mole^{-1}. In anisole the n-bonding ability of oxygen is decreased and π-complex-forming ability of the phenyl ring is enhanced. By comparison with the analogous phenol complexes it is predicted that the n- and π-complex equilibrium constants of anisole with I_2 are the same order of magnitude. Appreciable concentrations of both π- and n-bonded complexes are thus almost certainly present in solutions of I_2 with anisole.

The Coupling of 4-Chloro-4-methyl-2-pentyne with Alkyl and Phenyl Grignard Reagents

By Thomas L. Jacobs and Robert A. Meyers[1]

4-Chloro-4-methyl-2-pentyne reacted with methylmagnesium bromide to yield 4,4-dimethyl-2-pentyne (65–72%), 2-methyl-1-penten-3-yne (11–21%), and 2,4-dimethyl-1,3-pentadiene (24–7%) contrary to an earlier report that an allene was the main product. Similarly, phenylmagnesium bromide gave 4-methyl-4-phenyl-2-pentyne, 2-methyl-1-penten-3-yne, 4-methyl-2-phenyl-1,3-pentadiene, and 2-methyl-4-phenyl-1,3-pentadiene, rather than 2-methyl-4-phenyl-2,3-pentadiene. However, isopropylmagnesium bromide gave 2,4,5-trimethyl-2,3-hexadiene and 4,4,5-trimethyl-2-hexyne. The mechanism of formation of the rearranged products is discussed.

The coupling of propargyl halides RC≡CCClR'R'' with Grignard reagents has been used as a synthetic method for acetylenic hydrocarbons RC≡CCR'R''R''' on several occasions.[2-4] However, a hydrocarbon of unknown structure was reported as a by-product from reaction of 2-chloro-2,5,5-trimethyl-3-hexyne with methylmagnesium bromide[3] and the hydrocarbon obtained from reaction of 2-chloro-2-methyl-3-octyne with octylmagnesium bromide was shown by g.l.c. to be a mixture of three products even though the composition was that expected for 7,7-dimethyl-5-pentadecyne and the boiling range was narrow.[5] It has also been reported[6] that 4-chloro-4-methyl-2-pentyne yielded 2,4-dimethyl-2,3-pentadiene as the principal product (50%) by reaction with methylmagnesium bromide; only a small amount of 4,4-dimethyl-2-pentyne or 4,4-dimethyl-1,2-butadiene was observed. With phenylmagnesium bromide the only product isolated was 2-methyl-4-phenyl-2,3-pentadiene (40%). Similar results were reported for 4-chloro-4-methyl-2-hexyne[7] and 4-chloro-4,5,5-trimethyl-2-hexyne.[8] Reports of coupling of Grignard reagents with less highly substituted propargyl halides are similarly conflicting, although with certain of these recent evidence for allenic products appears to be more certain.[9-12]

A reinvestigation of the coupling reaction was undertaken in order to determine the synthetic value of the reaction and to study the acetylene–allene rearrangement which is involved in formation of allenic products. It was of special interest to examine such products because aliphatic tetrasubstituted allenes are difficult to prepare. The work reported in the present paper involves only 4-chloro-4-methyl-2-pentyne (I), which was chosen because it is the simplest trisubstituted propargyl chloride and because allenes were reported as principal products.

Results and Discussion

Coupling reactions were carried out with excess methyl-, phenyl- and isopropylmagnesium bromide (1.4 to 2.4 M) in ether at room temperature. Preliminary experiments were also carried out with tert-butylmagnesium bromide. With methyl and phenyl Grignard reagents no allenic hydrocarbons were detected among the products. In addition to the normal acetylenic coupling products the reactions gave conjugated dienes and the enyne which would result from elimination of hydrogen chloride from 4-chloro-4-methyl-2-pentyne. However, isopropylmagnesium bromide gave no conjugated diene or enyne, but 4,4,5-trimethyl-2-hexyne (X) and 2,4,5-trimethyl-2,3-hexadiene (XI) were obtained in the ratio 64:36. Products were separated by g.l.c. and identified by n.m.r. and infrared spectra. Raman spectra were also obtained for the acetylenic hydrocarbons and ultraviolet spectra for the conjugated dienes. The products are summaried in Table I and the spectral properties in Table II or in the Experimental.

