allowed to warm to room temperature. Workup as usual yielded a white solid. Trituration of the solid with a 50% ether–hexane solution afforded 6.5 g (56%) of **12**, mp 136–137 °C. The mother liquor was chromatographed on silica gel G, and elution with ether–hexane solutions and ether afforded an additional 675 mg (6%) of **12** and 1.2 g (15%) of **10**. Total yield of **12** was 62%. The NMR and TLC analyses of compounds **10** and **12** were consistent when compared with those of authentic[2] **10** and **12**.

1-Methyl-3,3-diphenylthio-2-piperidone (12). Inverse Quenching. A 1:2:2 Ratio. Following the general procedure B, the amide enolate (0.00885 mol) was prepared in the usual way in 13 mL of THF in the presence of LDA (0.0177 mol). The reaction was stirred at −78 °C for 10 min. The enolate solution was siphoned through a glass tube into a solution of phenyl disulfide (3.85 g, 0.0177 mol) dissolved in 10 mL of THF at 0 °C. The resulting reaction mixture was stirred at 0 °C for 1.5 h. Workup as usual yielded a solid. The solid was triturated with a 50% ether–hexane solution to afford 2.2 g (76%) of **12**, mp 136–37.5 °C. The NMR and TLC analyses of compound **12** were consistent when compared with those of authentic[2] **12**.

1-Methyl-3-phenylsulfinyl-2-pyrrolidinone (13). Following the general procedure A, LDA (0.0202 mol) was prepared in the usual manner in 10 mL of THF. The reaction mixture was cooled to −78 °C and 1-methyl-2-pyrrolidinone (1 g, 0.0101 mol) dissolved in 20 mL of THF was added over a 15-min period. The reaction mixture was allowed to stir at −78 °C for 1 h. Methyl benzenesulfinate (1.57 g, 0.0101 mol) dissolved in 5 mL of THF was added over a 5-min period. The reaction was stirred at −78 °C for 1 h, then allowed to come to room temperature, and stirred overnight. The reaction mixture was poured into a 10% hydrochloric acid solution and extracted with two 200-mL portions of $CHCl_3$. The chloroform extracts were combined, washed with a saturated NaCl solution, dried over anhydrous $MgSO_4$, filtered, and concentrated on a rotary evaporator, affording a yellow oil. The oil was chromatographed on silica gel G, and elution with ether–hexane solutions, ether, and ether–chloroform solutions afforded 2.2 g (96%) of pure **13** as a white solid: the NMR and TLC analyses of **13** were consistent when compared with those of authentic **13**.[3]

Registry No.—**1**, 14468-90-7; **2**, 65102-72-9; **3**, 65102-73-0; **4**, 65102-74-1; **5**, 931-46-4; **6**, 65138-32-1; **7**, 872-50-4; **8**, 931-20-4; **9**, 59953-50-3; **10**, 59953-51-4; **11**, 59953-53-6; **12**, 59953-54-7; **13**, 63914-40-9; **14**, 65102-75-2; phenyl disulfide, 882-33-7; methyl benzenesulfinate, 670-98-4.

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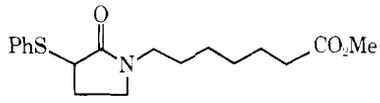

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Clarification of the Mechanism of the Reaction of Terminal Propargylic Chlorides with Alkyl Grignard Reagents

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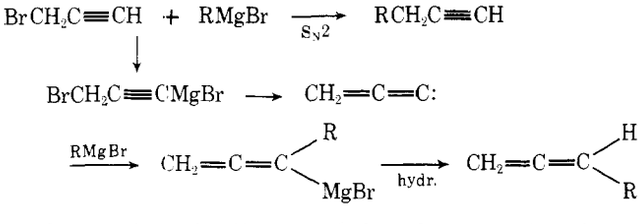
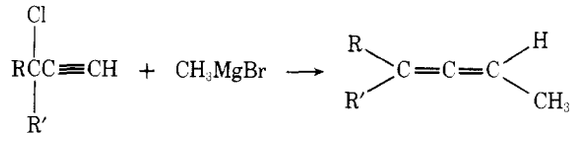
In the absence of transition metal impurities in the magnesium used to prepare the alkyl Grignard reagent, terminal propargylic chlorides react with Grignard reagents to form an allene carbene–zwitterion intermediate. Reaction of this intermediate with a second molecule of the Grignard reagent generates a mixture of propargyl and allenyl Grignard reagents which on hydrolysis generates a mixture of two alkynes and the allene. No evidence was found for the occurrence of carbonium ion, free radical, or S_N2' reaction pathways.

