Allene Formation in Reactions of Propargyl Chlorides with Dialkylcuprates and Alkylallenylcuprates[1]

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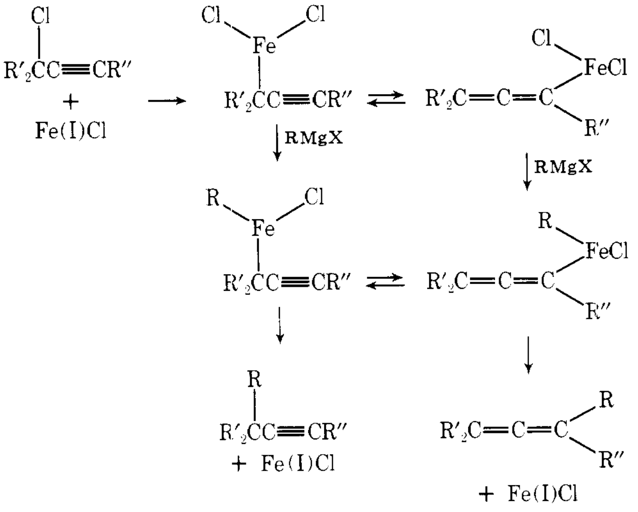
Dialkylcuprates react with propargyl chlorides to form allenes in generally excellent yield. The mixed *n*-butylmethyl- and *tert*-butylmethylcuprates react to preferentially transfer the *n*-butyl (67:29) and *tert*-butyl (97:3) groups, the latter providing an excellent means for the synthesis of *tert*-butylallenes. Small amounts of coupled product derived from the dialkylcuprates are formed, along with allene formally derived by net reduction of the propargyl chloride. It is shown that the "reduced" allene is formed by hydrolysis of an allenylcopper(I) compound formed during the reaction. Allenylcopper(I) compounds, alkylallenylcuprates, and bisallenylcuprates were prepared and their chemistry was explored in a preliminary manner. Reaction of alkylallenylcuprates with an alkyl halide produced alkane only, while reaction with propargyl chlorides resulted in the formation of only allenes. These reactions are compared with those of dialkylcuprates with alkyl halides and tosylates and the mechanisms of the reactions are discussed.

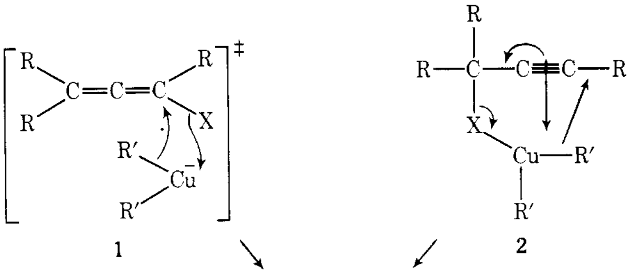
Introduction

In the preceding articles we have described the results of studies of the noncatalyzed[2] and transition metal catalyzed[3] reactions of propargyl chlorides with Grignard reagents. In the transition metal catalyzed process, allene formation was proposed to occur via a catalytic cycle in which a low-valence state metal species, formed by reaction of the metal salt (illustrated below with ferric chloride) with the Grignard reagent, undergoes insertion into the carbon–chlorine bond of the propargyl chloride to produce an equilibrium mixture of propargyl and allenyl metal derivatives. Displacement of the chloride bonded to the metal by an alkyl group produces a bisorganometal species which undergoes thermal decomposition to produce allene and regenerate the low-valence state metal species. Only when the alkyl group of the Grignard reagent is methyl and the propargyl chloride is not terminal is there an appreciable amount of the alkyl propargyl metal species present which undergoes decomposition to form alkyne. In all other cases only allene is formed. Transition metals found to be active at 5×10^{-5} M are Fe(III), Fe(II), Co(II), Ni(II), Cu(II), and Cu(I).

$$RMgX + FeCl_3 \longrightarrow R_2FeCl \longrightarrow RR + Fe(I)Cl$$



In view of the catalytic activity of Cu(II) and Cu(I) and the nature of the mechanism proposed, we decided to extend our investigations to the stoichiometric reactions of dialkylcuprates with propargyl chlorides, an area where only limited work had been carried out previously. Landor and co-workers[4] have reported that allenyl and propargyl halides react with dialkylcuprates to form allenes. These authors proposed that the allenyl halides react via a four-centered transition state (**1**), while the propargyl halides react via a π complex (**2**) which decomposes to allene with rearrangement of a π bond.



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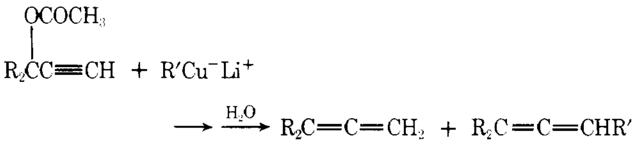
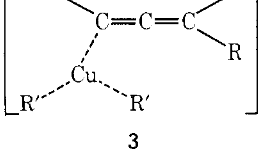
$$R_2C{=}C{=}CRR' + (R'CuX)^-$$

Crabbé and co-workers have reported that the reaction of propargyl acetates with dialkylcuprates produce allenes and proposed that the reactions proceeded via an S_N2' mechanism.[5] During the course of our investigation, Crabbé and co-workers reported that when the reaction of propargyl acetates with dialkylcuprates is carried out at low temperature and hydrolyzed immediately, a considerable amount of "reduced" allene is formed.[6] Based on these observations, Crabbé proposed formation of an intermediate represented as **3** which can undergo decomposition to produce allene, or be intercepted by hydrolysis to produce reduced allene.



$$R_2C(OCOCH_3)C{\equiv}CH + R'Cu^-Li^+ \xrightarrow{H_2O} R_2C{=}C{=}CH_2 + R_2C{=}C{=}CHR'$$



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In this article we describe the results of our studies on the synthetic aspects of the reaction of homo and mixed dialkylcuprates with propargyl chlorides, and on the preparation and reactions of allenyl-containing cuprates.