More extended investigation was made of the reaction with methylmagnesium bromide because it was easier to prepare authentic samples of the products and of the expected allene V when methyl was the substituent introduced (see Experimental). Direct comparison by g.l.c. and of spectral properties as well as other physical properties showed that II, III, and IV were the products; V was absent although it was readily detected in the presence of the other hydrocarbons. Compound V was added to a coupling run and shown to survive without rearrangement. It was also found that II was not rearranged to V or III and

(1) This paper is taken from the Ph.D. Thesis of Robert A. Meyers, U.C.L.A., 1963. The research was supported by a grant from the U. S. Army Research Office (Durham).

(2) K. N. Campbell and L. T. Eby, J. Am. Chem. Soc., **62**, 1798 (1940).

(3) G. F. Hennion and T. F. Banigan, Jr., ibid., **68**, 1202 (1946).

(4) H. Heel and W. Zeil, Z. Elektrochem., **64**, 962 (1960).

(5) G. Desgrandchamps, A. Deluzarche, and A. Maillard, Bull. soc. chim. France, 264 (1961).

(6) A. I. Zakharova, Zh. Obshch. Khim., **17**, 1277 (1947); Chem. Abstr., **42**, 3722 (1948).

(7) A. I. Zakharova, Zh. Obshch. Khim., **19**, 1297 (1949); Chem. Abstr., **44**, 1001 (1950).

(8) A. I. Zakharova and R. A. Sapozhnikova, Zh. Obshch Khim., **22**, 1804 (1952); Chem. Abstr., **47**, 6857 (1953).

(9) T. Y. Lai, Bull. soc. chim. France, [4] **53**, 1537 (1933).

(10) C. Prévost, M. Gaudemar, and J. Honigberg, Compt. rend., **230**, 1186 (1950).

(11) M. Gaudemar, ibid., **232**, 1945 (1951); Ann. chim., [13] **1**, 161 (1956).

(12) A. A. Petrov and K. A. Molodova, Zh. Obshch. Khim., **32**, 3510 (1962).

TABLE I

COUPLING PRODUCTS OF $(CH_3)_2CClC\equiv CCH_3$ (I)

Grignard reagent	Yield, %	Products[a]		
CH_3MgBr	77	$(CH_3)_3CC\equiv CCH_3$	$CH_3C=CHC=CH_2$ (with CH_3, CH_3)	$CH_2=CC\equiv CCH_3$ (with CH_3)
1^b		II, 65%	III, 24%	IV, 11%
2^b		72%	7%	21%
$C_6H_5MgBr^c$	77	$(CH_3)_2CC\equiv CCH_3$ (with C_6H_5)	$CH_3C=CHC=CH_2$ (with CH_3, C_6H_5)	$CH_2=CCH=CCH_3$ (with CH_3, C_6H_5)
		VI, 56%	VII, 41%	VIII, 3%
i-PrMgBr	70	$(CH_3)_2CC\equiv CCH_3$ (with $CH(CH_3)_2$)	$CH_3C=C=CCH(CH_3)_2$ (with CH_3, CH_3)	
		X, 64–65%[d]	XI, 36–35%[d]	

[a] Percentages indicate the proportions of the products shown. [b] Run 1, 2.4 M; run 2, 1.6 M and 2,4-dimethyl-2,3-pentadiene added. [c] A significant amount of 2-methyl-1-penten-3-yne was also formed. [d] Two runs.
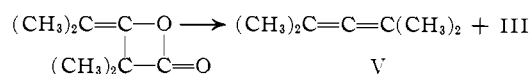
TABLE II