The history of the reaction of propargyl derivatives with Grignard reagents is one of confusion, widely divergent results being reported by various authors. Serratosa[1] has suggested that propargyl bromide can react with Grignard reagents via two mechanistic pathways, one being a direct S_N2 process to



produce exclusively alkyne, and the other occurring via an allene–carbene to give exclusively allene. Pasternak and Delépine[2] have reported that terminal tertiary propargylic halides react with methylmagnesium bromide to produce only allene in quantitative yields! (No mechanism was proposed.) These authors also suggested that the previous contradictory reports of the formation of mixtures of isomeric allenes, alkynes, and dienes were due to isomerization during the hydrolysis step.



Coulomb-Delbecq[3] and co-workers have investigated the reactions of propargylic acetates with Grignard reagents in the absence and presence of added magnesium iodide or cobalt chloride. In the presence of added magnesium iodide a mixture of products is obtained in which allene and alkyne are formed in greater amounts than in the absence of magnesium iodide, leading the authors to propose that a propargyl–allenyl cation was an intermediate. However, in the presence of cobalt chloride substantially higher yields of allene were formed, leading the authors to suggest that an intermediate propargyl–allenyl radical was involved as an intermediate. Substantial yields of dimeric products were also reported in both cases.

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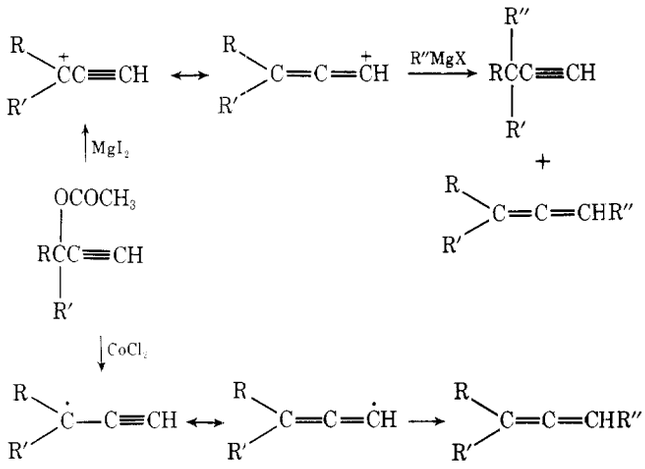


The reactions of nonterminal propargylic halides with Grignard reagents have been studied by Zakharova[4] and by Jacobs and Meyers.[5] Zakharova[4] reported that allenes are the major products formed and suggested a carbocation intermediate mechanism. Jacobs and Meyers[5] reported that alkynes and dienes were the major products; the dienes later were shown to be derived by isomerization of the initially formed allenes.[6]

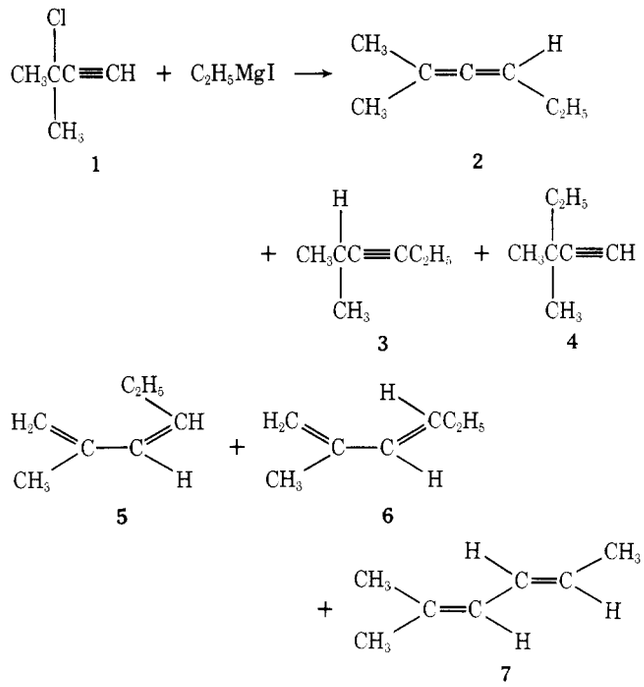
Finally, apparently accepting that allenes are formed in the reactions of propargylic halides with Grignard reagents, an S_N2'-type mechanism has also been suggested to account for their formation.[7]

In view of our need to develop a reliable synthesis of allenes, and the diverse results reported in the literature, we undertook a detailed study of the reaction of selected propargylic halides with Grignard reagents. During the course of this study we have derived evidence in favor of the allene–carbene mechanism for the direct reaction of Grignard reagents with terminal propargylic halides leading to the formation of a mixture of alkynes and allene, and a transition metal catalyzed process resulting in the exclusive formation of allene.[8] We describe herein the results of the study of the noncatalyzed reaction, while the study of the transition metal catalyzed reactions is described in detail in the accompanying article.[9]

