can be considerably larger.[8] Second, as in the case of CD measurements,[32] it may well be that the recorded absorption maximum at room temperature does not correspond to the actual one of a B component. We have confirmed this hypothesis by measuring the absorption spectrum of compound **3** at liquid nitrogen temperature in EPA (five parts of ether, five parts of isopentane, and two parts of ethanol). As expected, the spectrum is resolved into three components with maxima occurring at *409*, 393, and 375 nm (as compared to *405* nm with shoulders at about 394 and 375 nm at room temperature). The S-shaped magnetic Cotton effect observed on the blue side of the Soret band can be tentatively assigned either to the B_1 components (mostly x and y polarized around 380 and 366 nm, respectively) or to other transitions. In particular, it is possible that the additional π orbitals arising from the external double bonds of the vinyl and carbonyl groups lie in the same energy range as the B states.

Finally, in view of the great dependence of MCD on the polarization of the absorption components (and therefore on the substituents on the framework), it is hoped that these studies may provide a useful basis for a new approach to the problem of the role of substituents on the spectroscopic properties of chlorophyll-like molecules. Our experimental results complement the important earlier work on porphyrins.[11a,16,19]

However, although the *relative* sign of B values seems to be well understood, it is not yet clear to us why the *absolute* sign (corresponding to the Q_0^y band, for example) is different here from that observed in porphyrins. Additional theoretical studies are therefore required, as well as new data about the polarization of various transitions.

Acknowledgments. We are grateful to Professor A. Moscowitz (University of Minnesota) and Dr. E. A. Dratz (University of California) for stimulating discussions. We are also indebted to Mr. Gordon H. Scott for technical assistance and Mr. Lonnie Scott for help in the plotting of the spectra.

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(32) C. Djerassi, H. Wolf, and E. Bunnenberg, *J. Am. Chem. Soc.*, **85**, 324 (1963).

The Coupling of 4-Chloro-4-methyl-2-pentyne and Similar Propargyl Chlorides with Organometallic Compounds[1]

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Contribution No. 1855 from the Department of Chemistry, University of California, Los Angeles, California 90024. *Received May 18, 1967*

Abstract: Coupling of 4-chloro-4-methyl-2-pentyne (I) and similar substituted propargyl chlorides with Grignard reagents yields mixtures of acetylenic and allenic hydrocarbons; some enyne is also produced by an elimination reaction. Conjugated dienes reported earlier[2] as major products have been shown to arise by a facile, acid-catalyzed rearrangement of the allenes. The proportion of allenic product is increased by decrease in Grignard reagent concentration or decrease in temperature. Very different products are obtained from the radical reaction which occurs in the presence of cobaltous chloride. Organolithium compounds give high proportions of allenic products in improved yields; this reaction is an excellent method for the synthesis of tetrasubstituted allenes. 4-Methyl-1,2,3-pentatriene was synthesized; methyllithium and methylmagnesium bromide do not undergo addition reactions with this cumulene.

Recently it was reported[2] that the coupling of 4-chloro-4-methyl-2-pentyne (I) with methylmagnesium bromide gave a 77% yield of a hydrocarbon mixture which contained 65–72% of 4,4-dimethyl-2-pentyne (II, R = CH_3; the normal coupling product), 7–24% of 2,4-dimethyl-1,3-pentadiene (III, R = CH_3), and 11–21% of 2-methyl-1-penten-3-yne (IV), the elimination product. Phenylmagnesium bromide gave a similar mixture which in addition to IV contained 4-methyl-4-phenyl-2-pentyne (II, R = C_6H_5, 56%), 4-methyl-2-phenyl-1,3-pentadiene (VI, 41%), and 2-methyl-4-phenyl-1,3-pentadiene (III, R = C_6H_5, 3%). Earlier reports, summarized in ref 2, were conflicting but Zakharova[3] reported that tetrasubstituted allenes were the principal products in these reactions. Her results were confirmed in a very recent communication.[4]

Formation of conjugated dienes[2] rather than allenes seemed particularly surprising and several suggestions were made to explain their formation. It was shown[2] that they did not arise by coupling of the Grignard reagents with rearranged chlorides (allenic or conjugated dienic). Experiments were carried out[2] to show that III was not formed by rearrangement of 2,4-dimethyl-2,3-pentadiene (V, R = CH_3; the expected allene) in the reaction mixture or on the glpc column used to analyze the reaction mixture. These experiments have now been found to be in error and the

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[1] This paper is taken from the Ph.D. thesis of P. Prempree, University of California, Los Angeles, Calif., 1966. A summary of the work was presented before the Organic Chemistry Division at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Abstract 66S. This research was supported by grants from the National Science Foundation and from the U. S. Army Research Office (Durham).

[2] T. L. Jacobs and R. A. Meyers, *J. Am. Chem. Soc.*, **86**, 5244 (1964).

