3,3-Dimethylallenyllithium. Reaction with Electrophiles Leading to Carbenoid, Electron Transfer, and Nucleophilic Processes

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Abstract: Reaction of lithium dialkylamide bases with a benzyl halide–3,3-dimethylallene (**1**) mixture gave aryl carbenoid addition products via deprotonation of the benzyl halide. Competing deprotonation of **1** also occurs giving 3,3-dimethylallenyllithium (**8**). Products of reaction of **8** with benzyl halides were acetylenes (major) and allenes (minor) and were rationalized in terms of an electron transfer mechanism leading to the 3,3-dimethylallenyl radical–benzyl radical pair. Reaction of **8** with aldehydic and ketonic electrophiles gave acetylenic alcohols, **17**, and allenic alcohols, **18**, exemplifying the ambident nature of **8**. The ratio **17**:**18** was very dependent on steric factors with hindered ketones producing allenic alcohols, **18**. Reaction of **8** with water, carbon dioxide, and chlorotrimethylsilane gave exclusively allenic products which could be rationalized in terms of Pearson's HSAB principle. Reaction with disulfide electrophiles also gave allenic products which were inconsistent with the HSAB rationalization. Rearrangement of **8** on standing gave lithium isopropylacetylide (**20**). A mechanism is suggested to account for this transformation.

In connection with an attempt to generate methylenecyclopropanes, via reaction of carbenes with allenes, we have investigated the reaction of benzyl chloride with lithium tetramethylpiperidide in the presence of 3,3-dimethylallene (**1**). In principle α-elimination from benzyl halide yields the phenylcarbene (as the carbenoid).[1] Capture by the allene should give phenyl-substituted methylenecyclopropanes. In addition to promoting α-elimination in the benzyl halide the possibility of deprotonation of the allene must also be considered in view of a report that lithium diethylamide is strong enough to deprotonate certain allenes.[2] The attempted carbene reaction indeed gives the cyclopropanation products along with smaller amounts of isomeric products best explained in terms of competing deprotonation of the 3,3-dimethylallene. We report here on this reaction as well as other reactions of the 3,3-dimethylallenyllithium with electrophiles.

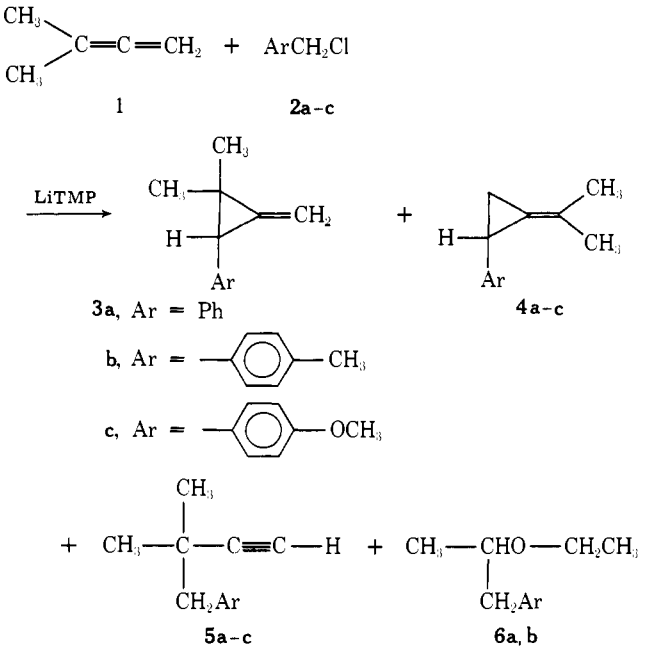
The Benzyl Halide–3,3-Dimethylallene–Lithium Tetramethylpiperidide System. The addition of an ethereal solution of lithium tetramethylpiperidide (LiTMP)[3] to a mixture of benzyl chloride and 3,3-dimethylallene (**1**) gave the cyclopropanation products **3a** and **4a** in a ratio of 4.1:1, presumably via the phenyl carbenoid intermediate. Methylenecyclopropane **4a** has been verified as a primary product of the reaction and does not arise by a methylenecyclopropane rearrangement of **3a**. However, it can be shown that thermally under more strenuous conditions (half-life of 35 min at 100 °C) **3a** rearranges to **4a**. The predominance of **3a** can be rationalized in terms of the expected greater preference of the electrophilic phenyl carbenoid for the more substituted allenyl bond of **1**.[4]

In addition to these cyclopropanation products, careful analysis of the reaction revealed the presence of both acetylene **5a** and ether **6a** in small amounts. Ether **6a** is readily rationalized in terms of insertion of phenylcarbene into the α position of diethyl ether. The formation of **5a** will be subsequently explained.

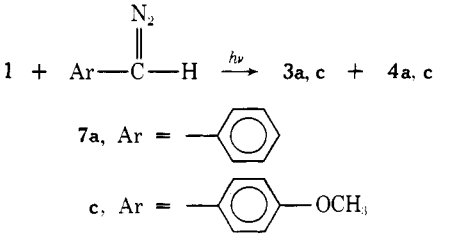
Reaction of *p*-methylbenzyl chloride under the conditions of Scheme I gave analogous cyclopropanation products **3b** and **4b** and an ether insertion product **6b**. However, an increased amount of acetylene **5b** is produced. With *p*-methoxybenzyl chloride, the acetylene **5c** now is a major product, produced in amounts comparable to the cyclopropanation products.

What is the source of the acetylenes **5a–c**? To rule out the carbene as the source of these products, the free carbene was generated photolytically from the corresponding diazo compounds, **7**, in the presence of 3,3-dimethylallene (Scheme II).

Scheme I



Scheme II



This procedure gave only the methylenecyclopropanes and none of the acetylenes, **5**. This rules out the free carbene as the source of **5** and argues against a carbenoid source since the properties of the free aryl carbene parallel those of the carbenoid species.[5]

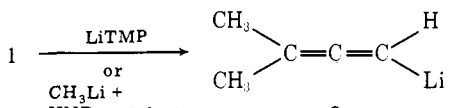
The reaction of **1** with LiTMP can be used to explain the formation of **5**. It has been found that such a reaction rapidly generates 3,3-dimethylallenyllithium (**8**). More conveniently **8** can be prepared by reaction of **1** with methyllithium and a

Table I. Reaction of Substituted Benzyl Chlorides and 3,3-Dimethylallene with LiTMP

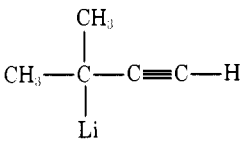
Benzyl chloride	Products: Methylenecyclopropanes 3 + 4 (%)	Ratio 3:4	Acetylene 5 (%)
$C_6H_5CH_2Cl$ **2a**	**3a** + **4a** (35)	4.1	**5a** (3)
p-$CH_3C_6H_4CH_2Cl$ **2b**	**3b** + **4b** (33)	3.9	**5b** (8)
p-CH_3O-$C_6H_4CH_2Cl$ **2c**	**3c** + **4c** (31)	Large (14)[a]	**5c** (22)