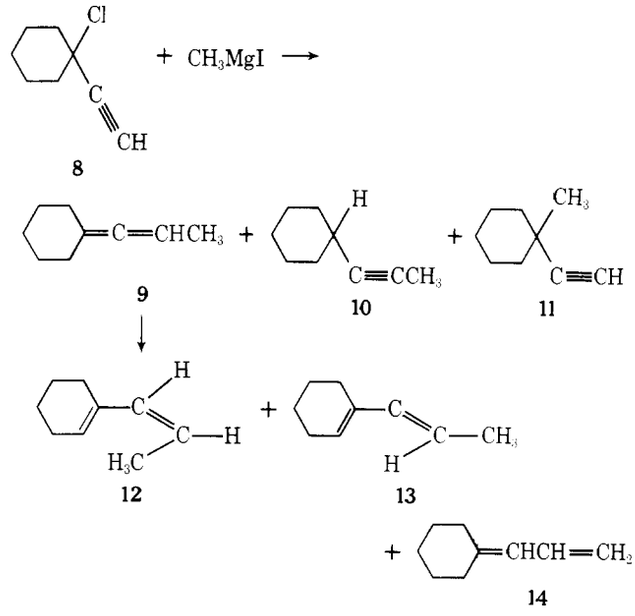
Results

Initial results derived from reactions of propargyl halides with Grignard reagents in our laboratories were not consistent. In some instances mixtures of alkynes and allene, and in some cases dienes, were formed, while in others only allene was formed. It finally became apparent that internally consistent, but different, results were being obtained using two different sources of magnesium, and that allene formation was the abnormal reaction in which transition metal catalysis was occurring.[8,9] Only the results of the noncatalyzed reactions are described here.

Treatment of 3-chloro-3-methyl-1-butyne (**1**) with 2 molar equiv of ethylmagnesium iodide at 0 °C resulted in the slow evolution of ethane. At the end of 24 h gas evolution had ceased. Hydrolysis of an aliquot of the reaction mixture indicated that ~75% of the Grignard reagent had been consumed. Distillation of the reaction product produced a volatile fraction containing **2, 3,** and **4** which were separated by preparative GLPC and identified by their spectral properties. The distillation residue was analyzed and separated by GLPC and shown to contain, in addition to **2,** the three dienes **5, 6,** and **7.** GLPC analysis of the crude reaction mixture immediately after hydrolysis showed the presence of only **2, 3,** and **4** in a 59:15:26 ratio. In contrast to the earlier suggestion that isomerization of the allene to dienes occurred during the hydrolysis step,[2] the ratio of **2:3:4** remained the same regardless of whether the reaction mixture was quenched with water, 5% sulfuric acid, saturated ammonium chloride, or 5% sodium hydroxide in either a normal or inverse manner. The isomerization of the allene appears to be a thermal process and is under further study in our laboratories. Quenching a reaction mixture with deuterium oxide followed by determination of the deuterium content in **2, 3,** and **4** by mass spectrometry showed the presence of 47.0% **2**-d_1, 48.8% **3**-d_1 and 8.9% **4**-d_1.



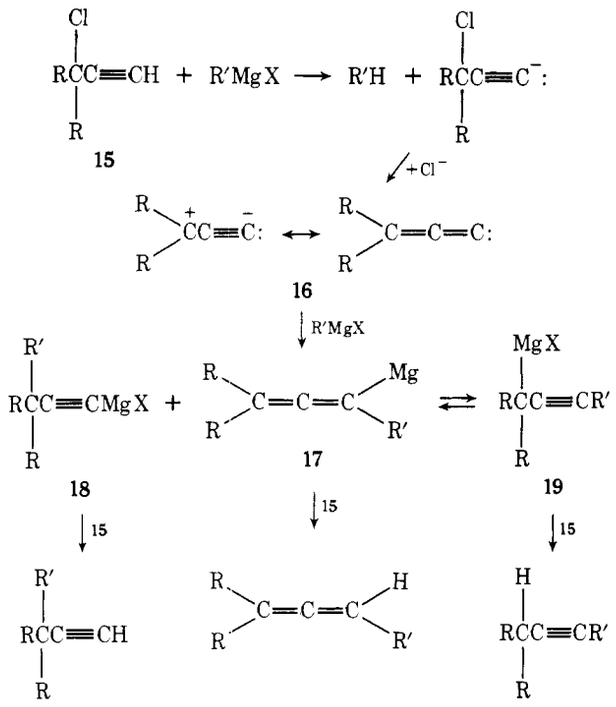
In a similar manner, 1-ethynylcyclohexyl chloride (**8**) on



reaction with 2 molar equiv of methylmagnesium iodide for 19.5 h at 0 °C produced **9, 10,** and **11** in a 100:15:46 ratio, along with lesser amounts of the rearranged dienes **12, 13,** and **14.**