[3] A. I. Zakharova, *Zh. Obshch. Khim.*, **17**, 1277 (1947); **19**, 1297 (1949); A. I. Zakharova and R. A. Sapozhnikova, *ibid.*, **22**, 1804 (1952); *Chem. Abstr.*, 42, 3722 (1948); 44, 100 (1950); 47, 6857 (1953).

[4] J. Bianchini and A. Guillemonat, *Compt. Rend.*, **C264**, 600 (1967).

Table I. Coupling Products of $(CH_3)_2CClC{\equiv}CCH_3$ (I)[a]

Organometallic reagent	Concn of reag, *M*	Products,[b] % $(CH_3)_2CRC{\equiv}CCH_3$ II	 $(CH_3)_2C{=}C{=}CRCH_3$ V	 $(CH_3)_2C{=}CH\underset{R}{C}{=}CH_2$ III	 $CH_3C{\equiv}C\underset{CH_3}{C}{=}CH_2$ IV	II/V[c]
CH_3MgBr[d]	~1.5	48.4 ± 2.0	40.2 ± 0.7	~1	10.4 ± 2.0	1.2
CH_3MgBr[e]	~4.0	71.1 ± 0.6	15.2 ± 0.2	2.4 ± 0.2	11.3 ± 0.1	4.0
CH_3MgBr[e]	2.3	68.3	23.1	...	8.6	3.0
CH_3MgBr[e]	1.15	31.0 ± 0.1	59.3 ± 0.9	...	9.7 ± 1.6	0.52
CH_3MgBr[e]	0.46	24.5 ± 0.2	63.4 ± 0.3	1.5 ± 0.1	10.6 ± 0.4	0.38
CH_3MgBr[f]	~1.5	25.6 ± 1.4	66.4 ± 2.5	3.3 ± 0.4	4.7 ± 2.0	0.37
CH_3MgCl	~2.0	61.1 ± 2.2	23.9 ± 1.0	2.3	12.7 ± 2.0	2.3
CH_3Li[g]	1.9	13.9 ± 2.4	83.5 ± 5.0	...	2.6 ± 0.1	0.16
C_2H_5MgBr[h]	~2.8	49.7	32.4	...	4.6	1.5
C_6H_5MgBr	1.2	45.8	49.1	5.1[i]	...	0.85[j]
C_6H_5MgBr[k]	~1.5	24.3 ± 0.9	~31.5[k]	~31.5[k]	12.7	0.32
C_6H_5Li[l]	~1.2	9.4	90.6	*m*	Trace	0.10

[a] The reactions were carried out in diethyl ether unless specified otherwise. I was added to the Grignard solution without cooling and refluxing occurred during much of the addition. Over-all product yields were 70–80%. [b] The figures are percentages and indicate the proportions of the products shown as determined by glpc. If more than one glpc determination was carried out for a given run (or runs under the same conditions) the deviation of the glpc determinations is indicated as a percentage variation from an average. R represents the group from the Grignard reagent. [c] III was believed to arise entirely by rearrangement of V on the glpc column; therefore the amount of III was added to V for calculation of II:V, the ratio of acetylenic product to allenic product. [d] Average of three runs in refluxing diethyl ether. [e] Single run. [f] Single run at 0°. [g] Average of three runs at 0°. Yields were 88–90% over-all. [h] Additional products: 2-methyl-2,3-pentadiene (2%) and 4-methyl-2-pentyne (11.3%). [i] Contained a small amount of $CH_2{=}C(CH_3)CH{=}C(CH_3)C_6H_5$ (VI). [j] Very nearly this same ratio of II:V was found by nmr on the mixture of products before glpc and no III was detected by nmr. This confirms the belief that III arises from V during glpc. [k] In tetrahydrofuran at room temperature; over-all yield 65%. On column B the enyne had the same retention time as the solvent; the enyne was determined separately on column A. V and III were not separated cleanly on column B, but their combined total was 63.0 ± 0.4; nmr indicated this fraction contained 50% V. The other conjugated diene did separate clearly and made up 12.7 ± 0.5% of the products. [l] Over-all yield 90%. [m] The percentage of the allenic isomer was calculated by combining the areas of the gas chromatogram peaks of products which arose from rearrangement of the allene; separate peak areas were not determined in this instance.

allene shown to be a product of the reaction. In earlier work[2] with phenylmagnesium bromide the allenic product, 2-methyl-4-phenyl-2,3-pentadiene (V, R = C_6H_5), was not available for direct examination; it has now been shown to undergo rearrangement to the conjugated dienes VI and III (R = C_6H_5) thermally or on glpc columns even more readily than does V (R = CH_3).

It was found that the rearrangement of tetramethylallene (V, R = CH_3) to 2,4-dimethyl-1,3-pentadiene (III, R = CH_3) is catalyzed by acids. The allene could be separated by glpc from accompanying isomers without rearrangement if column temperatures were kept low and a suitable packing material chosen; rearrangement occurred at higher temperatures on all of the columns tried. The rearrangement will be discussed in a separate paper.