[a] From photolysis of p-methoxyphenyldiazomethane.

catalytic amount of diisopropylamine. Without addition of the catalyst, the reaction is exceedingly slow. The NMR spectrum of **8** in benzene shows a doublet, J = 4.8 Hz, at δ 1.33, and a



8



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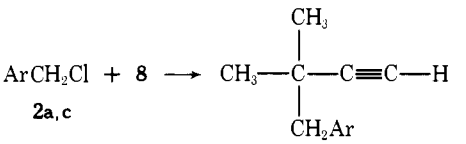
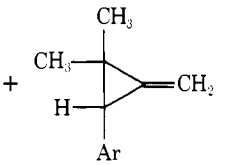
heptet, J = 4.8 Hz, at δ 4.70. A similar spectrum is seen in ether. The spectrum is therefore consistent with the major contribution from the allenyl structure **8** rather than an acetylenic structure such as **9** which should show an acetylenic proton in the δ 7–8 region of the spectrum. The unusual feature of the spectrum is the *downfield* shift of the allenyl proton of **8** relative to the parent hydrocarbon **1**. The allenyl protons of **1** appear at δ 4.05 in benzene. The origin of this reversed effect is uncertain at this time but may be due to bond angle effects in the allenyllithium reagent, **8**.

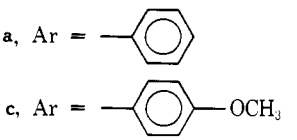
The generation of allenyllithium reagents is not unprecedented. Reaction of butyllithium with allene generates an allenyllithium reagent[6a] as does interaction of lithium diethylamide with certain alkoxyallenes.[2] Bromoallenes have also been converted to allenyllithium reagents.[6b] Polylithiated allenes have also been prepared using n-butyllithium. West has recently reported on some of the chemistry of these polylithiated allenes.[7] However, the chemistry of the monolithiated reagents has not been investigated in detail.

When p-methoxybenzyl chloride is added to an ethereal solution of **8**, a rapid reaction ensues giving **5c** (94%) and only a trace (6%) of cyclopropanation product **3c**. With benzyl chloride the acetylene is again the major product (64%) but increased amounts (36%) of cyclopropanation products arise. The most likely source of the acetylene in the cyclopropanation reaction (Scheme I) is therefore a competing deprotonation of the allene **1** by LiTMP followed by reaction of **8** with the benzyl chloride.[8] This competing reaction can be reduced by reacting p-methoxybenzyl chloride with LiTMP at −78 °C followed by addition of **1** at low temperature. In this case the relative yield of acetylene is reduced from 42% of the products to 31%. The formation of any acetylene under these conditions and the formation of cyclopropanation products under the conditions of Scheme III suggests that **8** can deprotonate the benzyl chlorides. Likewise the chlorobenzyl anion can deprotonate 3,3-dimethylallene (**1**). However, with benzyl bromide and p-methoxybenzyl bromide, proton transfer to **8** is not an important process. Negligible amounts of methylenecyclopropanes which would result via the bromobenzyl anion are

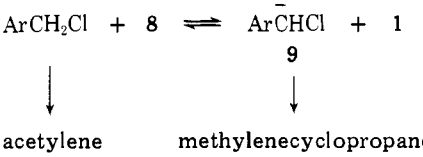
Scheme III







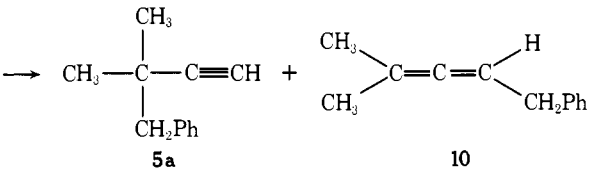
Scheme IV



formed in reaction of these two bromides with 3,3-dimethylallenyllithium (**8**).

What is the mechanistic origin of the acetylenes **5** in the reaction of **8** with benzyl halides? Careful analysis of the products of reaction of benzyl bromide with **8** shows the presence of about 13% of allene **10** along with the acetylene product **5a**. Simple nucleophilic displacement of halide by **8**,

Scheme V



5a **10**

showing ambident character, is a mechanistic possibility. The observed product distribution would require that the tertiary end of **8** be the more nucleophilic end. Such nucleophilic behavior would seem to contradict what is expected on the basis of steric factors. However, without evidence on the nucleophilic properties of **8**, a simple nucleophilic displacement cannot be ruled out.

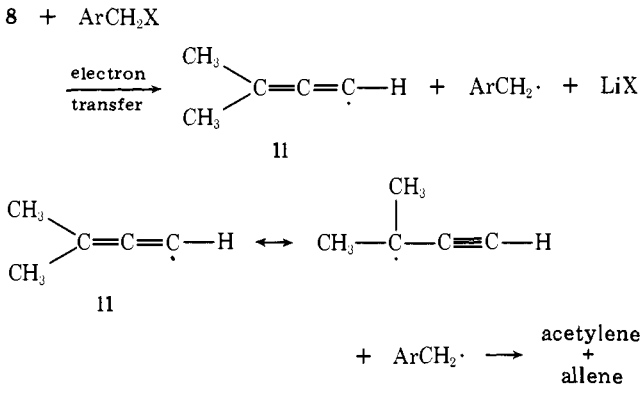
The reaction of alkyl halides with alkyllithium reagents has received attention lately with regard to mechanism. Reactions have been shown in some cases to be quite complex and often involve radical pathways. Evidence for the intervention of radicals includes racemization in the coupling reaction of n-butyllithium with optically active halides,[9a] trapping of radicals with α-methylstyrene in the reaction of ethyllithium with ethyl iodide,[9b] and the observation of the CIDNP phenomenon in certain coupling reactions[10] and lithium-halogen exchange reactions.[11] However, evidence is sometimes ambiguous. The reaction of allyl- and benzyllithium with optically active *sec*-octyl iodide gives mainly inversion in the coupled products.[12] We therefore sought to obtain evidence for the intervention of radical intermediates in the coupling reaction of benzyl bromide with **8**.

When benzyl bromide is introduced into a solution of **8** at 0 °C and the reaction is monitored by NMR, a rapid reaction

occurs. When the benzylic region of the spectrum of **5a** is scanned, emission is initially observed, implying that polarized acetylene **5a** is produced initially. While the observation of the CIDNP phenomenon does not prove the origin of **5a**, it strongly suggests that at least some of **5a** arises from a radical coupling mechanism. Additionally, scanning the methyl region the allene **10** also gives initially a strong emission signal, suggesting that a radical mechanism also accounts for the allenic product. The reaction of benzyl chloride is slower than that of benzyl bromide and no CIDNP is observed.