Results

Reaction of lithium di-*n*-butylcuprate (**4**) with 3-chloro-

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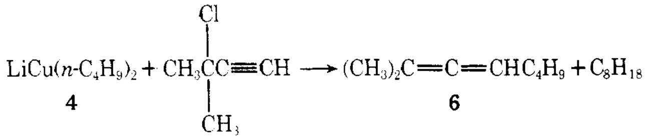
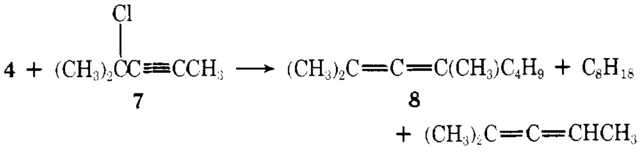
3-methyl-1-butyne (**5**) at −78 °C followed by hydrolysis produces 2-methyl-2,3-octadiene (**6**) along with a low yield of octane. In a similar manner **4** reacts with **7** at −78 °C to produce **8** along with octane and trimethylallene. At 0 °C, the reaction is very fast but the yield of **8** is lower, while the yield of trimethylallene is increased. Although **4** undergoes only very slow decomposition to give octane at −78 or 0 °C, monobutylcopper(I) undergoes decomposition to octane considerably faster. A comparison of the rate of formation of octane by decomposition of monobutylcopper(I) with that during the reaction of **4** with **7** shows that octane must be formed during the reaction of **4** with **7** (see Experimental Section). Monitoring the reaction with time shows that the yield of trimethylallene increases to a maximum and then decreases owing to decomposition of the allenylcopper(I) species formed in the reaction (vide infra).

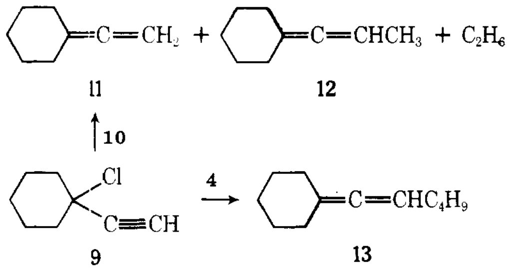


$$\underset{4}{\mathrm{LiCu}(n\text{-}C_4H_9)_2} + \underset{5}{CH_3\overset{Cl}{\underset{CH_3}{C}}C\equiv CH} \longrightarrow \underset{6}{(CH_3)_2C=C=CHC_4H_9} + C_8H_{18}$$

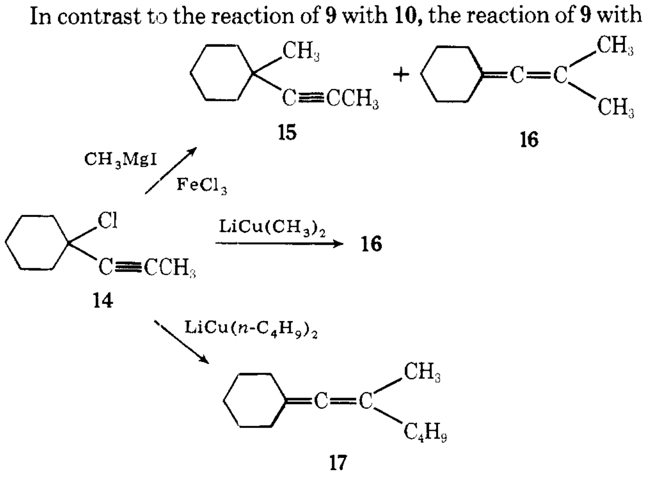


$$4 + \underset{7}{(CH_3)_2\overset{Cl}{C}C\equiv CCH_3} \longrightarrow \underset{8}{(CH_3)_2C=C=C(CH_3)C_4H_9} + C_8H_{18} + (CH_3)_2C=C=CHCH_3$$

The reaction of 1-chloroethynylcyclohexane (**9**) with lithium dimethylcuprate (**10**) produces the "reduced" allene **11** and 1-propenylidenecyclohexane (**12**) in a 1:4 ratio. A reaction mixture of **9** with **10** was maintained at −78 °C and aliquots were periodically removed, hydrolyzed, and analyzed by GLPC. The ratio of **11**:**12** remained constant although at room temperature slow decomposition occurred resulting in lower yields of **11**. Deuteriolysis of a reaction mixture derived from **9** and **10** produced **11** containing 1.0 deuterium atom at the allenyl position. During the reactions of **9** with **10** gas evolution occurred. A sample of the gas above a reaction mixture was analyzed by mass spectrometry showing the presence of ethane.

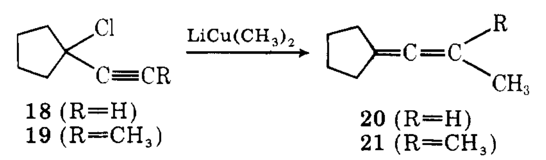


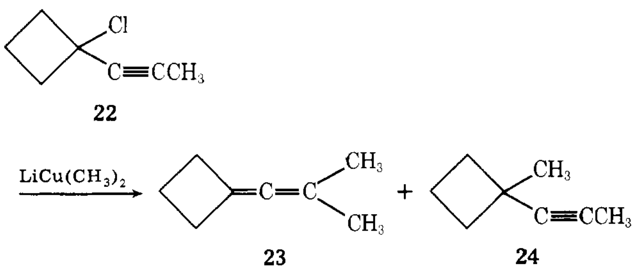
In contrast to the reaction of **9** with **10**, the reaction of **9** with di-*n*-butylcuprate (**4**) produces only the alkylated allene **13**. Only traces of octane are formed, and the reduced allene **11** could not be detected.