A more careful investigation of the reaction between methylmagnesium bromide and I was carried out; the concentration of the Grignard reagent was varied, and the effect of variation of other factors was examined briefly. The products from reactions of I with phenyl- and ethylmagnesium bromide were also determined. Results are summarized in Table I.

The ratio of acetylenic product II to allenic product V depended on the concentration of the Grignard reagent; higher yields of II were obtained with higher reagent concentrations. More carefully controlled experiments on this concentration effect are discussed below and summarized in Table IV. Changes in the concentration of the Grignard reagent appear to have little effect on the amount of IV produced, but when I was added to large excesses of the reagent less IV was produced (again with little dependence on the reagent concentration). More precise determinations of IV under more carefully controlled conditions are needed before this effect can be discussed. The yield of allene was improved when the reaction temperature was kept at 0°. Methylmagnesium chloride gave about the same II/V ratio as the bromide. The effect of changing from diethyl ether to tetrahydrofuran as solvent was not examined with methylmagnesium bromide because it was difficult to separate products from solvent, but with phenylmagnesium bromide, this change decreased the II/V ratio; the over-all yield of coupling products also decreased.

The reactions of methylmagnesium bromide with several other trisubstituted propargyl chlorides were examined under conditions employed with I; the results are summarized in Table II. The ratio of acetylenic isomer to allenic isomer increases as more branched groups are attached to the γ-carbon of the starting acetylenic chloride, but a comparison of methyl with ethyl in that position is out of line and two ethyl groups on the α-carbon decrease the acetylene/allene ratio by very little; the elimination reaction is much more important with the latter compound. The differences are very small in terms of free energies and a simple steric explanation appears inadequate.

The lowest ratio of acetylenic to allenic isomer (II/V) was obtained when I was coupled with methyl- and phenyllithium. The over-all yield of coupling products was also improved from 70–80% obtained with Grignard reagents to 88–90%; the yield of elimination product was substantially lower. It is possible to isolate by distillation excellent yields of the mixture of II and V in the proportions shown in Table I, but distillation was not a practical method of separating II from V. Pure tetramethylallene was obtained by glpc separation, but pure phenyltrimethylallene was

Table II. Products from Reaction of Substituted Propargyl Chlorides with Methylmagnesium Bromide in Diethyl Ether[a]

Propargyl chloride	Molar concn of CH_3MgBr[b]	Products,[c] % Acetylenic isomer	Products,[c] % Allenic isomer	Products,[c] % Enyne	Acetylene/ allene
$(CH_3)_2CClC{\equiv}CC_2H_5$ (X)[d]	1.23 ± 0.07	37.7 ± 0.2	58.8 ± 0.1	3.5 ± 0.3	0.64
	1.3 ± 0.1	37.8 ± 0.1	56.6 ± 0.5	5.6 ± 0.5	0.67
$(CH_3)_2CClC{\equiv}CCH(CH_3)_2$ (XI)	1.3 ± 0.1	46.1 ± 0.4	44.5 ± 0.4	10.4 ± 0.2	1.03
$(CH_3)_2CClC{\equiv}CC(CH_3)_3$ (XII)	1.3 ± 0.1	72.4 ± 1.0	17.0 ± 0.6	10.6 ± 0.3	4.26
$(C_2H_5)_2CClC{\equiv}CCH_3$ (XIII)[e]	1.4 ± 0.01	24.5 ± 0.5	44.6 ± 0.5	30.9 ± 0.9	0.55
$(CH_3)_2CClC{\equiv}CCH_3$ (I)	1.15 ± 0.05	31.0 ± 0.1	59.3 ± 0.9	9.7 ± 1.6	0.52

[a] The substituted propargyl chloride was added to the Grignard reagent without cooling and refluxing occurred during much of the addition. Over-all yields of products were 70–80% in all cases. The reaction was allowed to continue for ~24 hr unless otherwise specified. [b] Concentrations were determined by titration; two determinations were made for each concentration. [c] The figures are percentages and represent proportions of the products shown as determined by glpc (variation between duplicate glpc determinations indicated). [d] Reaction time 120 hr. [e] Reaction time 48 hr.

not isolated successfully because it rearranged at least partially to conjugated dienes on all columns tried. Both of these compounds appear to be liquids at room temperature; successful crystallization was not accomplished. Methyllithium was also coupled with chlorides X–XIII to give the products shown in Table III. Again it was observed that the acetylene/allene ratio increased as the group attached to the acetylenic carbon became more branched. These experiments suggest that the reaction of organolithium compounds with trisubstituted propargyl halides is the best method available for synthesis of tetrasubstituted allenes in which at least some of the substituents are alkyl and in which the groups at one end of the allenyl system are different from the groups at the other end. Symmetrical allenes of the type RR′C=C=CRR′ may be easier to prepare from keto ketene dimers.[2,5]

Table III. Products from Reaction of Substituted Propargyl Chlorides with Methyllithium in Ether[a]

Propargyl chloride	Yield, %	Allenic	Acetylenic
X	88	89	11
XI	84	83	17
XII	*b*	35	65
XIII	73	88	5.3[c]

[a] See Table I for the reaction of CH_3Li and C_6H_5Li with $(CH_3)_2CClC{\equiv}CCH_3$. [b] Yield of these products low. See Experimental Section. [c] The enyne 3-ethyl-2-hexen-4-yne was 6.7% of the product.