The mechanism shown in Scheme VI accounts for the ob-

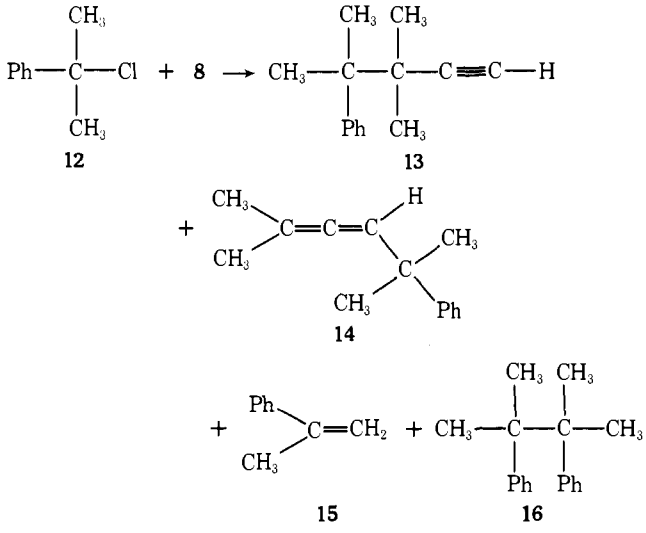
Scheme VI



served CIDNP and the predominance of the acetylenic product **5a**. Electron transfer to the benzyl halide results in formation of the 3,3-dimethylallenyl radical, **11**, and a benzyl radical. Coupling occurs preferentially at the propargyl position. Unpublished data[13] indicate that spin density is greatest at the propargyl position of **11** and coupling should occur preferentially at this site. Our results would seem to support these calculations. Additionally the 3,3-dimethylallenyl radical **11**, generated by thermal decomposition of the propargylic azo compound, couples preferentially at the propargyl position.[14]

Reaction of cumyl chloride (**12**) with **8** is substantially slower than that with benzyl chloride. This is in line with the expected increased difficulty in the electron transfer step as a result of the increased reduction potential of the cumyl chloride. Although the reduction potential of cumyl chloride has not been reported, the reduction potential of cumyl bromide[15a] (−2.18 V) is significantly larger than that of benzyl bromide (−0.82 V).[15b] The same trend in reduction potential of the chlorides is expected and accounts for the slower reaction of **12** relative to benzyl chloride. The products of the reaction (Scheme VII) are acetylene **13** and allene **14** in a ratio of 3.6:1

Scheme VII

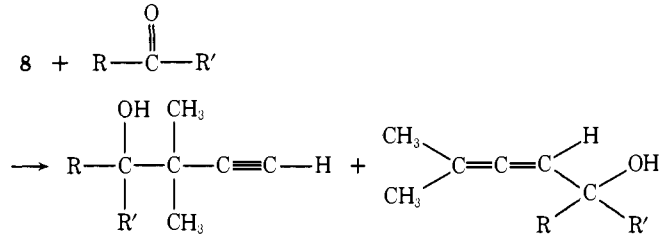


with the acetylene **13** being the major substitution product. Also produced are α-methylstyrene (**15**) and 2,3-dimethyl-2,3-diphenylbutane (**16**). It is difficult to envisage the formation of **13** and **14** by a simple nucleophilic process and we therefore suggest that the electron transfer, radical coupling mechanism (Scheme VI) is also operative in this case. The α-methylstyrene could arise *via* competing E2 processes or radical disproportionation. The 2,3-dimethyl-2,3-diphenylbutane (**16**) is a result of coupling of two cumyl radicals and provides convincing evidence for their involvement in this reaction.

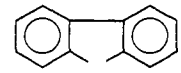
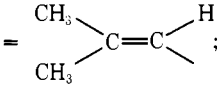
Nucleophilic Reactions of 3,3-Dimethylallenyllithium. While the data strongly favor a radical coupling mechanism in reaction of benzylic type halides, knowledge of the nucleophilic properties of **8** is desirable. Previous literature reports on reaction of allenyl-metal reagents with electrophiles establish no general pattern of reactivity. Acetylenes are sometimes produced,[6a] while at other times allenes are produced.[2,6,16] The reaction of **8** with a variety of electrophiles was therefore undertaken with the goal of understanding the ambident behavior of this nucleophile. Results are summarized in Table II.

Reaction of 3,3-dimethylallenyllithium (**8**) with aldehydes and ketones does establish the ambident nature of **8**. Both acetylenic and allenic alcohols **17** and **18** are produced in varying amounts depending on the nature of the carbonyl electrophile. The reactions are believed to occur by simple nucleophilic attack at the carbonyl center. Electron transfer processes such as those suggested to intervene in reaction of organocopper reagents with enones[17] and in certain Grignard reactions[18] are not believed to be important. If the reaction of **8** preceded partially by an electron transfer mechanisms, one

Scheme VIII

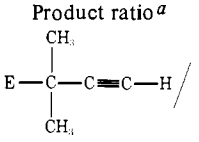
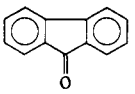
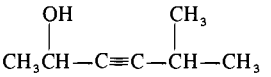
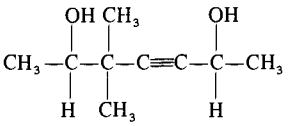
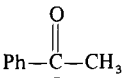
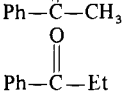
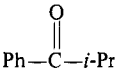
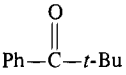
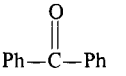
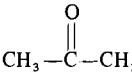
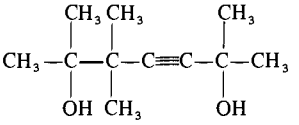
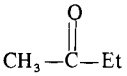
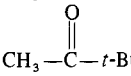
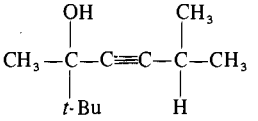
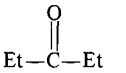
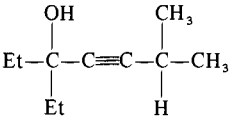
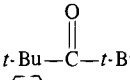
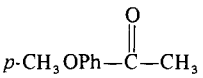
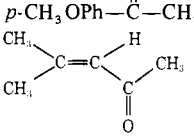


17a-q **18a-q**

a, R = R′ = H
b, R = Ph; R′ = H
c, R + R′ = 
d, R = CH_3; R′ = H
e, R = Ph; R′ = CH_3
f, R = Ph; R′ = Et
g, R = Ph; R′ = *i*-Pr
h, R = Ph; R′ = *t*-Bu
i, R = R′ = Ph
j, R = R′ = CH_3
k, R = CH_3; R′ = Et
l, R = CH_3; R′ = *t*-Bu
m, R = R′ = Et
n, R = R′ = *t*-Bu
o, R + R′ = $-CH_2(CH_2)_3CH_2-$
p, R = *p*-CH_3OPh; R′ = CH_3
q, R =  ; R′ = CH_3

would expect coupling at the center of the highest spin density in the 3,3-dimethylallenyl radical **11**. If this center is indeed the propargyl position as indicated by calculation and the coupling reactions with benzyl halides, then acetylenic alcohols