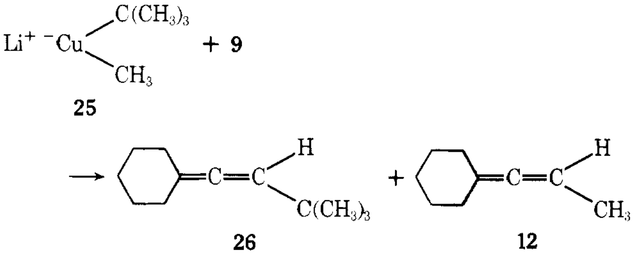
Although 1-(1-propynyl)cyclohexyl chloride (**14**) reacts with methylmagnesium iodide in the presence of ferric chloride to produce a 1:1 mixture of 1-(1-propynyl)methylcyclohexane (**15**) and (2-methyl-1-propenylidene)cyclohexane (**16**),[2] **14** reacts with **10** to form only **16**. No reduced allene of **14** was formed. In a similar manner **14** reacted with **4** to produce **17**.

Application of the reaction to the alkynylcyclopentyl and cyclobutyl chlorides provided interesting contrasts in both reactivity and mode of reaction. The cyclopentyl derivatives **18** and **19** reacted considerably slower than **9** and **14**, **18** requiring 18 h for completion. In both cases only the methylated allenes **20** and **21** were formed. The cyclobutyl derivative **22** underwent very slow reaction with **10** to produce in low yield a 60:40 mixture of allene **23** and alkyne **24**.

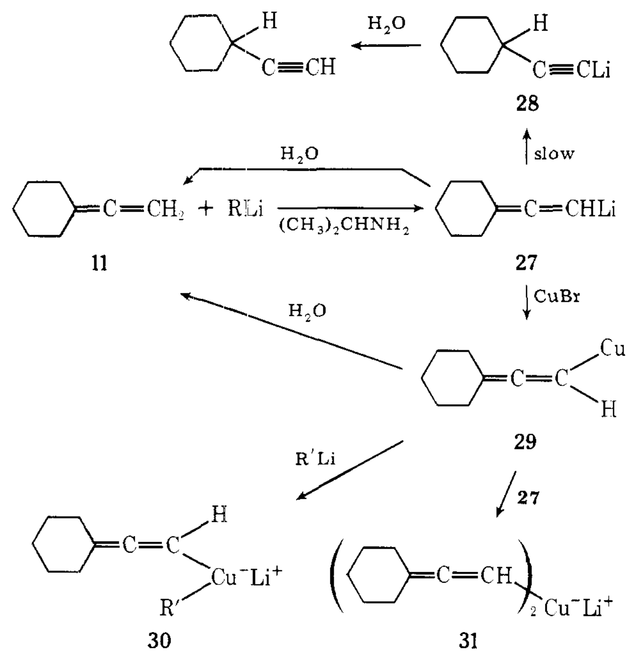




In the transition metal catalyzed reaction of propargyl chlorides with Grignard reagents it was not possible to introduce a *tert*-butyl group onto the allene. We therefore investigated the possibility of transfer of a *tert*-butyl group from a mixed dialkylcuprate,[8] specifically lithium *tert*-butylmethylcuprate (**25**).[9] Reaction of ethynylcyclohexyl chloride (**9**) with **25** gave an 80% yield of a 97:3 mixture of the *tert*-butyl and methyl allenes **26** and **12**. Much lower selectivity is exhibited by lithium *n*-butylmethylcuprate, reacting with **9** to produce **13** and **12** in 67:29 ratio along with 3.2% of reduced allene **11**. Magnesium cuprates, prepared from alkylcopper and Grignard reagents,[9] failed to react with the propargyl chlorides.

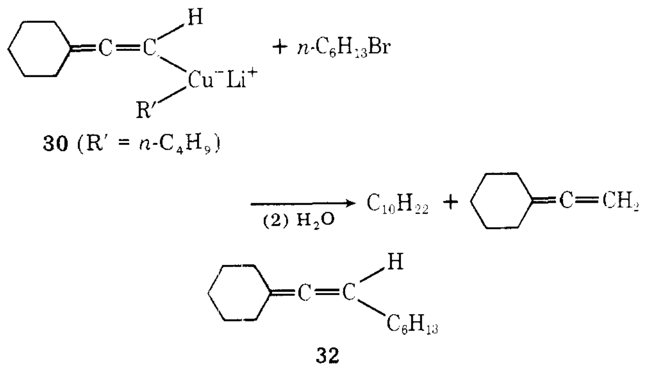


The formation of reduced allene in many of the instances described above and the formation of both allene and alkyne from **22** initially suggested that the propargyl–allenyl group becomes covalently bonded to the copper of the cuprate. In order to clarify this possibility we have prepared and studied in a preliminary manner the reactivity of allenylcopper(I) compounds and alkylallenyl- and bisallenylcuprates. Reaction of **11** with a methyllithium in the presence of a catalytic quantity of isopropylamine[10] at 0 °C rapidly produces the allenyllithium compound **27**. Immediate hydrolysis regenerates **11** uncontaminated by the isomeric alkyne. (If the solution of **27** is allowed to warm to room temperature for 30 min



extensive rearrangement to **28** occurs.[11] Addition of the solution of **27** to a suspension of cuprous bromide in ether produces an insoluble dark reddish-brown precipitate of **29**. Hydrolysis of **29** produces *only* allene **11**. The allenylcopper compound **29** appears to be quite stable in ether at room temperature. Addition of 1 molar equiv of an alkyllithium produces the mixed cuprate **30**, while addition of a second molar equiv of **27** produces the bisallenylcuprate **31**. Both **30** and **31** produce only **11** on hydrolysis.