The change in acetylene/allene ratio with change in Grignard reagent concentration indicates that more than one mechanism is operating in these coupling reactions. More acetylenic isomer is formed at higher Grignard reagent concentrations which shows that the reaction of higher kinetic order in the reagent produces more acetylenic compound. The simplest possibility would be that the acetylene is produced by one mechanism and the allene by another. To investigate this the coupling of I was carried out with large excesses of varying concentrations of methylmagnesium bromide so that the change in Grignard reagent concentration was negligible. Results are summarized in Table IV and a plot of acetylene/allene ratio against initial Grignard reagent concentration is shown in Figure 1. The linear relationship and the intercept of 0.04 on the acetylene/allene axis at zero Grignard reagent concentration show that the lower order reaction produces almost exclusively the allenic compound and that the reaction forming the acetylenic isomer is of higher order by one in methylmagnesium bromide. Moreover, the linearity of the plot indicates that the reaction of higher order produces only the acetylenic isomer within the experimental error.

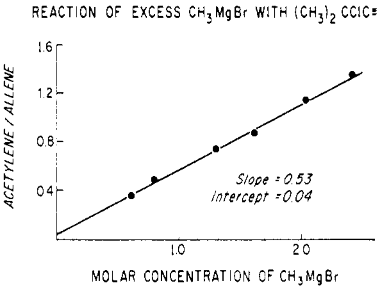

Figure 1.

Table IV. The Coupling of $(CH_3)_2CClC{\equiv}CCH_3$ (I) with Large Excess of CH_3MgBr at Various Concentrations

Concn of CH_3MgBr, *M*	CH_3MgBr/I	Acetylene/ allene[a]
0.61	10.5	0.36
0.80	14	0.49
1.30	22	0.74
1.62	17	0.87
2.04	22	1.14
2.42	26	1.35

[a] The enyne was also detected in each run in 5 ± 3% of the total yield.

A possible formulation for these reactions would involve simple SN1 and SN2 mechanisms. This appears improbable because the SN1 mechanism would have to give almost exclusively allenic product whereas most propargyl carbonium ions, $—C{\equiv}C—C^{+}< \leftrightarrow —C^{+}{=}C{=}C<$, react more rapidly at the propargyl position. Moreover, it seems rather unlikely that an SN2 process involving attack at a tertiary carbon would be fast enough to account for formation of the acetylenic isomer. Chart I gives an alternative formulation

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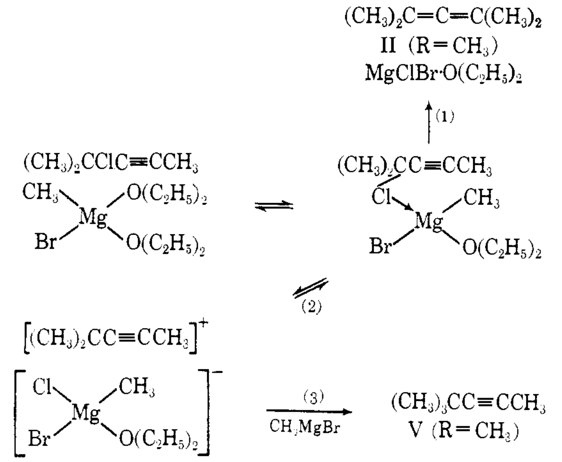
(5) J. C. Martin, private communication, 1962; Technical Data Report, Eastman Chemical Products, Inc., Kingsport, Tenn., Sept 1961. Some of the dimers have been available from Eastman Chemical Products; see, *e.g.*, *Chem. Eng. News*, 43, 11 (July 26, 1965).