Table II. Reaction of 3,3-Dimethylallenyllithium with Electrophiles

Reaction	Electrophile	Product ratio[a] 	% yield[b]	Other products	(% yield)[b]
1	HCHO	100:0	*c*		
2	PhCHO	100:0	45[b]		(24)[b]
3		100:0	*c*		
4	CH_3CHO	92:8[d]	36[e]		(6)[e]
					(26)[e]
5		92:8	71		
6		80:20	76		
7		0:100	90		
8		0:100	100		
9		49:51	*c*		
10		19:81	53		(6)
11		11:89	80		
12		0:100	91		(3)
13		0:100	89		(4)
14		0:100	100		
15		12:88	73		
16		75:25	62		
17		49:51	63		
18		8:92	46		
19	$ClSi(CH_3)_3$	0:100	67		
20	CO_2	0:100	91		
21	H_2O	0:100	*c*		
22	$CH_3-S-S-CH_3$	0:100	90		
23	Ph—S—S—Ph	0:100	90		

[a] Determined by NMR or VPC. See Experimental Section. [b] Yields are isolated and not optimized. [c] Absolute yield not determined. [d] Determined using 0.1 equiv of CH_3CHO. [e] Determined using 0.7 equiv of CH_3CHO. [f] Determined using 0.85 equiv of PhCHO.

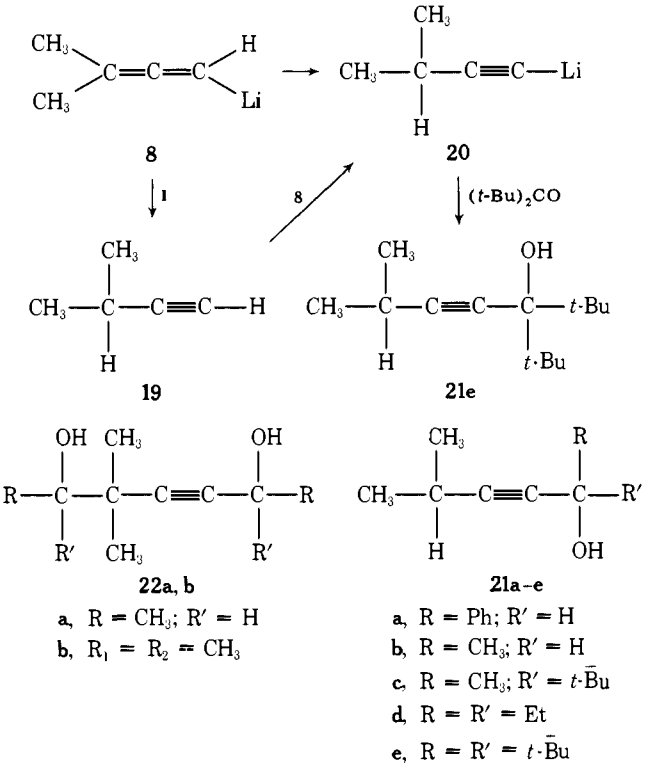
should be produced preferentially by electron transfer to the carbonyl compound. However, there is no general correlation between the amount of acetylenic alcohol produced and the reduction potential of the ketone (or aldehyde). Whereas fluorenone, with a very low reduction potential,[19] gave all acetylenic alcohol **17c**, aldehydes with much higher reduction potentials also tended to give acetylenes. Acetophenone also gave more acetylenic alcohol **17e** than the more easily reduced benzophenone.[19] It is therefore believed that some other factor controls the acetylene to allene ratio.

Examination of the data in Table II reveals certain trends. Aldehydes tend to produce acetylenic alcohols **17**, while hindered ketones produce more of the allenic alcohols **18**. In the homologous series benzaldehyde, acetophenone, propiophenone, isobutyrophenone, the amount of allenic alcohol **18** produced systematically increases. In the series acetaldehyde, acetone, 2-butanone, pinacolone, the same trend is observed. Steric factors are apparently quite important with increasing hindrance leading to large amounts of allenic alcohols **18**. The relatively uncongested aldehydes give acetylenic alcohols, **17** along with the planar unhindered ketone, fluorenone. Reaction tends to occur with the more hindered end of **8** when the carbonyl compound is relatively unhindered. Aromatic substrates give more acetylenic alcohol **17**, than their aliphatic analogues. For example, benzaldehyde gives 100% acetylenic alcohol **17b** while acetaldehyde gives amall amounts of allenic alcohol **18d**. Acetone gives allenic alcohol **18j** as the major product while acetophenone gives acetylenic alcohol **17e** as the major product. These results initially seem at odds with the expected steric trends previously discussed. If steric effects are the sole controlling factor, they seem to suggest that the methyl group processes greater steric bulk than the phenyl group. Conformational equilibrium data[20] and steric substituent constant data[21] suggest the opposite. The conclusion must be that steric effects are not only factors operating or alternately that the effective steric bulk of a phenyl group held in conjugation with a carbonyl group is less than in the methyl-substituted analogue.

While steric effects undoubtedly play a large part in determination of acetylene–allene ratios, other factors may be operative. West[7b] has suggested that Pearson's hard and soft acid and base principle (HSAB)[22] can account for some of the products seen in silation–alkylation reactions of polylithiated allenes. The propargyl site of these polylithiated allenes is characterized as soft, having high *p* character, while the sp-hybridized acetylide end is classified as hard. Leroux[6c] has also used this concept to rationalize formation of exclusively allenyl products in reaction of methoxy-substituted allenyllithium reagents with electrophiles. In an analogous manner, the propargyl end of **8** is softer than the allenyl end. The reactions of water, trimethylchlorosilane, and carbon dioxide (reactions **19–21**) might be explained in terms of HSAB theory. These electrophiles can be classified as relatively hard[23] and hence allenic products could result by preferred interaction with the "harder" end of the 3,3-dimethylallenyllithium. The HSAB theory can also be used to partially rationalize the differences in behavior of aliphatic and aromatic ketones and aldehydes. If the more polarizable aromatic substrates are considered to be softer electrophiles than their aliphatic analogues, then HSAB theory predicts preferential reaction at the propargyl end of **8** giving more acetylenic alcohols. This is what is observed. Used alone, however, the HSAB explanation breaks down when applied to the reactivity of the formaldehyde–acetaldehyde pair and benzophenone–acetophenone pair.