SPECTRAL DATA

	Z	Infrared,[a] cm.$^{-1}$	Nuclear magnetic resonance[b]			
			*	+	Z	Vinyl H's
			Acetylenes			
$(CH_3)_2CZC\equiv CCH_3$ (* on $(CH_3)_2C$, + on CH_3)	OH	2240	8.84	8.29	7.14	
	Cl	2240	8.22[f]	8.14		
	CH_3	c	8.86	8.31		
	C_6H_5	c	8.47	8.14	2.67 (m)	
	$(CH_3)_2CH^e$	c; 1375,[d] 1365[d]	8.93	8.28	9.09 (d) $J = 6$ c.p.s.	
$H_2C=C—C\equiv CCH_3$ (with CH_3; * on CH_3, + on CCH_3)		3090, 2235, 1612	8.18 $J = 1$ c.p.s.	8.08	5.02	
			Allenes			
$(CH_3)_2C=C=C(CH_3)_2$ (* on one end)			8.40			
$(CH_3)_2C=C=CCH_3^e$ (with $HC(CH_3)_2$; * on $(CH_3)_2C$, + on $HC(CH_3)_2$)		1962, 1368,[d] 1360[d] 1080, 1040	8.40	9.06 (d) $J = 6.05$ c.p.s.		
			1,3-Dienes			
$(CH_3)_2C=CHC=CH_2$ (* on $(CH_3)_2C$, with Z)	CH_3	3080, 1653, 1652 1600	8.29			5.43 (m), 5.25 (m) 4.56 (m)
	C_6H_5	1645, 1605	8.32 (d) $J = 1.8$ c.p.s. 8.14 (d) $J = 1.8$ c.p.s.		2.80 (m)	5.00 (m) 4.08 (m) 4.57 (d) $J = 2$ c.p.s.
$CH_3CZ=CHC=CH_2$ (* on CH_3CZ, + on CH_3)	C_6H_5	1625, 1595	7.81 (d) $J = 1$ c.p.s.	8.10 (m)	2.77 (m)	5.11 (m), 4.96 (m) 3.88 (m)

[a] Only bands for the significant structural features are given. Additional bands which are characteristic for the conjugated dienes are given in the section on spectral correlations. [b] Recorded as τ-values for 10% solutions in carbon tetrachloride with tetramethylsilane as internal standard. A doublet is indicated by (d) and a multiplet by (m). [c] Bands for $C\equiv C$ stretching frequencies not observed. Raman bands recorded in section on spectral correlations. [d] These strong bands of about equal intensity are probably deformation bands for $-C(CH_3)_2$ of the isopropyl group. [e] No n.m.r. signal was detected for the isopropyl hydrogen. [f] In agreement with value reported in ref. 32.

that III was similarly stable at 95° and on the chromatographic columns used.

Although tetramethylallene (V) has been reported a number of times,[6,13-16] the pure compound was never obtained and physical constants given are incorrect. Even the usually reliable method of Doering and La-Flamme[16] gave mainly 1-methyl-1-isopropenylcyclopropane.[17] Pure V was synthesized by pyrolysis of

3-hydroxy-2,2,4-trimethyl-3-pentenoic acid lactone.[18] This synthesis also gave a small amount of conjugated diene II which was very difficult to remove by distillation; separation was readily effected by g.l.c.

$$(CH_3)_2C=C—O \longrightarrow (CH_3)_2C=C=C(CH_3)_2 + III$$
$$(CH_3)_2C—C=O \qquad\qquad V$$

(13) L. Henry, *Ber.*, **8**, 398 (1875).

(14) B. K. Merezhkovskii, *J. Russ. Phys.-Chem. Soc.*, **45**, 1940 (1913).

(15) Ya. M. Slobodin, *Zh. Obshch. Khim.*, **6**, 1806 (1936).

(16) L. Skattebol, *Tetrahedron Letters*, 167 (1961).

(17) L. Skattebol, private communication, 1962; *Acta Chem. Scand.*, **17**, 1683 (1963).

(18) J. C. Martin, private communication, 1962; Technical Data Report X-129, Eastman Chemical Products, Inc., Kingsport, Tenn., Sept., 1961. We wish to thank Dr. Martin for sending us a sample of the allene.
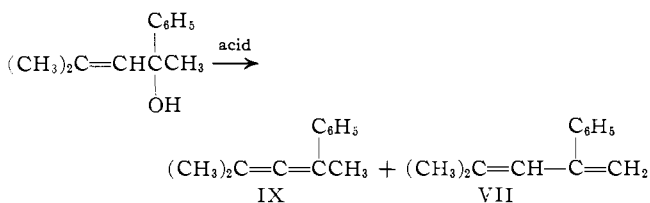
The earlier report[6] that coupling formed mainly V was based on isolation of acetone as principal product from alkaline permanganate oxidation and agreement of physical properties with those reported for V.[14,15] Small amounts of trimethylacetic and acetic acids suggested the presence of II, and qualitative tests for formic acid suggested that 4,4-dimethyl-1,2-pentadiene might be present. However, III would yield acetone and formic acid. Yields of oxidation products were not given so it is not possible to guess at the relative amounts of II and III obtained in the earlier work. Apparently a conjugated diene structure was considered unlikely because the hydrocarbons produced failed to give a maleic anhydride adduct. Compound III has been reported[19] to yield such an adduct, but we failed to obtain it under the usual conditions.