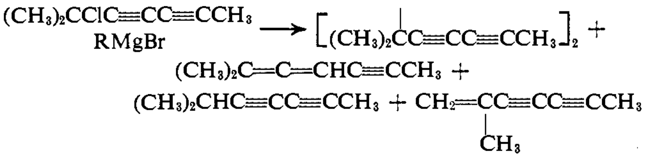
Chart I



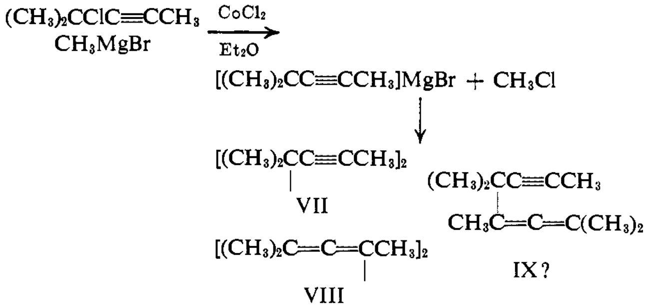
which we believe more reasonable. It involves preliminary formation of a complex which can either react by an internal mechanism to yield the allenic product II as shown in (1) or with a second molecule of Grignard reagent to form the acetylenic isomer V. This second reaction might be a simple SN2 attack on the complex, but could also involve the reversible ionization shown in (2) and reaction of the ion pair with methylmagnesium bromide to form V (reaction 3). One might also have both II and V formed from a properly oriented ion pair (II by internal collapse and V by reaction with external reagent). It seems to us surprising that the picture is as simple as it appears and that complications are not introduced by change in the state of aggregation or the composition of the reacting Grignard reagent species as a result of dilution.

The experiments described below indicate that these coupling reactions do not occur by a radical mechanism because different products are obtained in the radical reaction.

Skattebøl[6] reported that the diacetylenic chloride 6-chloro-6-methyl-2,4-heptadiyne reacted with methyl- or ethylmagnesium bromide in diethyl ether to give the products shown below along with ethane and methane or ethane and ethylene, respectively.



These products were explained by a functional exchange–elimination mechanism involving radicals. It seemed surprising that products which would be expected from such a radical mechanism were not encountered with I which appears so similar to Skattebøl's starting chloride, and an attempt was therefore made to initiate such a radical reaction with I by addition of cobaltous chloride. It was observed that the products from the catalyzed reaction, obtained in 74% yield, were very different from those obtained normally; less than 5% of the products usually found were obtained and the main one of these was the elimination product IV. The principal products were C$_{12}$ hydrocarbons, believed to have structures VII and VIII; glpc indicated that these were present in a ratio of about 4:1.



VII was easily isolated as a pure, crystalline solid which had the correct composition and nmr spectrum. VIII was not isolated as a pure compound and its presence was merely inferred from nmr spectra. It is possible that the compound of unsymmetrical structure IX was also present in the liquid mixture. Methyl chloride was isolated, which makes more probable the exchange postulated as the first step.

A puzzling reaction course which appears to indicate that products like those encountered in the presence of cobaltous chloride may not always result from a radical mechanism was encountered in the reaction of methyllithium with 2-chloro-2,5,5-trimethyl-3-hexyne. The principal product of the reaction was a solid with composition and nmr spectrum corresponding to 2,2,5,5,6,6,9,9-octamethyl-3,7-decadiyne, the symmetrical coupling product from the chloride. Further study is needed before this reaction can be discussed.

Before it was established that the conjugated dienes III obtained earlier[2] as the products of normal coupling could arise by rearrangement of V, the possibility was considered that I could undergo elimination to form 4-methyl-1,2,3-pentatriene which might react with Grignard reagents to yield III. Early in the present work this cumulene was synthesized from 3-methyl-1,2-butadiene by reaction with dibromocarbene to yield 1,1-dibromo-2,2-dimethyl-3-methylenecyclopropane which was debrominated with methyllithium. This synthetic method for cumulenes was devised by Skattebøl[7] who applied it to the synthesis of 2,5-dimethyl-2,3,4-hexatriene.

4-Methyl-1,2,3-pentatriene was moderately stable in ether solution at 0° but polymerized rapidly as soon as the solvent was removed. It did not react with excess methyllithium at 0° nor with methylmagnesium bromide at the same temperature.

Experimental Section

Infrared spectra were obtained on Perkin-Elmer Model 421 and 137 spectrophotometers (neat or 10% in carbon tetrachloride solution). Nuclear magnetic resonance spectra were obtained with a Varian Associates analytical NMR Model A-60 (10% in carbon tetrachloride with tetramethylsilane internal standard). Analytical and spectral data are given in Table V.

General Procedure. The Grignard reagent was prepared in the usual fashion from magnesium turnings in ether under nitrogen in a flask which was flame dried under nitrogen flow. The magnesium used was the same as in the earlier paper.[2] The reagent was transferred through a double layer of glass wool under nitrogen pressure to a three-necked flask which was previously dried and kept under nitrogen. Its concentration was determined by the usual acid–base titration (phenolphthalein end point).[8] The Grignard reagent was magnetically stirred as the substituted propargyl chloride (*e.g.*, I)

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[6] L. Skattebøl, *Tetrahedron*, **21**, 1357 (1965).

[7] L. Skattebøl, *Tetrahedron Letters*, 2175 (1965).

[8] M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-Metallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, pp 92–95.