While the HSAB principle may have some merit in explaining the reactions of water, trimethylchlorosilane, and carbon dioxide with **8**, it does not appear to be useful in rationalizing the reactions with dimethyl disulfide and diphenyl disulfide (reactions **22** and **23**). These "softer" electrophiles

Scheme IX



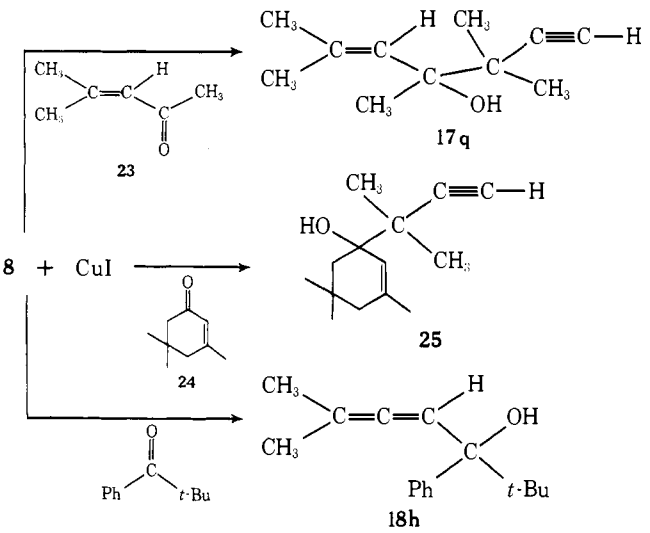
also give exclusively allenyl products. In light of these conflicting results, one must keep in mind the unknown nature of the charge distribution in **8** and the stability of the allene product vs. the acetylene. The charge distribution in **8**, along with product stability considerations, could outweigh the HSAB factor.

Reaction of **8** with certain ketones gave varying amounts of rearranged acetylenic alcohols, **21**. To determine the origin of these alcohols, the possibility of rearrangement of 3,3-dimethylallenyllithium (**8**) was investigated. It has been found that such a rearrangement does occur, giving lithium acetylide **20**. When a solution of **8** in ether, containing excess 1,1-dimethylallene and the catalytic amount of diisopropylamine catalyst, was allowed to stand at room temperature for 10 days, complete conversion to **20** was observed.[24] Such a rearrangement, in part, accounts for formation of acetylenic alcohols **21** in Table II. Reaction with di-*tert*-butyl ketone gave exclusively **21e** with none of the allenyl alcohol **18**. Rearrangement of **8** to the thermodynamic lithium acetylide **20** is a forbidden concerted process.[25] A mechanism is favored which involves protonation of **8** by the conjugate acid **1** at the propargyl position followed by deprotonation of **19**. This rearrangement is relatively slow compared to generation of **8** from the hydrocarbon **1** and does not significantly interfere when freshly prepared solutions of **8** are employed.

The rearrangement of **8** to **20** may not be the only source of the rearranged acetylenic alcohols **21**. With acetaldehyde and benzaldehyde the ratio of rearranged internal acetylenic alcohol **21** to terminal acetylenic alcohol increases as the amount of aldehyde used in the reaction increases. For example, **21a** comprises only 2% of the monoaddition products when 0.1 equiv of benzaldehyde is added to excess **8**. When 0.85 equiv of benzaldehyde is added to **8** (reaction **2**), **21a** now is 35% of the monoaddition products. The amount of **21a** produced in reaction of 0.85 equiv of benzaldehyde with **8** is too great to be accounted for solely on the basis of rearrangement of **8** to **20**. The complete origin of **21** remains unclear and investigations are continuing. The products of addition of 2 equiv of carbonyl compounds to the allenyllithium reagent, diols **22**,

are probably a result of in situ reaction of the acetylenic proton of alcohol **17** (as the lithium salt) with **8** followed by further reaction of the acetylide with the carbonyl compound.

Also perplexing is the attempted addition of the lithium diallenylcopper reagent to ketones. When a solution of **8** is treated with cuprous iodide, followed by addition of mesityl oxide (**23**) or isophenone (**24**), no products of 1,4-addition were



isolated.[26] The only characterized products were the acetylenic alcohols **17q** and **25**, respectively. None of the allenic alcohols, **18**, were produced. However, reaction with phenyl *tert*-butyl ketone gave all allenic alcohol **18h**. In contrast, the reaction of mesityl oxide (**23**), with 3,3-dimethylallenyllithium (**8**) gave a mixture of acetylenic alcohol **17q** and allenic alcohol **18e** (reaction 17, Table II). The unusual behavior in the "cuprate" reaction remains under investigation.

Experimental Section

Reaction of 3,3-Dimethylallene (1) with Benzyl Chloride–LiTMP. A solution of LiTMP[3] in ether was prepared from 1.07 g of tetramethylpiperidine and 4.1 mL of 1.84 M methyllithium in ether. The LiTMP solution was added dropwise to a solution of 2.7 g of 3,3-dimethylallene,[28] 0.65 g of benzyl chloride, and 2.5 mL of ether at 0 °C over a 2-h period. The mixture was stirred for an additional 1.5-h period at room temperature. Water was then added. The organic phase was separated, washed with dilute hydrochloric acid, and dried over anhydrous sodium sulfate. Solvents were removed in vacuo and the residue was distilled through a short-path condenser to give 0.37 g (45%) of a mixture of **3a**, **4a**, **5a**, and **6a**. Product ratios were determined by gas chromatography using a 5 ft, 5% SE-30 on Chromosorb G column at 90 °C. With the injection port lowered to 120 °C no isomerization of **3a** to **4a** was observed. The yields of **3a**, **4a**, and **5a** are given in Table I. The yield of **6a** was 5%. Samples of all products were isolated by preparative gas chromatography. The following spectral data were obtained. **3a**: NMR ($CDCl_3$) δ 7.23 (5 H, bs), 5.56 (2 H, t, J = 2 Hz), 2.48 (1 H, t, J = 2 Hz), 1.35 (3 H, s), 0.85 (3 H, s); mass spectroscopic mol wt, 158.1087 (calcd for $C_{12}H_{14}$, 158.1096). **4a**: NMR ($CDCl_3$) δ 7.18 (5 H, m), 2.55 (1 H, m), 1.92 (3 H, m), 1.78 (3 H, m), 1.65 (1 H, m), 1.13 (1 H, m); mass spectroscopic mol wt, 158.1097 (calcd for $C_{12}H_{14}$, 158.1096). **5a**: NMR (CCl_4) δ 7.18 (5 H, m), 2.67 (2 H, s), 1.97 (1 H, s), 1.18 (6 H, s); IR 2.93, 4.70 μ; mass spectroscopic mol wt, 158.1106 (calcd for $C_{12}H_{14}$, 158.1096). The NMR of **6a** was identical with that previously reported.[27]

