyne is converted by [*sec*-BuCuI]Li.LiBr into both possible adducts from which 8 and 9 are obtained in a ratio of 90:10 upon protonolysis (yield: 60-70%).

The vinylic cuprates described above are useful precursors of di- and trisubstituted alkenes. For example, the vinylic bromide 13 is obtained in high yield if cyanogen bromide or N-bromo-succinimide (NBS) is added to [Ph(Bu)C=CH-Cu-Bu]Li in diethyl ether, or to [Ph(Bu)C=CH-Cu-Bu]Li.LiBr in THF (Scheme 5). When NBS is used as a halogenating agent, some hexamethylphosphoric triamide (HMPT) has to be added to the reaction mixture. In the absence of this co-solvent a considerable amount of dimerization of the vinylic cuprates takes place (cf[5]).

Similarly, a good yield of the vinylic chloride 14 is obtained only from these vinylic cuprates and N-chloro-succinimide (NCS) if HMPT is added prior to NCS.

Scheme 5



13

13: X = Br

14: X = Cl

The experimental data will be published in a forthcoming paper.

Acknowledgement

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7. A. Alexakis, J.F. Normant and J. Villieras, Tetrahedron Lett., 1976, 3461.
8. The lithium organocuprates were prepared from a salt-free solution of RLi in hexane and CuI in diethyl ether or THF.
9. The lithium dialkylcuprates contain one mole equivalent of LiI, which is due to the manner of preparation (cf[8]).
10. When the homocuprate is prepared from BuLi and a CuBr-LiI complex, the same result is obtained. When the homocuprate is prepared from BuLi and CuBr, proton abstraction occurs only. No influence of LiBr on the conversions is observed when diethyl ether is used as a solvent.
11. Both Bu groups can be transferred to $PhC\equiv CH$ with formation of $[Ph(Bu)C{=}CH]_2CuLi.LiBr$.