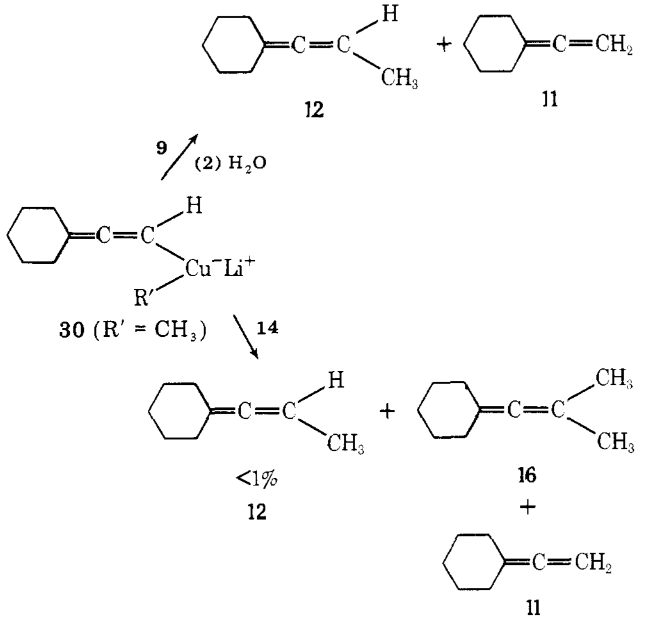
Reaction of **30** (R' = $-n$-C_4H_9) with n-hexyl bromide followed by hydrolysis produced decane (80%) and allene **11**. No butyl- or hexylallene (**13** and **32**) could be detected.

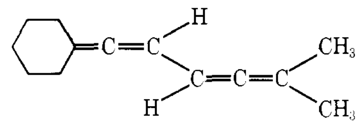


Reaction of **30** (R' = $-CH_3$) with propargyl halide **9** produced an excellent yield (>80%) of **16**, along with **11** formed during hydrolysis. Reaction of **30** (R' = $-CH_3$) with **14** gave **16**. Careful GLPC analysis indicated the possible presence of a very small amount (<1%) of **12**. Whether **12** is formed by methyl transfer to the allenyl portion in **30** (R' = CH_3) or by hydrolysis of an allenyl fragment attached to copper derived from **14** could not be determined. The other data presented herein, however, would suggest that the **12** is formed via the latter pathway. In neither case was any of the bisallenes **33** or **34** formed.

Similar results are obtained in reactions of **30** (R' = n-C_4H_9) with propargyl halides **5**, **7**, and **9**, producing only the butylated allenes **6**, **8**, and **13** derived from the propargyl chlorides. In none of these reactions was any bisallene detected.

Reaction of the diallenylcuprate **31** with n-butyl bromide for 30 min at room temperature resulted in no apparent reaction. GLPC analysis after hydrolysis showed the presence of unreacted n-butyl bromide and allene **11**. Reaction of **31** with **5** at 0 °C led to the complete disappearance of **5**, yet none





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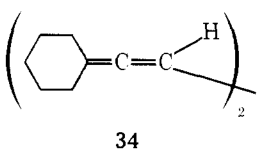

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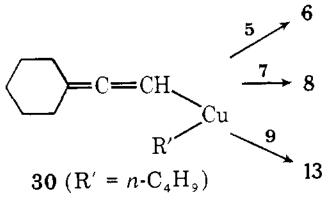
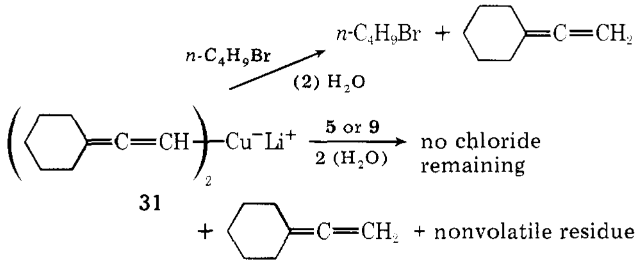




of the bisallene **33** could be detected. Hydrolysis of the reaction mixture resulted in the formation of allene **11** with ~70% recovery. Considerable noncharacterizable residue remained after removal of **11**. Similarly, reaction of **31** with **9** resulted in the disappearance of the propargyl halide, yet GLPC analysis after hydrolysis showed the formation of **11** (70%, recovery) and no bisallene. Evaporation of **11** again left considerable noncharacterizable residue. These reactions of bisallenylcuprates are under further scrutiny.