Discussion

The formation of the isomeric alkynes and allene as the primary products from the tertiary propargylic halides is best rationalized as occurring via a zwitterion–allene carbene intermediate (**15**) which is formed by proton abstraction of the acetylenic hydrogen by the Grignard reagent followed by loss of chloride ion.[10] Nucleophilic attack on **16** by a second molecule of the Grignard reagent at either the propargyl or allenyl



carbon[11] produced the new organomagnesium intermediates **17, 18,** and **19.** The incomplete utilization of 2 molar equiv of the Grignard reqgent, and the incomplete deuterium incorporation on deuterolysis, is due to the fact that the newly formed Grignard reagents **17–19** compete with the original Grignard reagent in proton abstraction from the propargyl halide.

The competitive proton abstraction by **17** unfortunately does not allow one to gain any information concerning the possible formation of allene via an S_N2' displacement process. Accordingly, we reinvestigated the reaction of propargyl bromide with a Grignard reagent as reported by Serratosa.[1] As reported, only allene is formed (<1% of any isomeric alkyne was present). However, careful analysis of the reaction mixture showed that *no* hexane had been formed as would have been required by the allene carbene mechanism. The formation of only allene is most consistent with its being formed via a transition metal catalyzed process,[9] propargyl bromide being very much more reactive than the propargyl chlorides in the transition metal catalyzed process and thus occurring at much lower concentrations of transition metal impurities in the magnesium. At best, an S_N2' process cannot be occurring to more than a few percent, even in the most favorable cases.

Experimental Section

Reaction of 3-Chloro-3-methyl-1-butyne (1) with Ethylmagnesium Iodide. To a solution of 0.25 mol of ethylmagnesium iodide in 135 mL of ether was rapidly added 10.25 g (0.1 mol) of **1** at 0 °C. The reaction mixture was allowed to warm to room temperature during which slow gas evolution ensued (mostly ethane containing a small amount of butane by mass spectroscopy). After 24 h gas evolution had ceased. An aliquot of the reaction mixture was removed and hydrolyzed in a gas evolution apparatus indicating ~75% consumption of the ethylmagnesium iodide. The reaction mixture was hydrolyzed by the cautious addition of cold water (30 mL). The organic layer was decanted, washed once with water and saturated NaCl, and dried ($MgSO_4$). The ether was removed by distillation and the residue was distilled (63–95 °C) giving 2.48 g of a colorless liquid and 3.95 g of distillation residue. Analysis of the distillate by GLPC on a 10-ft Carbowax 20M column showed the presence of **4** (26.6%), **3** (15.5%), and **2** (58.9–) which were isolated by preparative GLPC.

4: NMR ($CDCl_3$) δ 0.98 (distorted triplet, J = 6.5 Hz, 3 H), 1.17 (s, 6 H), and 1.47 (distorted quartet, J = 6.5 Hz, 2 H), and 2.07 (s, 1 H); MS M^+· 96.

3: NMR ($CDCl_3$) δ 1.11 (t, J = 6.7 Hz, 3 H), 1.14 (d, J = 6.3 Hz, 6 H) and 2.18 (s, J = 6.3 Hz, 1 H); MS M^+· 96.

2: NMR ($CDCl_3$) δ 0.98 (t, J = 7.3 Hz, 3 H), 1.67 (d, J = 2.7 Hz, 6 H), 1.97 (m, 2 H), and 5.02 (m, 1 H); MS M^+· 96.

GLPC analysis of the distillation residue showed the presence of allene **2,** dienes **5** and **6,** and **7** in a ratio of 0.26:0.45:1.00. **5, 6,** and **7** were isolated by preparative GLPC.

5: NMR ($CDCl_3$) δ 0.98 (t, J = 6.7, 3 H), 1.89 (m, 3 H), ~2.13 (m, 2 H), 4.86 (m, 1 H), 4.97 (m, 1 H), 5.46 (m, 1 H), and 5.84 (broadened doublet, J = 12.2 Hz, 1 H); MS M^+· 96.