Table V. Analytical Data[a]

Compound	Nmr[b]		Infrared, cm^{-1}	Calcd, %		Found, %	
	Peak positions, τ	Peak ratios		C	H	C	H
$(CH_3)_2C{=}C{=}C(CH_3)_2$	8.4 (s)	...	...	87.42	12.58	87.58	12.59
$(CH_3)_2C{=}C{=}\underset{\underset{C_2H_5}{\vert}}{C}{-}CH_3$	8.38 (s)	9	1960 (weak)	87.19	12.81	87.03	12.82
	7.94–8.31 (q)	2					
	J = 7.5 cps						
	8.93–9.19 (t)	3					
	J = 7.5 cps						
$(CH_3)_2C{=}C{=}\underset{\underset{CH(CH_3)_2}{\vert}}{C}CH_3$	8.40 (s) 8.38 (s)	9	1960 (weak)				
	7.88–8.30 (m)	1					
	8.98–9.10 (d)	6					
	J = 7.0 cps						
$(CH_3)_2C{=}C{=}\underset{\underset{C(CH_3)_3}{\vert}}{C}{-}CH_3$	8.38 (s)	2	1960 (weak)	86.88	13.12	86.92	13.15
	8.40 (s)	1					
	9.0 (s)	3					
$(CH_3)_2C{=}C{=}\underset{\underset{C_6H_5}{\vert}}{C}{-}CH_3$	2.77 (m)	...					
	7.98 (s)	1	1950 (weak)	91.08	8.92	91.23	8.86
	8.24 (s)	2					
$(C_2H_5)_2C{=}C{=}C(CH_3)_2$	8.3 (s)	3					
	9.03 (t)	3	1950 (weak)	87.09	12.91	87.23	13.00
	7.88–8.26 (q)	2					
	J = 7.5 cps						
$(CH_3)_2\underset{\underset{C_2H_5}{\vert}}{C}{-}C{\equiv}C{-}CH_3$	8.87 (m)			87.19	12.81	86.95	12.81
	8.25 (s)						
$(CH_3)_2\underset{\underset{C_6H_5}{\vert}}{C}{-}C{\equiv}C{-}CH_3$	8.47 (s)	2					
	8.24 (s)	1					
	2.77 (m)						
$(CH_3)_3CC{\equiv}CCH_2CH_3$	8.83 (s)	9					
	7.71–8.09 (q)	2					
	8.79–9.03 (t)	3					
$(CH_3)_3CC{\equiv}CCH(CH_3)_2$	8.84 (s)	9					
	7.3–7.9 (m)	1					
	8.84–8.96 (d)	6					
	J = 7.0 cps						
$(CH_3)_3CC{\equiv}C{-}C(CH_3)_3$	8.84 (s)	...	...	86.88	13.12	87.06	12.91
$(C_2H_5)_2\underset{\underset{CH_3}{\vert}}{C}{-}C{\equiv}C{-}CH_3$	8.14 (s)	3	...	87.02	12.98	86.99	13.06
	8.9 (s)		...				
	8.3–9.2 (m)	13[c]					
$CH_3\underset{\underset{H}{\vert}}{C}{=}\underset{\underset{C_2H_5}{\vert}}{C}{-}C{\equiv}C{-}CH_3$	4.07–4.5 (q)	1					
	J = 7.0 cps						
	7.68–8.14 (m)	2		88.82	11.18	88.81	11.04
	J = 7.5 cps						
	7.96 (s)	3	2220 (weak)				
	8.14–8.25 (d)	3					
	J = 7.0 cps						
	8.93 (t)	3					
	J = 7.5 cps						
$\begin{array}{l}(CH_3)_2C{-}C{\equiv}C{-}CH_3\\ \qquad\ \ \vert\\ (CH_3)_2C{-}C{\equiv}C{-}CH_3\end{array}$	8.22 (s)	1	...	88.82	11.18	88.67	11.35
	8.78 (s)	2	...				
$\begin{array}{l}(CH_3)_2C{=}C{=}C{-}CH_3\\ \qquad\qquad\quad\ \vert\\ (CH_3)_2C{=}C{=}C{-}CH_3\end{array}$	8.25 (s)	1	...	...		...	
	8.32 (s)	2	...	...		...	
$[(CH_3)_2\underset{\vert}{C}C{\equiv}CC(CH_3)_3]_2$	8.80 (s)	2		87.80	12.20	87.84	12.38
	8.83 (s)	3					
$(CH_3)_2C{=}C{=}C{=}CH_2$	5.2 (m)	1	2070 (strong)				
	8.12 (t)	3		...		...	
	J = 1.5 cps						
$(CH_3)_2CClC{\equiv}CC_2H_5$	8.22 (s)	6	2270				
	7.61–7.98 (q)	2					
	8.73–8.90 (t)	3					
	J = 7.5 cps						
$(CH_3)_2CClC{\equiv}CCH(CH_3)_2$	8.21 (s)	6	2240				
	7.16–7.75 (m)	1					
	8.76–8.88 (d)	6					
	J = 7.0 cps						
$(CH_3)_2CClC{\equiv}CC(CH_3)_3$	8.22 (s)	2	2240	68.13	9.53	68.34	9.71
	8.80 (s)	3					
$(C_2H_5)_2CClC{\equiv}C{-}CH_3$	8.13 (m)	7[d]	2250	66.43	9.06	66.31	9.24
	8.9 (t)	6					