Reaction of 3,3-Dimethylallene with *p*-Methylbenzyl Chloride–LiTMP. A solution of LiTMP, prepared from 2.15 g of tetramethylpiperidine in 6 mL of ether and 8.1 mL of 1.84 M methyllithium, was added dropwise to a mixture of 4 g of 3,3-dimethylallene, 10 mL of ether, and 1.44 g of *p*-methylbenzyl chloride, over a 2-h period. After stirring at room temperature for an additional 2 h, water was added. After an aqueous workup, the products were isolated by distillation at 0.07 mm. The products distilled at less than 35 °C at this pressure. The yields of products **3b**, **4b**, **5b**, and **6b** was 0.81 g (46%). The major product, **3b**, was not stable to gas chromatographic conditions and therefore could not be separated by gas chromatography. The ratio of **3b** to **4b** was therefore determined by NMR of the mixture. The following spectral data were obtained. **3b**: NMR (CCl_4) δ 7.00 (5 H, bs), 5.53 (2 H, d, J = 2 Hz), 2.40–2.20 (4 H, 3 H singlet at δ 2.28), 1.33 (3 H, s), 0.83 (3 H, s). **4b**: NMR ($CDCl_3$) δ 7.04 (5 H, s), 2.51 (1 H, m), 2.30 (3 H, s), 1.89 (3 H, m), 1.80 (3 H, m), 1.67 (1 H, m), 1.05 (1 H, m); mass spectroscopic mol wt, 172.1252 (calcd for $C_{13}H_{16}$, 172.1252). **5b**: NMR ($CDCl_3$) δ 7.14 (4 H, m), 2.69 (2 H, s), 2.33 (3 H, s), 2.14 (1 H, s), 1.22 (6 H, s); IR (CCl_4) 3.02, 4.73 μ; mass spectroscopic mol wt, 172.1222 (calcd for $C_{13}H_{16}$, 172.1252). The NMR of **6b** was identical with that previously reported.[27] The product mixture was heated to 150 °C for 1 h which converted **3b** completely to **4b**. Products **4b**, **5b**, and **6b** could then be separated by preparative gas chromatography. The yield of **5b** was 8% and **6b** was 5%.

Reaction of 3,3-Dimethylallene with *p*-Methoxybenzyl Chloride–LiTMP. A solution of LiTMP, prepared from 2.14 g of tetramethylpiperidine in 3 mL of ether and 8.1 mL of 1.84 M CH_3Li in ether, was added dropwise over a 2-h period to a mixture of 5.4 g of 3,3-dimethylallene, 1.60 g of *p*-methoxybenzyl chloride, and 5 mL of ether at 0 °C. The mixture was stirred for an additional 2 h at room temperature and then water was added. After an aqueous workup, the solvent was removed in vacuo. The residue was distilled to give 1.19 g (62%) of products **3c** and **5c**, along with two unidentified minor impurities, bp 57–61 °C (0.04 mm). The pot temperature was kept below 75 °C at all times during the distillation. The major product, **3c**, was not stable to gas chromatographic conditions. The ratio of **3c** to **4c** was too large to be measured by NMR. The following spectral data were obtained. **3c**: NMR (CCl_4) δ 6.86 (4 H, AA′BB′ quartet), 5.52 (2 H, d, J = 2 Hz), 3.72 (3 H, s), 2.35 (1 H, t, J = 2 Hz), 1.31 (3 H, s), 0.82 (3 H, s). **5c**: NMR ($CDCl_3$) δ 7.04 (4 H, AA′BB′ quartet), 3.81 (3 H, s), 2.68 (2 H, s), 2.13 (1 H, s), 1.21 (6 H, s); IR 2.93, 2.70 μ; mass spectroscopic mol wt, 188.1210 (calcd for $C_{13}H_{16}O$, 188.1201).

When the product mixture was heated at 160 °C for 1 h, complete conversion of **3c** to **4c** was observed. Acetylene **5c** could then be separated from **4c** by preparative gas chromatography. The ratio of **4c** (via **3c**) to **5c** was 1.38:1 as measured by gas chromatography. Methylenecyclopropane **4c** showed the following NMR: ($CDCl_3$) δ 6.93 (4 H, AA′BB′ quartet), 3.76 (3 H, s), 2.53 (1 H, m), 1.89 (3 H, m), 1.81 (3 H, m), 1.66 (1 H, m), 1.00 (1 H, m); mass spectroscopic mol wt, 188.1207 (calcd for $C_{13}H_{16}O$, 188.1201).

Reaction of 3,3-Dimethylallene with Phenyldiazomethane. phenyldiazomethane[5] (200 mg) and 5.5 mL of **1** were freeze degassed and sealed under vacuum in a Pyrex tube. The solution was irradiated for 5 h using a Hanovia 450-W source (Pyrex filtered). Upon completion of the irradiation, the color due to the diazo compound had almost completely disappeared. Gas chromatographic analysis showed the presence of **3a** and **4a** in a ratio of 4.1:1. Removal of the solvent in vacuo and distillation of the residue gave 157 mg (59%) of **3a** and **4a**. Samples of each were isolated by preparative gas chromatography and were shown to be identical spectrally with the products of the benzyl chloride–LiTMP reaction. No trace of acetylene **5a** was detected.

Reaction of 3,3-Dimethylallene with *p*-Methoxyphenyldiazomethane. A mixture of 80 mg of *p*-methoxyphenyldiazomethane[5] and 2.5 mL of **1** was freeze degassed and sealed under vacuum. The solution was irradiated for 5 h with Pyrex filtered light from a Hanovia 450-W source. Distillation of the product after completion of the irradiation gave 50 mg (49%) of a mixture of **3c** and **4c**. The ratio of **3c** to **4c** was 14:1 as determined by NMR. A sample of the product was heated at 160 °C for 1 h, upon which complete conversion to **4c** occurred. Gas chromatographic analysis showed no trace of acetylene **5c**.

Reaction of 3,3-Dimethylallenyllithium (8) with Benzyl Chloride. Lithium diisopropylamide was prepared from 1.01 g of diisopropylamine and 5.4 mL of 1.84 M methyllithium. 3,3-Dimethylallene (2.5 g) was added and the mixture was stirred at room temperature for 0.5 h. Benzyl chloride (0.62 g) was added to the solution at 0 °C and the mixture was removed from ice. The reaction became exothermic and after 20 min water was added. After an aqueous workup, distillation gave 0.38 g (48%) of a mixture of **5a** and **3a** as determined by NMR spectroscopy. Acetylene **5a** and methylenecyclopropane **3a** were not separable by gas chromatography. A sample of the distillate was heated to 165 °C for 45 min to convert **3a** to **4a**. Gas chromatographic analysis gives a ratio of **5a** to **4a** of 1.81:1. Samples of each product were isolated by preparative gas chromatography and were

spectrally identical with products previously obtained in reaction of benzyl chloride-LiTMP with **1**.

Reaction of 3,3-Dimethylallenyllithium (8) with *p*-Methoxybenzyl Chloride. LiTMP was prepared from 0.83 g of tetramethylpiperidine and 3.1 mL of 1.84 M methyllithium. 3,3-Dimethylallene (2 g) was added and the mixture was stirred at room temperature for 40 min. *p*-Methoxybenzyl chloride (0.73 g) was added at 0 °C and the mixture was stirred at this temperature for 1 h. After the mixture was stirred at room temperature for an additional 1 h, water was added. After an aqueous workup, solvents were removed in vacuo. NMR analysis shows 50% unreacted *p*-methoxybenzyl chloride along with **5c** and traces of **3c**. The ratio of **5c** to **3c** was 16:1 as determined by NMR.