Earlier identification[6] of the coupling product from I and phenylmagnesium bromide as 2-methyl-4-phenyl-2,3-pentadiene (IX) was based on oxidation products, failure to yield an adduct with maleic anhydride, and correspondence of physical properties with those reported for the allene. However, it seems very probable that reported[20,21] syntheses of IX by dehydration of 4-methyl-2-phenyl-3-penten-2-ol gave mainly or exclusively VII.[22-25]

$$(CH_3)_2C=CHCCH_3 \xrightarrow{acid}$$

with C_6H_5 and OH substituents

$$(CH_3)_2C=C=CCH_3 + (CH_3)_2C=CH-C=CH_2$$
$$\quad\quad\quad IX \quad\quad\quad\quad\quad\quad VII$$
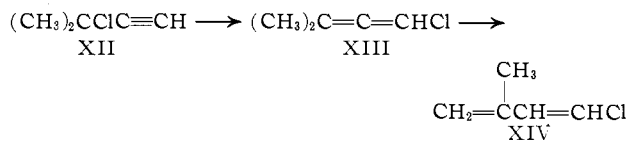
with C_6H_5 substituents

It was shown[25] that VII adds maleic anhydride under forcing conditions only. Finally, distillation of the coupling product gave several fractions, one of which had the refractive index reported by Zakharova[6] for IX and a composition corresponding to a mixture of VI, VII, and VIII which would give approximately the proportions of oxidation products observed[6] for supposed IX.

We have not yet synthesized IX, but it was shown that VI, VII, and VIII did not rearrange at 100° even in the presence of dilute hydrochloric acid; VI was also shown to be stable to phenylmagnesium bromide in refluxing ether.

Reaction of t-butylmagnesium bromide with I gave a complex mixture from which none of the expected products (4,4,5,5-tetramethyl-2-hexyne, 2,4,-5,5-tetramethyl-2,3-hexadiene, 4-t-butyl-2-methyl-1,3-pentadiene, 2-t-butyl-4-methyl-1,3-pentadiene) could be isolated. The infrared and n.m.r. spectra of the undistilled reaction mixture suggested that the starting chloride had rearranged partially to 2-chloro-4-methyl-2,3-pentadiene. Attempted distillation resulted in extensive polymerization.

A possible explanation for formation of rearranged coupling products would be reaction of Grignard reagents with rearranged chlorides. It is known that

3-chloro-3-methyl-1-butyne (XII) is rearranged by cuprous chloride to the chloroallene XIII which in turn is converted to conjugated diene XIV.[26,27] The

$$(CH_3)_2CClC\equiv CH \longrightarrow (CH_3)_2C=C=CHCl \longrightarrow$$
$$XII \quad\quad\quad\quad\quad\quad\quad XIII$$

$$CH_2=CCH=CHCl$$
with CH_3 substituent
$$XIV$$

corresponding bromo compounds rearrange even more readily.[28] 4-Chloro-4-methyl-2-pentyne (I) had a sharp freezing point (−50°) and an n.m.r. spectrum in agreement with the structure shown. It could be stored at 0° for as long as 4 months without change. However, it was sensitive to heat; g.l.c. at temperatures which permitted separation of C_6H_9Cl isomers caused rearrangement to conjugated dienic chlorides and elimination of hydrogen chloride. Simple heating in a glass tube produced similar changes. Rearrangement occurred in an infrared cell; the spectrum of I was that expected, but double bond bands characteristic of dienic compounds developed fairly rapidly. Cuprous chloride also caused rearrangement to a chloroallene and then to conjugated chlorides. No detailed study of these rearrangement products has yet been made but a mixture of them failed to couple with phenylmagnesium bromide. This showed that the coupling products with conjugated diene structures were not formed by coupling with rearranged chlorides.

