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ALLENYLCOPPER(I) COMPOUNDS: SUITABLE REAGENTS FOR THE SYNTHESIS OF ALLENYNES

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Summary

Allenylcopper(I) compounds react smoothly and highly regioselectively with 1-iodo-1-alkynes to give allenynes in excellent yields.

Introduction

The preparation and reactions of allenyllithium compounds have received considerable attention [1—4], but their copper(I) analogs have hardly been explored. To our knowledge only two papers deal with the synthesis of allenylcopper(I) compounds or their cuprate derivatives, viz. one involving the reaction of lithio-1-trimethylsilylpropyne with copper(I) iodide * [5], and another dealing with the preparation of lithium diallenylcuprates starting from allenyllithium compounds [6].

Although there are several papers dealing with the reactions of 1-iodo-1-alkynes with organocopper(I) reagents [7], no data are available for reactions of allenylcopper(I) compounds or their cuprate derivatives, with 1-iodo-1-alkynes. In principle this reaction could give allenynes, compounds which are of interest, among other reasons, because some mould metabolites involve allenyne structures [8—10]. We describe below a new, efficient route to allenynes.

Results and discussion

Our initial experiments concerned the reaction of lithium diallenylcuprates with 1-iodo-1-alkynes. It soon became apparent that this approach is not satisfactory for preparation of allenynes, because of the occurrence of substantial

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* The resulting copper(I) compound has been described as a propargylic copper(I) compound, it may of course, also be regarded as an allenic one, which is how we describe it here.

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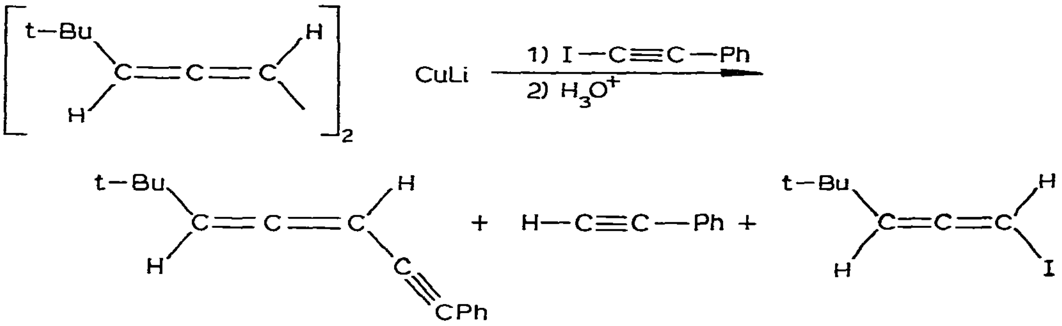
metal—halogen exchange. It was found, for instance, that the reaction of the diallenylcuprate given in Scheme 1 with 1-iodo-2-phenylacetylene gives a mixture of products (solvent = tetrahydrofuran (THF)) consisting of the desired allenyne, phenylacetylene (after protolysis), and presumably an 1-iodoallene (see Scheme 1). The last two compounds arise by metal—halogen exchange.

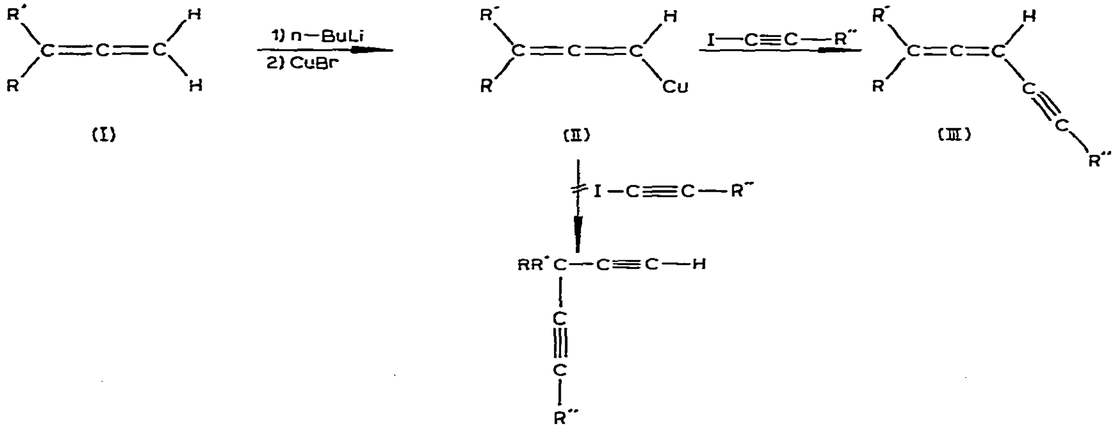
SCHEME 1



It is well-known that metal—halogen exchange is often observed during reactions of lithium diorganocuprates with, e.g., aryl iodides [11]. This is presumably why organocopper(I) compounds RCu are commonly used to bring about the cross-coupling with aryl iodides [11].