[a] Also see ref 2. [b] s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. [c] Combination of 13 protons, all from the left-hand substituents. [d] Combination of seven protons: three protons from the right-hand methyl group and four protons from two methylene groups.

was added. The reaction became slightly warm. Stirring was continued for varying time after addition was complete. The reaction mixture was decomposed by slow addition with stirring of iced ammonium chloride solution. The organic layer was separated and dried over Drierite; it was then analyzed by glpc. The ether was next removed by distillation, and the residual liquid was investigated. The yield was calculated from the weight of residual liquid.

Products were separated into components by glpc and collected. Each component was identified by nmr and infrared spectroscopy; spectra were compared with those of authentic samples.

Coupling of I with Methylmagnesium Bromide. The Grignard reagent was prepared from 6.5 g of magnesium turnings in various amounts of ether to obtain the desired concentrations. I (15.0 g, 0.129 mole), prepared as described earlier,[2] was added dropwise with stirring during 30–40 min. Stirring was continued overnight. Glpc was performed on a 10.5-ft column of 30% di-*n*-decyl phthalate on 80–100 mesh, acid-washed Firebrick (column A); the column temperature was kept between 60 and 65°. At these temperatures, very little rearrangement of V to III occurred as shown by the data in Table I. At higher temperatures, far more rearrangement occurred.

Coupling of I with Methyllithium.[9] I (30.0 g, 0.26 mole) was added dropwise with stirring during 45 min to 200 ml of 1.92 *M* methyllithium in ether. The flask was kept in an ice bath. Stirring was continued overnight. Glpc was performed on column A.

Coupling of I with Ethylmagnesium Bromide. I (65 g, 0.56 mole) was added dropwise with stirring during 1.5 hr to ethylmagnesium bromide prepared from 21.9 g (0.9 g-atom) of magnesium and 98.1 g (0.9 mole) of ethyl bromide, and the reaction mixture was stirred overnight. The yield of crude product was 73% calculated as C_8H_{14}. Glpc on column A gave the products shown in Table I. 2-Methyl-2,3-pentadiene and 4-methyl-2-pentyne were not completely separated on column A and no conclusive evidence for their structures was obtained, although both nmr and infrared spectra agreed with the suggested structures. These products could arise by an exchange mechanism which would form the Grignard reagent of I; if this survived further reaction it would yield these C_6H_{10} products on hydrolysis. Further work is needed before it is worthwhile to comment further.

Coupling of I with Phenylmagnesium Bromide. I (13.0 g, 0.11 mole) was added dropwise with stirring to 1.2 *M* phenylmagnesium bromide prepared from 7.0 g of magnesium turnings in 190 ml of ether and 45 g of freshly distilled bromobenzene. Stirring was continued for 3 days. Glpc was performed on a 6-ft column of 30% Apiezon L on 80–100 mesh Chromosorb W (column B) at column temperatures between 120 and 130°. Before glpc the nmr spectrum of the residual liquid after ether was removed revealed the absence of vinyl protons. Trimethylphenylallene rearranged to the conjugated dienes on this column. The amount of allene formed in the coupling reaction was calculated from the combination of peaks corresponding to the allene itself and the conjugated dienes. Area ratios corresponded to an acetylene/allene ratio of 0.85. The same procedure was applied for the coupling in tetrahydrofuran.

Coupling of I with Phenyllithium. Phenyllithium was prepared by the method of Jones and Gilman[10] from 70 g (0.45 mole) of freshly distilled bromobenzene in 100 ml of diethyl ether and 6.25 g (0.9 mole) of lithium wire in 250 ml of ether under argon atmosphere. It was transferred under argon pressure to a second dried flask. I (25 g, 0.216 mole) was added dropwise with stirring during 50 min. Stirring was continued for 2 hr. Glpc was performed on column B.