Another possible explanation for formation of abnormal conjugated diene products is elimination of hydrogen chloride from I or a rearranged chloride followed by addition of the Grignard reagent. The only elimination product isolated was enyne IV. No addition of Grignard reagents to conjugated enynes has been reported, but alkyllithiums add to give allenic hydrocarbons.[29] Thus it seems unlikely that the

$$RLi + H_2C=CHC\equiv CR' \longrightarrow RCH_2CH=C=CR'Li \xrightarrow{H_2O}$$
$$RCH_2CH=C=CHR'$$
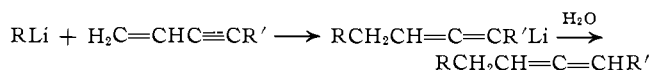
conjugated dienes arise from IV. Another possible elimination product would be 4-methyl-1,2,3-pentatriene, $(CH_3)_2C=C=C=CH_2$. This hydrocarbon is unknown but would be expected to be highly reactive; it is difficult to predict whether it would yield an addition product with a Grignard reagent or what the structure of such an adduct would be.

Another possible explanation for the abnormal conjugated diene products involves prototropy during the coupling reaction. Although there is no proof that the coupling of Grignard reagents with reactive organic halides occurs by an S_N1 mechanism, the halides that couple readily also solvolyze readily by this mechanism. It has been suggested[30] that the Grignard reagent provides a suitable polar medium for such a coupling mechanism. Compound I should present a favorable example for such a process because it readily

(19) R. Jacquemain, Compt. rend., 214, 880 (1942).
(20) A. Klages, Ber., 37, 2301 (1904).
(21) V. I. Pansevich-Kolyada and Z. B. Idel'chik, Zh. Obshch. Khim., 24, 1617 (1954).
(22) C. K. Ingold and C. L. Wilson, J. Chem. Soc., 1493 (1933).
(23) H. Ravier, Compt. rend., 198, 1786 (1934).
(24) E. A. Braude and C. J. Timmons, J. Chem. Soc., 2000 (1950).
(25) K. Alder, K. H. Decker, and R. Lienau, Ann., 570, 214 (1950).

(26) T. A. Favorskaya, Zh. Obshch. Khim., 9, 386 (1939).
(27) G. F. Hennion, J. J. Sheehan, and D. E. Maloney, J. Am. Chem. Soc., 72, 3542 (1950).
(28) T. L. Jacobs and W. L. Petty, J. Org. Chem., 28, 1360 (1963).
(29) A. A. Petrov, et al., Zh. Obshch. Khim., 30, 216, 3845, 3890 (1960); 31, 1518 (1961); Dokl. Akad. Nauk S.S.S.R., 125, 1041 (1959).
(30) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice–Hall, Inc., New York, N. Y., 1954, pp. 1046–1052; see these discussions for pertinent references. More recent references include C. Prévost, et al., Bull. soc. chim. France, 679 (1959); L. Maginiac-Groizeleau, Ann. chim. (Paris), [13] 6, 1071 (1961).

Chart I

$$CH_3CC\equiv CCH_3 \text{ (Cl, CH}_3\text{)} \quad I \longrightarrow$$

$$\left[\begin{array}{c} CH_3 \\ CH_2=CC\equiv CCH_3 \\ H^\oplus \\ \updownarrow \\ (CH_3)_2 \overset{\oplus}{C}C\equiv CCH_3 \\ \updownarrow \\ (CH_3)_2 C=C=\overset{\oplus}{C}CH_3 \\ \updownarrow \\ (CH_3)_2 C=C=C=CH_2 \\ H^\oplus \end{array}\right]$$

$$CH_3 \atop CH_2=CCH=CRCH_3 \quad \uparrow RMgX$$

$$CH_3 \atop CH_2=CCH=\overset{\oplus}{C}CH_3 \quad XVI$$

$$(CH_3)_2C=CH\overset{\oplus}{C}=CH_2 \quad XV \quad \downarrow RMgX$$

$$(CH_3)_2C=CHCR=CH_2$$

forms carbonium ions; in aqueous ethanol it solvolyzes 2000 times faster than 3-chloro-3-methyl-1-butyne and 100 times faster than *t*-butyl chloride.[31] The prototropy might be formulated as a unique carbonium ion rearrangement as shown in Chart I, or the rearrangement might occur in a complex with the Grignard reagent in which the C–Cl bond was only partly broken at the time the hydrogen migrated. It has recently been shown that the hyperconjugation of the right hand methyl is considerable.[32] Rearrangement to XV might be expected to occur more readily than to XVI because a short migration of hydrogen along the linear chain yields XV as a resonance-stabilized allylic ion; this is shown in XVII → XVIII; XV would be expected to be more stable with the geometry shown in XVIII than in a form which allowed conjugative π-overlap of the 1,3-diene type. Ion XVI can have only the latter type of stabilization.