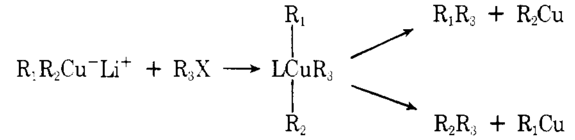
Discussion

The results reported herein differ in several aspects from those reported previously for reactions of dialkylcuprates with alkyl halides and tosylates. Mandeville and Whitesides[8] have reported that reactions of mixed dialkylcuprates with an alkyl halide result in coupling of only the alkyl groups attached to copper to the alkyl group of the halide. No coupling products derived from the two alkyl groups attached to the copper are formed. In the reactions of dialkylcuprates with propargyl halides, coupling of the alkyl groups attached to copper does occur.

$$R_1R_2Cu^-Li^+ + R_3Hal \rightarrow R_1R_3 + R_2R_3 \ (\textit{no}\ R_1R_2)$$

Mandeville and Whitesides[8] have also correlated rates of reactions of dibutylcuprate with alkyl halides with other typical S_N2 displacement reactions and suggest that the dialkylcuprate reactions occur via "unexceptional S_N2" pathways; however, distinction between attack by copper or an alkyl anion could not be made.

On the basis of Mandeville and Whitesides'[8] and earlier results, and the results of reactions of dialkylcuprates with alkyl tosylates, Johnson and Dutra[12] suggested that the mechanism of coupling involved formation of a square-planer Cu intermediate in which the alkyl groups attached to the Cu are trans located. Rapid decomposition before rearrangement results in coupling of only groups which are cis located.

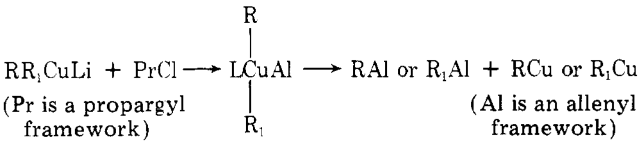


$$R_1R_2Cu^-Li^+ + R_3X \longrightarrow L\overset{R_1}{\underset{R_2}{Cu}}R_3 \longrightarrow R_1R_3 + R_2Cu \text{ or } R_2R_3 + R_1Cu$$

35

(L is a liganded solvent molecule)

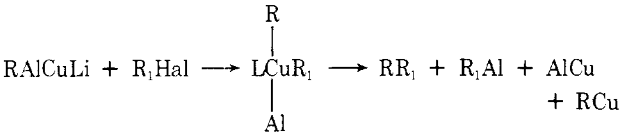
The results of the present study cannot be accommodated by such a mechanism. Assuming that the groups attached to copper become trans-located intermediates **36–39** would have been formed. Coupling of cis-located groups would have produced only those products shown. However, intermediate **36** produced not only allene, but also alkane; **37** gave alkane and no allene, **38** gave only allene RAl_1 and no bisallene or RAl, while **39**, if formed, did not give any coupled bisallenes. Obviously these results are not consistent with the Johnson and Dutra mechanism. It is also obvious that when an allenyl group is bonded to the copper it is not capable of being coupled with an alkyl or propargyl halide, being similar in reactivity with an alkynyl group attached to copper.



$$RR_1CuLi + PrCl \longrightarrow L\overset{R}{\underset{R_1}{Cu}}Al \longrightarrow RAl \text{ or } R_1Al + RCu \text{ or } R_1Cu$$

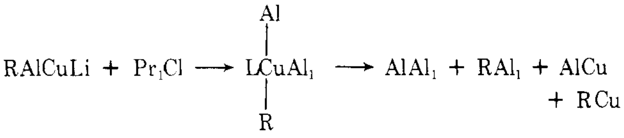
(Pr is a propargyl framework) (Al is an allenyl framework)

36



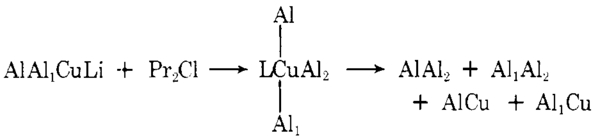
$$RAlCuLi + R_1Hal \longrightarrow L\overset{R}{\underset{Al}{Cu}}R_1 \longrightarrow RR_1 + R_1Al + AlCu + RCu$$

37



$$RAlCuLi + Pr_1Cl \longrightarrow L\overset{Al}{\underset{R}{Cu}}Al_1 \longrightarrow AlAl_1 + RAl_1 + AlCu + RCu$$

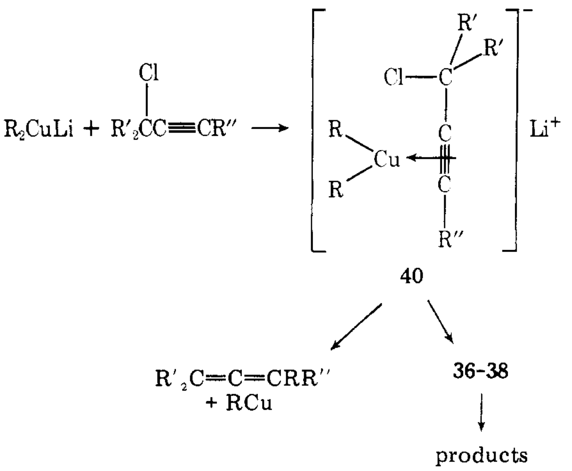
38



$$AlAl_1CuLi + Pr_2Cl \longrightarrow L\overset{Al}{\underset{Al_1}{Cu}}Al_2 \longrightarrow AlAl_2 + Al_1Al_2 + AlCu + Al_1Cu$$

39

In view of the above, we believe that allenes are not formed via the intermediates **36** and **38**, but arise by alkyl transfer from copper to the propargyl halide in a π-type complex (**40**). In general, allene is formed except when the allene contains considerable strain energy as in the case of the reaction with **22** where alkyne is also formed. In competition with alkyl transfer to the propargyl halide, nucleophilic attack by Cu to produce **36–39** must also occur. Competition between nucleophilic attack by alkyl and copper must be controlled by the nucleophilicity of the alkyl group attached to the Cu. This feature of the reaction is under further study. If groups must be cis related to couple, an intermediate such as **36** must be sufficiently stable to undergo rearrangement to **37** prior to decomposition.