Because of the disappointing results obtained with diallenylcuprates we decided to study the behaviour of monoallenylcopper(I) compounds (compounds II in Scheme 2) towards 1-iodo-1-alkynes. The copper(I) compounds II are prepared in situ by treating allenes I successively with n-butyllithium and copper(I) bromide in THF. The resulting brown solution is completely homogeneous. Addition of various 1-iodo-1-alkynes to II gives rise to a smooth cross-coupling reaction with formation of allenynes III in excellent yields (see Table 1). In no case were contaminants of type IV, detected; these would arise if II reacted as a propargylic group. This implies that the reaction is very regioselec-

SCHEME 2



(R,R' = H,H ; t-Bu,H or Me, Me ;
R'' = Me, Ph Me_3Si, Me—C≡C— or H_2C=C(Me)—)

TABLE 1

SPECTRAL DATA FOR COMPOUNDS III

Compound III				B.p. (°C/mmHg)	n_D^{20}	Yield [a, b] (%)	^{1}H NMR data (CCl_4) [c] δ(=C=CH)	^{13}C NMR data ($CDCl_3$) [c] δ(=C=)	Remarks
	R	R′	R″						
a	H	H	Me_3Si	66—67/18	1.4871	85	5.00 (d, 2 H); 5.37 (t, 1 H)	217.0	
b	H	H	Ph		1.6382	89	5.02 (d, 2 H); 5.56 (t, 1 H)	216.6	*d*
c	t-Bu	H	Me	65—66/18	1.4900	75	5.25—5.28 (m, 2 H)	209.3	
d	t-Bu	H	Me_3Si	50—52/0.3	1.4818	77	5.37 (s, 2 H)	210.4	
e	t-Bu	H	$H_2C{=}C(Me)$	85—86/18	1.5171	85	5.31 (d, 1H); 5.47 (d, 1H)	210.3	
f	t-Bu	H	Ph		1.6027	90	5.38 (d, 1 H); 5.57; (d, 1 H)	209.9	*d*
g	t-Bu	H	$MeC{\equiv}C$	45—47/0.3	1.5397	75	5.37 (s, 2 H)	211.9	
h	Me	Me	Me_3Si	79—80/18	1.4942	80	5.18 (m, 1 H)	210.1	
i	Me	Me	$H_2C{=}C(Me)$	62—63/18	1.5292	85	5.22 (m, 1 H)	210.5	
j	Me	Me	Ph		1.5723	90	5.39 (m, 1 H)	210.2	*d*
k	t-Bu	H	H	72—73/65	1.4710	74	5.22—5.60 (m, 2 H)	210.9	*e, f*

[a] Yields refer to purified products (purity of III: >97%). [b] All compounds gave, inter alia, IR bands in the region 1940—1955 cm^{-1} (>C=C=C<). The mass spectrum showed the expected parent peaks in all cases. [c] δ(Me_4Si) = 0 ppm. [d] The compounds were purifed by column chromatography (Al_2O_3-5% H_2O/n-hexane).
[e] Compound IIIk was obtained by treatment of IIId according to the procedure given in ref. 23. [f] The ^{1}H NMR spectrum was recorded on a $CDCl_3$ solution of IIIk.

tive, if not regiospecific. It is noteworthy in this connection that diallenylcuprates have also been reported to react regioselectively with n-alkyl iodides and methyl propynoate [see ref. 6] to give allenic compounds. On the other hand, the copper(I) compound derived from lithio-1-trimethylsilylpropyne gives mixtures of allenic and acetylenic 1,6-addition products when it is added to $\Delta^{2,4}$-dienoic esters [see ref. 5].

In Table 1 are listed the compounds III which have been prepared according to Scheme 2. Of special interest are those in which R″ is the trimethylsilyl group (compounds IIIa, IIId, and IIIh). The trimethylsilyl group is a very suited protecting group for 1-alkynes and is easily split off under mild conditions [12,13], and this removal of the protecting group was carried out for compound IIId. The resulting ethynylallene IIIk was obtained pure and in good yield (see Table 1). Compound IIIg shows that the new method is also applicable to the preparation of allenediynes, compounds which are produced in nature by microorganisms [14]. From the synthetic point of view there is the further attraction that the whole reaction sequence given in Scheme 2 can be performed as a "one-pot" procedure.

To summarize, the new route to allenynes, which is complementary to the reaction of 1-haloallenes with 1-alkynes in the presence of cuprous ions and an amine [15,16], is very attractive, as it starts from readily accessible allenes [17,18] and proceeds with high regioselectivity and in high yields.

Experimental

All operations with organometallic reagents were performed under dry nitrogen. The products were analysed by GLC (SE 33 column) and NMR (Varian EM-390 and CFT-20 spectrometers) and IR spectroscopy.

1,2-Propadiene was prepared according to the method given by Cripps and Kiefer [19], tert-butylallene according to the method given in ref. 20, and 1,1-dimethylallene according to the method given in ref. 4. The 1-iodo-1-alkynes were obtained according to ref. 21. Copper(I) bromide was prepared according to the procedure of Keller and Wycoff [22].

General procedure for the preparation of III

To a stirred solution of I (0.030 mol) in dry THF (60 ml) is added at −60°C a solution of n-BuLi (0.030 mol) in n-hexane (20 ml). The mixture is stirred for 1 h at −60°C. Copper(I) bromide (0.030 mol) is then added and the temperature of the mixture is allowed to rise to −20°C. A homogeneous, brown solution results, and this is cooled to −40°C and 1-iodo-1-alkyne (0.027 mol) is added. The temperature is then gradually raised to 0°C (within 30 min), and the mixture is poured into a saturated solution of ammonium chloride in water (200 ml) containing NaCN (2 g). The product is extracted with pentane (3 × 100 ml). The combined extracts are washed with water (3 × 150 ml) and dried with $MgSO_4$. The solvent is evaporated in vacuo and the residue distilled or purified by column chromatography (Al_2O_3-5% H_2O/n-hexane). Physical constants, yields, and characteristic spectroscopic data for III are given in Table 1.

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