XVII

XVIII
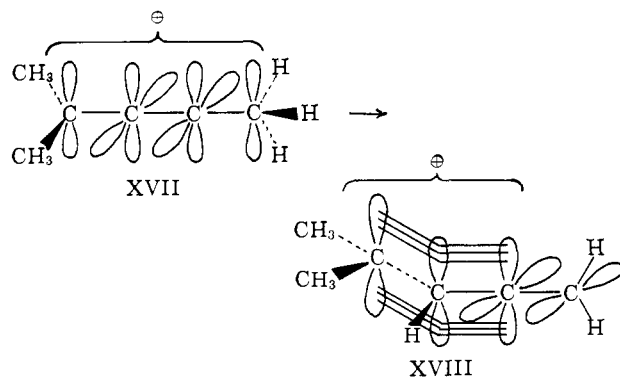
If this formulation of the reaction is correct, one would expect that similar 1,3-dienic products would be produced in reactions of I which involve carbonium ions. Preliminary experiments[33] indicate that solvolysis in acetic acid yields such products.

It is puzzling that isopropylmagnesium bromide does not yield conjugated dienes, but instead the tetrasubstituted allene is formed. This result cannot be discussed except in the most qualitative terms because the nature of Grignard reagents and reactions is still

so uncertain. Relative carbanion stabilities are in the order phenyl > methyl > isopropyl[34] and the reactivity of the corresponding Grignard reagents may be in the reverse order. Thus the isopropyl reagent may react more rapidly, or compound I may have less carbonium ion character in the transition state for the coupling reaction with this reagent, so that the prototropy does not occur. The appearance of allenic product may be the result of increased hindrance at the propargyl position which leads to X so that attack at the other end of the system to yield XI may become important. Further discussion is postponed until more facts are available.

Spectroscopic Correlations (see Table II). Acetylenes.—In the infrared the triple bond stretching mode was strong for the disubstituted acetylenic chloride I and its alcohol precursor. None of the disubstituted acetylenic hydrocarbons II, VI, and X had triple bond bands in the infrared. However, Raman spectra of these compounds showed strong acetylenic absorptions typical of disubstituted acetylenes[35]; n.m.r. shielding values for terminal methyl of the disubstituted acetylenes varied from 8.08 to 8.31 τ which is about the range for allylic methyl hydrogens. The nonpropargylic hydrogens absorbed in the normal *t*-butyl hydrogen region (except for the chloride which was 0.6 p.p.m. low as expected, and the phenyl-substituted derivative which was 0.4 p.p.m. low).[36] Our values for II are in relatively good agreement with reported values[37] for which water was the standard. The reported difference in chemical shift between the two kinds of protons in II is 0.55; our difference, 0.53.

Allenes.—2,4,5-Trimethyl-2,3-hexadiene (XI) had a medium infrared band at 1962 cm.$^{-1}$ characteristic of allenes and also showed strong bands at 1040 and 1080. The latter may correspond to the 1060 band reported for allene. The symmetrical 2,4-dimethyl-2,3-pentadiene failed to absorb in either of these regions.

Nuclear magnetic resonance spectra of tetrasub-

(31) A. Burawoy and E. Spinner, *J. Chem. Soc.*, 3752 (1960).

(32) V. J. Shiner, Jr., and G. S. Kriz, Jr., *J. Am. Chem. Soc.*, **86**, 2643 (1964). It was pointed out earlier [E. R. H. Jones, G. H. Whitham, and M. C. Whiting, *J. Chem. Soc.*, 3201 (1954)] that all three σ-bonds in this methyl are in position to permit delocalization to the π-orbitals of the acetylenic bond.

(33) Unpublished work with P. Prempree. The product, $(CH_3)_2C=CHC(OAc)=CH_2$, might also result from addition of acetic acid to 4-methyl-1,2,3-pentatriene. The details and mechanism of this reaction are under investigation.

(34) The relative stabilities of carbanions have been discussed in various places; recent references include J. E. Leffler, "The Reactive Intermediates of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1956, pp. 184–199, and R. E. Dessy, *Chem. Eng. News*, 136 (Feb. 18, 1963).