In a recent article, Pearson and Gregory[13] proposed that the structure of lithium dimethylcuprate is that shown as **40.** These authors favor a rate-determining oxidative addition with inversion followed by a rapid reductive elimination with retention of configuration, all occurring within a dimeric species. Although the reaction involves reaction between a dimeric cuprate and organic halide or tosylate, no evidence is available indicating whether the dimeric species remains intact or forms intermediates of the type suggested by Johnson and Dutra. Regardless, the Pearson and Gregory mechanism is not consistent with the results of our present study for the reactions of dialkylcuprates with propargyl chlorides.

As in the previous article describing the transition metal catalyzed formation of allenes in the reactions of Grignard reagents with propargyl halides,[2] special reactivity is attributed to the presence of the C≡C. We currently believe that the mechanisms of the two reactions differ, in the former a covalent carbon–metal bond being formed and the latter occurring via a π complex.

Experimental Section

General Procedure for the Preparative Reactions of Propargyl Chlorides with Lithium Dialkylcuprates 4 and 10. To a solution of 5 mmol of lithium di-*n*-butylcuprate (**4**) [prepared at −78 °C by the addition of 10 mmol of *n*-butyllithium in hexane to a suspension of 5 mmol of cuprous bromide in hexane (10 mL)] or lithium dimethylcuprate (**10**) (prepared at −78 °C from 10 mmol of methyllithium and 5 mmol of cuprous bromide suspended in 10 mL of ether) under a helium atmosphere at 0 °C was added 2.5 mmol of propargyl chloride in 5 mL of ether. The reaction mixtures were stirred at 0 °C for 30 min and were hydrolyzed by the addition of 2 mL of water. The organic layer was decanted and the aqueous layer extracted with 10 mL of ether. The organic layers were combined and dried ($MgSO_4$), and the solvent was removed by fractional distillation. The reaction mixtures were analyzed and separated by GLPC and the products were characterized by NMR and MS. Products and yields are given in Table I.

In the case of reaction of **10** with **9** a sample of the gas above the reaction mixture was removed in an evacuated MS sampling bulb. High-resolution MS analysis showed the presence of large amounts of ethane: *m/e* for C_2H_6 calcd 30.0470; found 30.0468.

All allenes formed in this study have been characterized previously except the following.

13: NMR ($CDCl_3$) δ 1.12 (distorted t, 3 H), 1.45–1.78 (bm, 10 H), 1.78–2.45 (bm, 6 H), 4.85 (bm, 1 H); MS calcd for $C_{12}H_{20}$ 164.1565, found 164.1570.

26: NMR (CCl_4) δ 1.01 (s, 9 H), 1.42–1.83 (bm, 6 H), 1.9–2.4 (bm, 4 H) 5.95 (p, 1 H); MS calcd for $C_{12}H_{20}$ 164.1565, found 164.1568.

23: NMR ($CDCl_3$) δ 1.66 (s, 6 H), 1.68 (p, *J* = 7.5 Hz, 2 H), 2.93 (t, *J* = 7.5 Hz, 4 H); MS calcd for C_8H_{12} 108.0939, found 108.0940.

Table I. Reactions of Dialkylcuprates with Propargyl Chlorides

Dialkyl-cuprate	Registry no.	Propargyl chloride	Registry no.	Products (%)
4	24406-16-4	**5**	1111-97-3	**6** (60)
4		**7**	999-79-1	**8** (60–65), $(CH_3)_2C{=}C{=}CHCH_3$ (~15)
4		**9**	6209-75-2	**13** (90)
4		**14**	60820-36-2	**17** (75)
10	15681-48-8	**9**		**12** (70), **11** (20)
10		**14**		**16** (70)
10		**18**	40185-07-7	**20** (20)
10		**19**	65149-99-7	**21** (50)
10		**22**	65150-00-7	**23** (12), **24** (8)
25	58096-49-4	**9**		**26** (85), **12** (2.5)
$(n\text{-}C_4H_9)(CH_3)Cu^-Li^+$	42278-64-8	**9**		**13** (42), **12** (28)

24: NMR ($CDCl_3$) δ 1.34 (s, 3 H), 1.83 (s, 3 H), 1.50–2.25 (m, 6 H); MS calcd for C_8H_{12} 108.0939, found 108.0941.

Reaction of 7 with 4. To a solution of 2.2 mmol of **4** in 3 mL of hexane at −78 °C under a helium atmosphere containing toluene as a GLPC internal standard was added 2.2 mmol of **7** in ether. Aliquots were periodically removed, hydrolyzed, and analyzed by GLPC. Aliquots were removed after 40 and 90 min, hydrolyzed, and analyzed by GLPC. The yields of products were at 40 min 18.6% octane, 3.3% trimethylallene, and 19.3% **8**, and at 90 min 51.9% octane, 15.2% trimethylallene, and 34.5% **8**. After 150 min the field of **8** approached 65%.

In a similar reaction maintained at 0 °C yields were after 5 min 42.9% octane, 18.5% trimethylallene, and 33% **8**, after 10 min 53.5% octane, 23.0% trimethylallene, and 37.8% **8**, and after 60 min 77.1% octane, 15.6% trimethylallene, and 40.8% **8**.