Coupling of I with Methylmagnesium Bromide in the Presence of Anhydrous Cobaltous Chloride. The Grignard reagent (1.5 *M*) was prepared from 6.5 g of magnesium turnings in 200 ml of ether. To this solution 2.0 g of anhydrous cobaltous chloride was added slowly with cooling and stirring. I (12 g) was added dropwise with stirring during 20 min. A cold trap was also set up to collect the low-boiling component. Stirring was continued overnight; before work-up the reaction mixture was refluxed for 15 min to expel low-boiling components into the cold trap. Traces of normal coupling products were observed on column A. The nmr spectrum of the residual liquid after ether was removed revealed the presence of VII and VIII in the ratio of about 4:1. A solid precipitated when the residue was cooled; it was filtered and recrystallized from petroleum ether (bp 20–40°) to give pure VII, mp 120–121°. Pure VIII could not be isolated from the crude reaction product nor from residual material after crystalline VII had been removed; attempts to distil these substances at reduced pressure gave extensive isomerization and polymerization. Various attempts at isolation by glpc failed. The nmr values reported for VIII in Table III were obtained from mixtures. Glpc of the liquid collected in the cold trap on a 20-ft version of column A and on a 10-ft column packed with 30% dimethylsulfolane on C-22[11] revealed the presence of methyl chloride (retention time the same as that of an authentic sample.)

Coupling of Other Substituted Propargyl Chlorides with Methylmagnesium Bromide. The chlorides listed in Table II were prepared from the corresponding alcohols and concentrated hydrochloric acid by Hennion's method[12] in 60–80% yields; all were stable and remained colorless when stored over anhydrous potassium carbonate at −20°. All had the expected acetylenic infrared band near 2240 cm^{-1} and displayed the expected nmr spectra (Table V). The starting alcohols were prepared from ketones and acetylenic Grignard reagents by the method of Hurd and Cohen[13] in 64–82% yields. Chlorides X, XI, and XII as well as the corresponding alcohols have been reported in the literature.[14,15] 3-Ethyl-4-hexyn-3-ol was prepared from 3-pentanone and the Grignard reagent from propyne in 65% yield, bp 63° (5 mm). It was converted to 4-chloro-4-ethyl-2-hexyne (XIII) in 66% yield, bp 54° (3 mm).

Table II gives the results of the Grignard reactions. The products from X were separated on an 8-ft glpc column packed with 25% didecyl phthalate on C-22,[11] from XI on a 10-ft column packed with 10% squalane on a 60–80 mesh Chromosorb W, from XII on a 10-ft column of 5% didecyl phthalate on Fluoropak, and from XIII on an 8-ft column of 25% Carbowax 20-M[16] on 80–100 mesh acid-washed Firebrick. The products from XII rearranged extensively when the support material for the glpc column was Firebrick.

Coupling of Other Substituted Propargyl Chlorides with Methyllithium. Chlorides X and XI were added to a 50% excess of 1.25 *M* methyllithium under the conditions used for I; chloride XIII was treated similarly but an equivalent amount of methyllithium was used. Table III details the results.

When 24 g (0.15 mole) of XII was added dropwise with cooling to 110 ml of 1.25 *M* methyllithium in ether and the reaction mixture treated as for I, removal of solvent left 17.5 g of a residual liquid which deposited 12 g of a solid when cooled. The solid was isolated and recrystallized from petroleum ether to give white crystals, mp 100–102°. This compound is believed to be 2,2,5,5,6,6,9,9-octamethyl-3,7-decadiyne on the basis of analysis and nmr spectrum (Table V).

Preparation of 4-Methyl-1,2,3-pentatriene and Its Reaction with Methyllithium and Methylmagnesium Bromide. Methyllithium (65 ml, 1.9 *M*) was added dropwise with stirring to 1,1-dibromo-2,2-dimethyl-3-methylenecyclopropane[17] (25 g) in 25 ml of ether in a Dry Ice–acetone bath during 1 hr. The system was kept under argon atmosphere. Stirring was continued for another hour at −78°. Water was added, and the ether layer separated and dried over anhydrous sodium sulfate. Only one peak of retention time longer than that of ether was observed on column A. Upon standing at room temperature a white solid was gradually formed. Only polymeric material was obtained when ether was removed by heating.

The ether solution of 4-methyl-1,2,3-pentatriene was added to both methyllithium and methylmagnesium bromide at 0°. No addition products were detected. Only white polymeric material was obtained and some of the triene was recovered.

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(9) Methyllithium was purchased from Lithium Corporation of America.

(10) R. G. Jones and H. Gilman, *Org. Reactions*, 6, 353 (1951).

(11) C-22 is a calcinated diatomaceous silica similar to Chromosorb P.

(12) G. F. Hennion, J. J. Sheehan, and D. E. Maloney, *J. Am. Chem. Soc.*, 72, 3542 (1950).

(13) C. D. Hurd and F. L. Cohen, *ibid.*, **53**, 1068 (1931).

(14) A. Burawoy and E. Spinner, *J. Chem. Soc.*, 3752 (1954).

(15) G. F. Hennion and T. F. Banigan, Jr., *J. Am. Chem. Soc.*, 68, 1202 (1946).

(16) Carbowax 20-M is a polyethylene glycol obtained from Union Carbide Chemicals Co.

(17) W. J. Ball and S. R. Landor, *Proc. Chem. Soc.*, 246 (1961).