Reaction of 3,3-Dimethylallenyllithium (8) with Benzyl Bromide. Methyllithium (5 mL of 1.84 M) and 2.5 g of 3,3-dimethylallene were stirred with 4 drops of diisopropylamine for 2 h at room temperature. The mixture was cooled to 0 °C and 0.78 g of benzyl bromide was added. The mixture was allowed to warm to room temperature, water was added, and an aqueous workup followed. Solvents were removed in vacuo and the residue was distilled to give 0.54 g (75%) of an 87:13 mixture of acetylene **5a** and allene **10**, bp 32 °C (0.07 mm). Samples of each product were isolated by preparative gas chromatography. Allene **10** showed the following: NMR ($CDCl_3$) δ 7.27 (5 H, bs), 5.05 (1 H, m), 3.30 (1 H, d, J = 7 Hz), 1.69 (6 H, d, J = 2.8 Hz); IR 5.06 μ; mass spectroscopic mol wt, 158.1087 (calcd for $C_{12}H_{14}$, 158.1096).

For the CIDNP experiments, a solution of **8** was prepared from 1 g of **1** and 3 mL of 1.84 M methyllithium with 2 drops of diisopropylamine at room temperature for 4 h. A 0.4-mL sample of this solution was introduced into an NMR tube via syringe followed by 0.1 mL of ether to prevent crystallization of **8** upon cooling. The mixture was cooled in an ice bath to 0 °C. A 0.1-mL portion of a solution of benzyl bromide (0.47 g in 1 mL of ether) was injected via syringe into the cold solution of **8**. The mixture was rapidly shaken and placed into the probe of the NMR. The region between the ether solvent peaks was scanned. Emission signals were seen at the positions corresponding to the benzylic protons of **5a**, the acetylenic proton of **5a**, and the methyl protons of **10**. The emissions ceased in less than 1 min following introduction of the benzyl bromide. The experiments which monitored the methyl region of **10** were carried out using solutions from which excess **1** had been removed in vacuo and the solvent replaced with fresh ether. The NMR spectrum of the solution before reaction showed no excess **1**. The methyl region of **5a** in ether solution was obscured by the ether solvent peaks and was not monitored. The benzylic protons of **10** were also obscured by the solvent peaks.

Upon completion of the reaction, an aqueous workup of the NMR tube contents of two runs followed by gas chromatographic analysis showed **5a** and **10** in a ratio of 6.4:1 and 5.4:1, respectively.

Reaction of 3,3-Dimethylallenyllithium (8) with *p*-Methoxybenzyl Bromide. A solution of **8** was prepared from 2.5 g of **1** and lithium diisopropylamide prepared from 1.06 g of diisopropylamine and 5.6 mL of 1.84 M methyllithium. *p*-Methoxybenzyl bromide (1.4 g) was added at 0 °C. An immediate exothermic reaction ensued. After stirring for an additional 1.5 h at room temperature, water was added. After an aqueous workup, solvents were removed in vacuo. NMR analysis of the crude product showed approximately 10% unreacted *p*-methoxybenzyl bromide[8] along with **5c**. No trace of **3c** could be detected by NMR. After heating a portion of the product at 150 ° for 0.5 h, no trace of **4c** could be detected by gas chromatography. The spectral properties of a sample of the product, isolated by preparative gas chromatography, were identical with those previously determined for **5c**.

Reaction of α-Chloro(*p*-methoxy)benzyllithium with 1. LiTMP was prepared from 0.85 g of tetramethylpiperidine and 3.2 mL of 1.84 M methyllithium. The mixture was cooled to −78 °C and a solution of 0.75 g of *p*-methoxybenzyl chloride in 3 mL of ether was added over a 10-min period. Stirring was continued at −78 °C for 40 min. 3,3-Dimethylallene (**1**, 2 g) was added at −78 °C and stirring was continued for 15 min. The mixture was then allowed to warm to room temperature and stirring was continued for 1.5 h. Water was then added. After an aqueous workup and removal of solvents in vacuo, distillation of the residue gave 0.528 g (59%) of **3c** and **5c**. Since **3c** was not stable to gas chromatographic analysis, a portion of the products was heated to 170 °C for 0.5 h. Gas chromatographic analysis now showed **4c** and **5c** in a ratio of 2.20:1. In a separate run, similar results were obtained when the *p*-methoxybenzyl chloride and LiTMP were allowed to react at −78 °C for 1.5 h followed by warming to −50 °C for 15 min before addition of **1**.

Reaction of Cumyl Chloride (12) with 8. A solution of 3,3-dimethylallenyllithium was prepared from 3 mL of 1.84 M methyllithium and 0.75 g of **1** with 3 drops of diisopropylamine. Cumyl chloride (0.43 g) was added and the mixture was refluxed for 36 h. Water was then added. After an aqueous workup, solvents were removed in vacuo and the residue was distilled to give 0.17 g (34%) of a mixture of **13** and **14**, bp 48 °C (0.08 mm). Hydrocarbon **16** (0.05 g, 15%) could also be sublimed from the mixture after removal of **13** and **14** by distillation. Acetylene **13** and allene **14** were not separable by gas chromatography. The ratio of **13** to **14** was 3.6:1 as determined by NMR spectroscopy. Acetylene **13** had the following spectral properties: NMR (CCl_4) δ 7.6–7.0 (5 H, m), 1.98 (1 H, s), 1.48 (6 H, s), 1.09 (6 H, s); IR 2.93, 4.07 μ; mass spectroscopic mol wt, 186.1430 (mixture of **13** and **14**) (calcd for $C_{14}H_{18}$, 186.1408). Allene **14** showed the following: NMR (CCl_4) δ 5.12 (1 H, heptet, J = 3 Hz), 1.73 (6 H, d, J = 3 Hz), 1.37 (6 H, s). Hydrocarbon **16** showed the following: NMR (CCl_4) δ 7.08 (5 H, bs), 1.31 (6 H, s). A sample of **16** was recrystallized from methanol, mp 116–117 °C (lit.[29] mp 118–118.5 °C).

Reaction of Aldehydes and Ketones with 3,3-Dimethylallenyllithium (8). General Procedure. A solution of **8** in ether was prepared from methyllithium and 2–3 equiv of **1** with a few drops of diisopropylamine as catalyst. The mixture was stirred at room temperature for about 3 h, cooled to −78 °C, and about 0.9 equiv of the aldehyde or ketone was added dropwise. The mixture was warmed to room temperature, and water was added. After an aqueous workup, solvents were removed and the products were isolated usually by distillation. Mixtures were separated by preparative gas chromatography. Spectral data for the products in Table II are given as supplementary material.

Reaction of Trimethylchlorosilane with 8. A solution of **8** in ether was prepared from 4 mL of 1.84 M methyllithium, 1 g of **1**, and 4 drops of diisopropylamine. The mixture was cooled to −78 °C and 0.88 g of trimethylchlorosilane in 1 mL of ether was added. The mixture was warmed to room temperature and stirring was continued for 30 min. After an aqueous workup, solvents were removed by distillation through a Vigreux column. Distillation of the residue gave 0.87 g (67%) of 3,3-dimethyltrimethylsilylallene, bp 63–65 °C (82 mm). No acetylene was present by NMR.