Measurement of Rate of Decomposition of *n*-Butylcopper(I) at −78 °C. *n*-Butylcopper(I) was prepared by the addition of 1 mmol of *n*-butyllithium in hexane to 1.0 mmol of cuprous bromide suspended in 2 mL of hexane at −78 °C containing 35 mg of toluene as a GLPC internal standard. The reaction mixture was maintained at −78 °C and aliquots were periodically removed, hydrolyzed, and analyzed by GLPC. The yields of octane are at 5 min 5.6%, 1 h 9.5%, and at 3 h 21.1%.

Deuteriolysis of Reaction Mixture of 9 with 10. To a solution of 1 mmol of **10** in 2 mL of ether at −78 °C was added 1 mmol of **9** in 2 mL of ether. The reaction mixture was stirred at −78 °C for 30 min and 1 mL of deuterium oxide was added. The reaction mixture was allowed to warm to room temperature and the organic layer was decanted, washed with water, and dried ($MgSO_4$). The **11** was isolated by preparative GLPC on a 10-ft Carbowax 20 M column at 150 °C. The NMR spectrum showed δ 1.55 (bm, 6 H), 2.2 (bm, 4 H), and 4.55 (m, 1 H). The mass spectrum was identical with that of **11** except the peaks in the parent ion region were at 1 amu higher; *m/e* calcd for $C_8H_{11}D$ 109.1002, found 109.1000.

Preparation and Hydrolysis of 27.[10] To 0.2 g (1.85 mmol) of **11** at 25 °C containing 40 mg of diisopropylamine was added 1.8 mmol of *n*-butyllithium in hexane. The NMR spectrum of the resulting solution (methyllithium in ether) showed a new resonance at δ 4.9 (m). Hydrolysis of an aliquot produced only **11**. Deuteriolysis produced **11** containing one deuterium (NMR and MS) at the allenyl position.

Hydrolysis and analysis of the reaction solution from above after stirring at 25 °C for 4 h showed the presence of ethynylcyclohexane and **11** in a 75:25 ratio.

Preparation and Hydrolysis of 29. To a solution 1.8 mmol of **27** in 1.0 mL of hexane at −78 °C was added 0.9 mmol of cuprous bromide. The reaction mixture was allowed to warm to −20 °C for 10 min resulting in the formation of a dark gray suspension. An aliquot of the reaction mixture was removed and hydrolyzed giving >95% recovery of **11**.

Preparation and Hydrolysis of 30. To the suspension of 1.8 mmol of **29** in hexane at −78 °C was added 1.1 mmol of RLi (R = CH_3 in ether or *n*-C_4H_9 in hexane) and the reaction mixture was allowed to warm to ~−20 °C for 10 min resulting in the formation of a very dark gray solution. Hydrolysis of an aliquot of the solution gave >95% **11**.

Reaction of 30 (R′ = *n*-C_4H_9) with 1-Bromohexane. To a solution of 1.0 mmol of **30** (R = *n*-C_4H_9) in 3 mL of hexane at 0 °C was added 1.0 mmol of 1-bromohexane. The reaction mixture was stirred at 0 °C for 30 min and hydrolyzed by the addition of 1 mL of water. The organic layer was removed, dried ($MgSO_4$), and analyzed by GLPC showing the presence of decane (80%) and **11**. No **13** or **32** could be detected by GLPC.

Table II. Reactions of 30 with Various Propargyl Chlorides

30, R	Propargyl chloride	Product[a] (yield)
CH_3	**9**	**12** (>80%)
CH_3	**14**	**16** (>80%)
n-C_4H_9	**5**	**6** (85%)
n-C_4H_9	**7**	**8** (90%)
n-C_4H_9	**9**	**13** (80%)

[a] **11**, formed by hydrolysis of **29**, was present in all cases.

Reaction of 30 with Various Propargyl Chlorides. To a solution of 1.0 mmol of **30** in 3 mL of ether or hexane at 0 °C was added 1.0 mmol of the propargyl chloride. The reaction mixture was stirred for 30 min at 0 °C and hydrolyzed with 1 mL of water. The organic layer was removed, dried ($MgSO_4$), and analyzed by GLPC. The results are given in Table II. No reduced allenes or bisallenes could be detected by GLPC.

Preparation and Hydrolysis of 31. To a solution of 0.3 g (2.78 mmol) of **11** at 0 °C was added 2.0 mmol of methyllithium in ether. After stirring at 25 °C for 10 min, the solution of **27** was chilled to −78 °C and 1.0 mmol of cuprous bromide was added giving a dark green solution. The reaction mixture was allowed to warm to 0 °C giving a very dark solution. Hydrolysis of an aliquot of the solution and analysis by GLPC showed the presence of only **11**.

Attempted Reaction of 31 with 1-Bromobutane. To a solution of 1.0 mmol of **31** at 0 °C was added 1.0 mmol of 1-bromobutane and the reaction mixture stirred at 0 °C. Aliquots were periodically removed, hydrolyzed, and analyzed by GLPC showing only the presence of **11** and 1-bromobutane.

Attempted Reaction of 31 with 5 and 9. To a solution of 1.0 mmol of **31** at 0 °C were added 1.0 mmol of **5** and **9**. Aliquots taken immediately after the addition of **5** and **9** showed the complete consumption of **5** and **9**, but no bisallenes **33** or **34** could be detected by GLPC.[14] Allene **11** was formed on hydrolysis. Hydrolysis of the reaction mixtures followed by separation of the organic phase, drying ($MgSO_4$), and removal of the solvent gave considerable quantities of nonvolatile residues which were not further investigated.

