

CONJUGATE ADDITION OF 1 - TRIALKYLSILYLPROPYNILCOPPER DERIVATIVES;

A NEW SYNTHESIS OF 1,5-ALLENIC AND ACETYLENIC OLEFINS

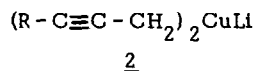
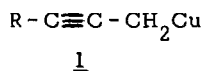
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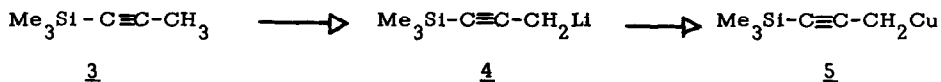
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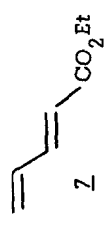
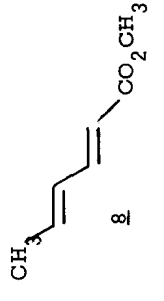
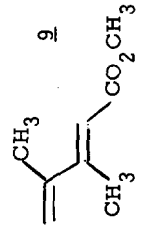
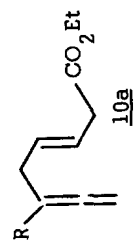
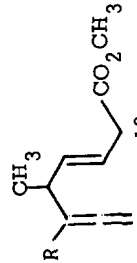
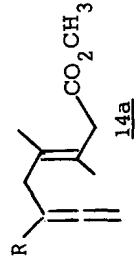
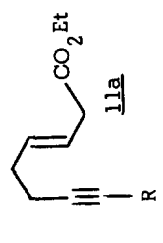
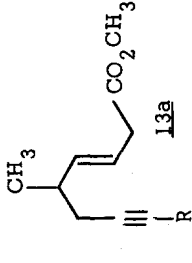
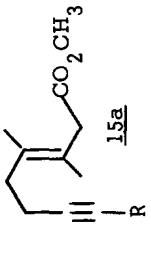
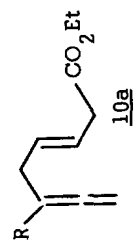
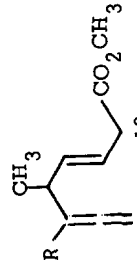
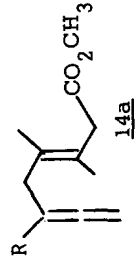
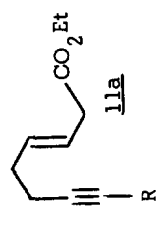
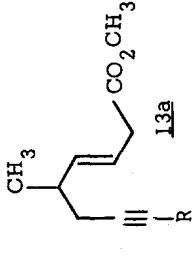
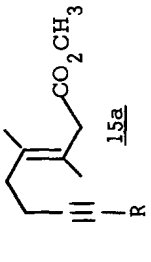
The coupling and conjugate addition reactions of organocopper and lithium diorganocuprates have become increasingly important developments in modern synthetic technology. In many cases the nature of the copper-carbon bond exerts a profound influence on the reactivity of these organometallic substances. This point has been well documented in the chemistry of alkyl, alkenyl, alkynyl and allylic copper and cuprate species.<sup>1</sup> Notably absent from these investigations, however, has been the preparation and characterization of propargylic copper compounds such as 1 or 2.<sup>2</sup>



We envisioned that any propensity on the part of 1 for 1,6-addition to  $\Delta^{2,4}$  dienolic esters in the manner described by Corey and Chen<sup>3</sup> might furnish a new stereoselective route to 1,5 acetylenic or allenic olefins. The successful lithiation of 1-trimethylsilylpropyne 3<sup>4</sup> prompted us to investigate copper derivatives of this reagent and herein are disclosed those results.

Addition of lithio-1-trimethylsilylpropyne 4, prepared in ether using *n*-butyllithium and tetramethylethylenediamine, to an ether slurry of purified cuprous iodide (1.1 equiv) at -78° under nitrogen followed by gradual warming produces a dark brown heterogeneous solution of 5 formed between -20° and -10°.



			
	Prod.	Prod.	Prod.
	Ratio	Ratio	Ratio
<p>a R = TMS</p> <p>b R = <i>i</i>-BuMe<sub>2</sub>Si</p>			
	80	18	85
<p>(CH<sub>3</sub>)<sub>3</sub>SiC≡C-CH<sub>2</sub>Cu</p>			
	20	82	15
1.2 eq.	Yield	Yield	Yield
3.5 eq.	Yield	Yield	Yield
	42%	32%	35%
	80%	70%	-----
<p>(CH<sub>3</sub>)<sub>2</sub>SiC≡C-CH<sub>2</sub>Cu</p>			
	95	3	85
<p><i>i</i>-Bu(CH<sub>3</sub>)<sub>2</sub>SiC≡C-CH<sub>2</sub>Cu</p>			
	5	97	15
1.2 eq.	Yield	Yield	Yield
	36%	25%	20%

Addition of aqueous ammonium chloride at this point enables an excellent recovery of 3 contaminated with less than 5% of trimethylsilyllallene, providing some support for the assignment of structure 5 to this intermediate.<sup>5</sup> When 5 is recooled to  $-78^{\circ}$ , treated with .85 equivalents of ethyl trans-2,4-pentadienoate 7<sup>6</sup> and held at  $-20^{\circ}$  for 12 hours, a 4:1 ratio of allenic and acetylenic products is formed in 42% yield.<sup>7</sup> That these products 10a and 11a are derived from 1,6 addition of 5 to the dienoate is fully supported by nmr, ir, and mass spectral data.<sup>3,8,9</sup> The assignment of trans geometry about the disubstituted olefin in these adducts is indicated both by the characteristic strong infrared absorption at  $976\text{ cm}^{-1}$  and by an H-H coupling constant of 16 Hz, as revealed in contact shift nmr studies using  $\text{Eu}(\text{fod})_3$ . Table I summarizes the results obtained with 7 as well as with two other dienoates.