3,3-Dimethyltrimethylsilylallene showed the following: NMR (CCl_4) δ 4.80 (1 H, heptet, J = 3 Hz), 1.72 (6 H, d, J = 3 Hz), 0.15 (9 H, s); mass spectroscopic mol wt, 140.1022 (calcd for $C_8H_{16}Si$, 140.1021).

Reaction of Carbon Dioxide with 8. A solution of **8** was prepared from 4 mL of 1.84 M methyllithium, 1.5 g of **1**, and 4 drops of diisopropylamine. The solution was diluted with 5 mL of ether and added dropwise to a stirred excess of dry ice in 25 mL of ether. Water was added after evaporation of the excess dry ice and the organic phase was separated. The aqueous phase was acidified with 10% hydrochloric acid, saturated with sodium sulfate, and extracted with two portions of ether. The combined ether extracts were dried over anhydrous sodium sulfate. Solvents were removed in vacuo. The crude residue, 3,3-dimethylallenecarboxylic acid, weighed 0.75 g (91%), mp 84–86 °C. No acetylenic acid was present by NMR. The carboxylic acid showed the following: NMR (CCl_4) δ 11.13 (1 H, s), 5.40 (1 H, heptet, J = 3 Hz), 1.83 (6 H, d, J = 3 Hz); mass spectroscopic mol wt, 112.0548 (calcd for $C_6H_8O_2$, 112.0524).

Reaction of Water with 8. A solution of **8** in ether was cooled to −10 °C and quenched with water. The ether phase was dired over anhydrous sodium sulfate and analyzed by NMR spectroscopy. Only allene **1** was present and no trace of acetylene within the limits of NMR.

Reaction of Dimethyl Disulfide with 8. A solution of **8**, prepared from 3 mL of 1.84 M methyllithium and 0.75 g of **1** with 3 drops of diisopropylamine, was cooled to −78 °C. A solution of 0.44 g of dimethyl disulfide in 2 mL of ether was added and the mixture was allowed to warm to room temperature. After an aqueous workup, solvents were removed by distillation through a Vigreux column. The residue was distilled to give 0.48 g (90%) of 1-thiomethoxy-3,3-dimethylallene: bp 44–45 °C (14 mm); NMR (CCl_4) δ 5.59 (1 H, heptet, J = 2.8 Hz), 2.05 (3 H, s), 1.77 (6 H, d, J = 2.8 Hz).

Anal. Calcd for $C_6H_{10}S$: C, 63.10; H, 8.83. Found: C, 62.89; H, 9.04.

Reaction of Diphenyl Disulfide with 8. The procedure was analogous to the reaction with dimethyl disulfide. Reaction of 1.00 g of diphenyl disulfide gave 0.72 g (90%) of 1-thiophenoxy-3,3-dimethylallene: bp

60-61 °C (0.06 mm); NMR (CCl_4) δ 7.5-7.0 (5 H, m), 5.74 (1 H, heptet, J = 2.8 Hz), 1.72 (6 H, d, J = 2.8 Hz).

Anal. Calcd for $C_{11}H_{12}S$: C, 74.95; H, 6.86. Found: C, 75.24; H, 6.92.

Rearrangement of 8 to 20. Reaction of 20 with Di-*tert*-butyl Ketone. A solution of **8** in ether was prepared from 2 mL of 1.84 M methyllithium, 0.66 g of **1**, and 2 drops of diisopropylamine. The solution was kept at room temperature for 10 days and cooled to 0 °C and excess di-*tert*-butyl ketone was added. The mixture was warmed to room temperature and water was added. After an aqueous workup, gas chromatography showed a single product, alcohol **21e** with no allenic alcohol **18n**. After removal of the solvents in vacuo, **21e** was isolated by distillation, bp 41 °C (0.05 mm). Alcohol **21e** showed the following: NMR (CCl_4) δ 2.58 (1 H, heptet, J = 7 Hz), 1.58 (1 H, s), 1.19 (6 H, d, J = 7 Hz), 1.13 (18 H, s); IR 4.42 μ.

Anal. Calcd for $C_{14}H_{26}O$: C, 79.94; H, 12.46. Found: C, 80.20; H, 12.56.

Reaction of Mesityl Oxide with 3,3-Dimethylallenyllithium–Cuprous Iodide. A solution of **8**, prepared from 10 mL of 1.84 M methyllithium and 2.5 g of **1** with 10 drops of diisopropylamine, was added dropwise to a stirred mixture of 1.82 g of cuprous iodide in 35 mL of ether at −30 °C. After stirring for 0.5 h at −30 °C, a solution of 0.80 g of mesityl oxide in 5 mL of ether was added over a 10-min period. The mixture was warmed to 0 °C and then added to a rapidly stirred solution of ammonium chloride and dilute hydrochloric acid at 0 °C. The ether extract was washed with ammonia water to remove the copper salts and dried. After removal of the solvents in vacuo, the residue was distilled to give 0.52 g (38%) of alcohol **17q**. Gas chromatographic analysis showed no trace of alcohol **18q** and approximately 5% of a higher boiling unidentified impurity.

Reaction of Isophorone (24) with 3,3-Dimethylallenyllithium–Cuprous Iodide. A solution of **8** prepared from 5 mL of 1.84 M methyllithium, 1.25 g of **1**, and 5 drops of diisopropylamine was added dropwise to a mixture of 0.9 g of cuprous iodide in 20 mL of ether at −78 °C. The mixture was warmed to −50 °C and recooled to −78 °C, and a solution of 0.50 g of isophorone (**24**) in 3 mL of ether was added dropwise over a 15-min period. The mixture was warmed to 0 °C and then added to a rapidly stirred mixture of ammonium chloride and dilute hydrochloric acid at 0 °C. The mixture was then washed with ammonia water solution to remove the copper salts and the ether phase was dried. After removal of the solvents in vacuo, the residue was distilled to give 0.29 g (38%) of alcohol **25**, bp 55-60 °C (0.2 mm). The NMR spectrum of **25** showed no trace of allene. Alcohol **28** showed the following: NMR (CCl_4) δ 5.53 (1 H, m), 2.02 (1 H, s), 1.85-1.55 (5 H, m), 1.53 (1 H, bs, exchanges with D_2O), 1.45 (1 H, bs), 1.22 (3 H, s), 1.12 (3 H, s), 1.02 (3 H, s), 1.00 (3 H, s), 0.93 (1 H, bs); IR 2.95, 4.72 μ.

Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.02; H, 10.50.

Reaction of Phenyl *tert*-Butyl Ketone with 3,3-Dimethylallenyllithium–Cuprous Iodide. The reaction conditions and workup procedures were identical with those used in the reaction of isophorone. Reaction of 0.49 g of phenyl *tert*-butyl ketone gave 0.78 g (93%) of alcohol **18h**. NMR analysis showed no trace of acetylenic alcohol.

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Supplementary Material Available: Physical properties and spectral data for the products of reactions 1-17 (Table II) (7 pages). Ordering information is given on any current masthead page.

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