Registry No.—**11**, 5664-20-0; **13**, 20023-45-4; **23**, 65150-01-8; **24**, 65150-02-9; **26**, 59643-61-7; **27**, 65150-03-0; **29**, 65150-04-1; **30** (R = Bu), 65150-22-3; **30** (R = Me), 65150-23-4; **31**, 65150-24-5; 1-bromohexane, 111-25-1.

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Synthesis of Highly Branched, β-Arylated Nitroparaffins[1]

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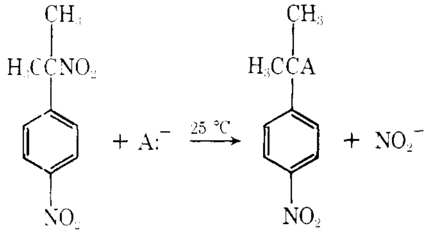
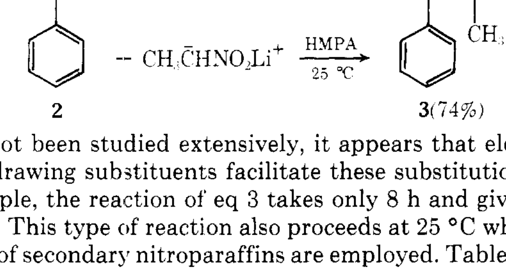
A synthetically useful one-step procedure for converting α-arylated tertiary nitro compounds into highly branched β-arylated nitroparaffins is described. These reactions appear to proceed via a chain mechanism in which radical anions and free radicals are intermediates.

Ten years ago it was discovered that the aliphatic nitro group of α,*p*-dinitrocumene (**1**) is readily displaced by a wide variety of nucleophiles as is shown in eq 1.[2] A large body of evidence now exists in support of the view that these are electron-transfer processes in which radical anions and free radicals are intermediates.[3] When the chemistry of α,*p*-dinitrocumene (**1**) was first described it was emphasized that the *p*-nitro group facilitates the displacements of eq 1; in no instance did α-nitrocumene (**2**) react with nucleophiles under conditions which resulted in complete reaction when α,*p*-dinitrocumene was employed.[2]

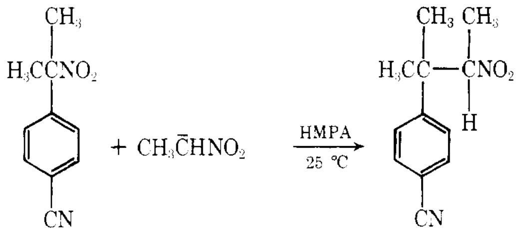


1 (1)

We have now found that the aliphatic nitro group of α-nitrocumene (**2**), and of substituted α-nitrocumenes and homologues thereof, can be displaced by nitroparaffin salts, albeit at a distinctly slower rate than when α,*p*-dinitrocumene is used. What is required is the use of hexamethylphosphoramide (HMPA) as the solvent, rather than the DMF or Me_2SO originally employed, and a relatively long reaction time (see Table I). Thus, in 45 h α-nitrocumene and the lithium salt of nitroethane react smoothly (eq 2). While the matter has not been studied extensively, it appears that electron-withdrawing substituents facilitate these substitutions; for example, the reaction of eq 3 takes only 8 h and gives 94% yield. This type of reaction also proceeds at 25 °C when the salts of secondary nitroparaffins are employed. Table I summarizes our results; it should be noted that the yields given there refer to pure, isolated products.



2 **3**(74%) (2)



4 **5**(94%) (3)

Simple, synthetically useful methods for preparing α-arylated tertiary nitro compounds are now available.[4,5] Consequently, the facile one-step conversion of α-arylated nitro compounds into highly branched β-arylated nitroparaffins makes the latter readily accessible. Manifestly, the synthesis of the highly ramified nitro compounds of Table I by classical means would be a matter of some difficulty. The relative insensitivity to steric hindrance of the processes of Table I is consonant with the view that they are radical anion reactions (vide infra) and serves to emphasize, once again, the utility of radical anion reactions for the preparation of highly branched structures.[3]

Several of the transformations listed in Table I have been studied in regard to the matter of mechanisms; in each case the characteristics of electron transfer substitution processes have been observed. Thus, the reaction of the lithium salt of nitroethane with α-nitrocumene (**2**) requires 45 h to proceed to completion and produces pure 2-phenyl-2-methyl-3-nitrobutane (**3**) in 74% yield (eq 2). But if di-*tert*-butyl nitroxide is present at the 9 mol % level the reaction is completely inhibited for 45 h. *m*-Dinitrobenzene (20 mol %) also retards this reaction; after 45 h it proceeds only 4% to completion. *m*-Dinitrobenzene is recognized as a diagnostic for radical anions,[1] di-*tert*-butyl nitroxide is a free-radical scavenger[1,6,7] and clearly the reaction of eq 2 is a chain process.

Two reactions employing *p*-cyano-α-nitrocumene (**4**) have also been investigated. At 25 °C the transformation of eq 3 requires 8 h and gives a 94% yield of the pure β-arylated nitroparaffin **5**. In contrast, if di-*tert*-butyl nitroxide is present at the 10 mol % level there is no reaction after 8 h and 91% of the *p*-cyano-α-nitrocumene is recovered. Furthermore, *m*-dinitrobenzene (20 mol %) completely inhibits this reaction for at least 8 h.

The second reaction of *p*-cyano-α-nitrocumene which was studied from the standpoint of mechanism is shown in eq 4; after 50 h a 68% yield of the pure β-arylated nitro compound