Yields may be substantially increased when 3.5 equivalents of organocopper reagent are employed. Most importantly, the allene:acetylene ratio is strikingly sensitive towards the steric environment around the  $\delta$ -carbon of the dienoate, but rather independent of alkyl substitution within the conjugated system. To test this hypothesis, 1-tert-butyldimethylsilylpropyne has been synthesized by the reaction of tert-butyldimethylchlorosilane with propynylmagnesiumbromide in dimethoxyethane (59% yield).<sup>10</sup> Preparation of the corresponding copper derivative 6 proceeds as with 5. The 1,6-addition reactions of 6 with 7, 8, and 9 are also shown in Table I and although analogous to those of 5, exhibit more regio-specificity in the position of attack within the nucleophile.

Since the trimethylsilyl moiety may be removed from allenic and acetylenic silanes using base<sup>11</sup> or by exposure to  $\text{AgNO}_3$  then  $\text{NaCN}$ <sup>12</sup>, the 1,6-addition reactions described here constitute a simple route to 1,5 enynes and 1,4,5 trienes.<sup>13,14</sup>

References and Footnotes

1. For a good review, see G. H. Posner, Organic Reactions, **19**, 1 (1972).
2. The 1,4 addition of trimethylsilylpropynylcopper to cyclohexenone in low (<30%) yield has been carried out, but we were unaware of these experiments until most of our work had been completed; cf. H. A. Kirst, Ph.D. Thesis, Harvard Univ. (1972).
3. E. J. Corey, R. H. K. Chen, Tetrahedron Lett., 1611 (1973).
4. E. J. Corey, H. A. Kirst, Tetrahedron Lett., 5041 (1968).
5. While protonation of **4** furnished exclusively **3**, addition of **4** to acetone led to a 9:1 mixture of acetylenic:allenic carbinol. Reaction of **4** with methyl sorbate produced a complex mixture derived from carbonyl attack, with no measurable amount of 1,4 or 1,6 addition.
6. E. J. Corey, C. U. Kim, R. H. K. Chen, M. Takeda, J. Amer. Chem. Soc., **94**, 4395 (1972). See also footnote 1 in reference 3.
7. Use of the soluble CuI-isopropylsulfide complex neither affected this ratio nor improved the yield.
8. The isomeric acetylenes and allenes were all easily separated by glc analysis and each was completely homogeneous on three different systems: 6' Union Carbide W982 on acid-washed 80/100 Chrom W; 12' OV-17 (10%) on 80/100 Gaschrom A; 6' Carbowax 20M (10%) on acid-washed 60/80 Chrom W.
9. For **10a**: nmr ( $\delta$ , CDCl<sub>3</sub>) 5.62 (m, 2H, olefin), 4.36 (t, 2H, allene), 4.25 (q, 2H, J=7), 3.05 (broad m, 2H, CH<sub>2</sub>CO<sub>2</sub>-), 2.77 (m, 2H, C=C=C-CH<sub>2</sub>), 1.20 (t, 3H, J=7); ir ( $\lambda$  max film) 5.20, 5.76, 10.21 $\mu$  inter alia; mass spec., M-15 = 223.  
For **11a**: nmr ( $\delta$ , CDCl<sub>3</sub>) 5.65 (m, 2H, olefin), 4.15 (q, 2H, J=7), 3.08 (m, 2H), 2.25 (m, 2H), 1.25 (t, 3H, J=7); ir ( $\lambda$  max film) 4.61, 5.75, 10.22 $\mu$  inter alia; mass spectrum, M-15 = 223.  
All other products had nmr and ir data completely in accord with the assigned structures.
10. tert-Bu(CH<sub>3</sub>)<sub>2</sub>SiC $\equiv$ C-CH<sub>3</sub>: b.p. 149-150<sup>o</sup>; nmr ( $\delta$ , CDCl<sub>3</sub>) .08 (s, 6H), .83 (s, 9H), 1.82 (s, 3H); ir ( $\lambda$  max film) 4.59 $\mu$  inter alia.
11. (a) R. Eastmond, D. R. M. Walton, Chem. Commun., 204 (1968); (b) H. Gilman, A. G. Brook, L. S. Miller, J. Amer. Chem. Soc., **75**, 4531 (1953).
12. H. M. Schmidt, J. F. Arens, Rec. Trav. Chim., **86**, 1138 (1967).
13. We have also studied the conjugate addition of **5** to other unsaturated systems including 2-cyclohexenone, ethyl acrylate, and ethyl propiolate, but with little success.<sup>2</sup>
14. The author thanks the Department of Chemistry at Cornell University for generous financial support.