6: NMR ($CDCl_3$) δ 1.02 (t, J = 7.2 Hz, 3 H), 1.82 (m, 3 H), 2.14 (dq, J = 7.2, 5.9 Hz, 2 H), 4.87 (m, 2 H), 5.74 (dt, J = 16.8, 5.9 Hz, 1 H), and 6.16 (d, J = 16.8 Hz, 1 H); MS M^+· 96.

7: NMR ($CDCl_3$) δ 1.72 (overlapping broad singlets, 6 H), 1.78 (broad singlet, 3 H), 5.49 (bdd, J = 14.8, 6.6 Hz, 1 H), 5.9 (dm's, J = 14.8, ~1.5 Hz, 1 H), and 6.23 (ddq, J = 14.8, 10.6, 1.5 Hz, 1 H); MS M^+· 96.

GLPC analysis of the crude reaction product immediately after hydrolysis indicated the presence of essentially only **3, 2,** and **4** in a 26:59:15 ratio. The product distribution remains the same regardless of whether the reaction mixture is quenched with water, 5% sulfuric acid, saturated ammonium chloride, or 5% sodium hydroxide.

Deuterolysis of Reaction of 1 with Ethylmagnesium Iodide. The reaction of **1** with ethylmagnesium iodide was carried out as described above except that hydrolysis was carried out by addition of 20 mL of deuterium oxide. **2, 3,** and **4** were isolated by preparative GLPC and their deuterium content was determined by mass spectrometry indicating the presence of 8.9% **4**-d_1, 48.8% **3**-d_1, and 47.0% **2**-d_1.

Reaction of 1-Ethynylcyclohexyl Chloride (8) with Methylmagnesium Iodide. To 0.1 mol of methylmagnesium iodide in 150 mL of ether was added 0.04 mol of 1-ethynylcyclohexyl chloride (**8**). A slow evolution of methane (identified by MS analysis) ensued. Aliquots were periodically removed, hydrolyzed, and analyzed by GLPC on a 10-ft Carbowax 20M column for unreacted **8.** After stirring for 19.5 h at 25 °C the reaction was complete. The reaction mixture was hydrolyzed by the addition of 25 mL of water. The organic layer was removed, washed twice with water, and dried ($MgSO_4$), and the solvent removed under reduced pressure giving a pale yellow liquid (85%). Analysis by GLPC showed the presence of **9–14** in a 100:15:46:1:12:9 ratio. The products were separated by preparative GLPC and characterized by IR, NMR, and MS.

9: NMR ($CDCl_3$) δ 1.56 (bm, 6 H), 1.59 (d, J = 7.0 Hz, 3 H). 2.11 (m, 4 H), 4.91 (quartet of quintets, J = 7.0, 2.2 Hz, 1 H); IR (cap film) 1920 cm^{-1} ($\nu_{C=C=C}$); MS calcd for C_9H_{14} 122.1096, obsd 122.1098.

10: NMR ($CDCl_3$) δ 1.56 (s, 3 H), 1.5–1.8 (bm, 11 H); MS calcd for 122.1096, obsd 122.1098.

11: NMR ($CDCl_3$) δ 1.19 (s, 3 H), 1.58 (bm, 10 H), and 2.07 (s, 1 H); IR (cap film) 3330 ($\nu_{\equiv C-H}$) and 2110 cm^{-1} ($\nu_{C\equiv C}$); MS calcd for 122.1096, obsd 122.1097.

12: NMR ($CDCl_3$) δ 1.62 (m, 4 H), 1.79 (d, J = 7.2 Hz, 3 H), 2.14 (m, 4 H), 5.32 (dq, J = 12.3, 7.2 Hz, 1 H), 5.65 (m, 1 H), and 5.78 (bd, J = 12.3 Hz, 1 H); MS M^+· 122.

13: NMR ($CDCl_3$) δ 1.62 (m, 4 H), 1.75 (d, J = 6.2 Hz, 3 H), 2.11 (m, 4 H), 5.56 (dq, J = 15.4, 6.2 Hz, 1 H), 5.61 (m, 1 H), and 6.05 (bd, J = 15.4 Hz, 1 H); MS M^+· 122.

14: NMR ($CDCl_3$) δ 1.62 (m, 6 H), 2.10 (m, 4 H), 4.8–5.2 (m, 3 H); MS M^+· 122.

Registry No.—**1,** 1111-97-3; **2,** 29212-09-7; **3,** 36566-80-0; **4,** 918-82-1; **5,** 65150-07-4; **6,** 20626-38-4; **7,** 32763-68-1; **8,** 6209-75-2; **9,** 20023-43-2; **10,** 18736-95-3; **11,** 28509-10-6; **12,** 5680-41-1; **13,** 54354-35-7; **14,** 5664-10-8.

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