(35) L. G. Akishin, L. G. Maisova, E. A. Victorova, and R. Ya. Levina, *Vestnik Moskov. Univ.*, **8**, No. 5, *Ser. Fiz. -Mat. i Estestven, Nauk*, No. 3, 59 (1953); *Chem. Abstr.*, **48**, 8653e (1954); A. A. Petrov and Yu. I. Porfir'eva, *Dokl. Akad. Nauk S.S.S.R.*, *Otdel. Khim. Nauk*, **89**, 876 (1953); *Chem. Abstr.*, **48**, 6373 (1954); P. A. Kishin and V. M. Tatevskii, *Dokl. Akad. Nauk S.S.S.R.*, *Otdel. Khim. Nauk*, **89**, 287 (1953); *Chem. Abstr.*, **47**, 10349 (1953).

(36) L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, London, 1959.

(37) H. Heel and W. Zeil, *Z. Elektrochem.*, **64**, 962 (1960).

stituted allenic hydrocarbons were not found in the literature. Both such compounds cited in the present work had methyl groups attached to the allenic system; the characteristic shielding value for such protons appears to be 8.40 τ. No signal could be detected for the tertiary hydrogen of the isopropyl group in 2,4,5-trimethyl-2,3-hexadiene.

Conjugated Dienes.—2,4-Dimethyl-1,3-pentadiene (III) showed characteristic infrared C=C stretching bands in the 1600–1650 cm.$^{-1}$ region. Three bands were observed but one (1600) was weak; the medium band at 1625 was stronger than that at 1653. A well-defined band at 3080 cm.$^{-1}$ (=CH$_2$ stretching) was observed but bands nearer 3000 were not resolved. Bands in the region for out-of-plane and in-plane C–H deformations were observed at 885 (s), 840 (m), 814 (w), and 1445 (s) cm.$^{-1}$. A weak band at 1780 might be the usual overtone band.

The infrared spectra of 4-methyl-2-phenyl-1,3-pentadiene (VII) and 2-methyl-4-phenyl-1,3-pentadiene (VIII) were complicated by the absorptions of the aromatic ring. In addition to the bands near 1600 (Table II), VII showed strong bands (not completely resolved) at 3078, 3050, and 3020 as well as at 1407 (m), 1370 (s), 890 (s), and 840 (m) cm.$^{-1}$; VIII similarly had bands at 3080, 3050, 3010, 1440 (s), 1375 (s), 890 (s), 850 (m), and 835 (shoulder) cm.$^{-1}$. The usual pattern of weak bands between 1700 and 2000 cm.$^{-1}$ was present in the spectra of VII and VIII and a considerable number of bands in addition to those recorded above were present in the 600–1700 region.

The n.m.r. spectra of III, VII, and VIII displayed three vinyl hydrogen peaks each in the region 3.5 to 5.5 τ. The allylic hydrogen absorption at 8.29 τ exhibited by III is in the normal allylic hydrogen region. The apparent absence of 1,3-coupling across the double bond may be ascribed to the low magnitude of 1,3-coupling constants,[38] and to the limits of the spectrometer. The terminal methyl groups are formally in different environments, but interaction with the rest of the molecule fails to bring about differences in shielding. The two pairs of doublets observed for the methyl groups of VII reflect different environments for these protons. The phenyl group (or possibly the vinyl group) may lie in close proximity to one of the methyls, cause deshielding, and account for the low τ-value (8.14).

Compound VIII can exist in *cis* and *trans* forms. The 1,3-coupling constant of terminal methyl with vinyl hydrogen (1 c.p.s.) lies between values reported[38] for *cis*- and *trans*-α-methyl-β-d-styrene so that it is not certain which stereoisomer of VIII was obtained.[38a] The product may have been a mixture of these with the coupling constant of the *trans* form too small to permit observation. The low value of the protons of the internal methyl may imply proximity of phenyl.

Ultraviolet absorption of conjugated dienes is greatly affected by deviation from planarity between the π-orbitals. Increasing nonplanarity results in decreasing intensity of absorption and usually in slightly decreasing λ_{max}. III showed normal λ_{max} for a trialkyl-

substituted butadiene (231 mμ) but low ϵ_{max} (8000); values agreed with reported values[39] (λ_{max} 232 mμ, ϵ 8500). Models suggest that either transoid or cisoid coplanar alignments of the double bonds would give marked interference between the 2- and 4-methyls or between the terminal methylene and the 4-methyl, respectively; a skew structure should be more stable. Interference appears to be even more marked in VII and VIII (VII, λ_{max} 262, ϵ 4700; VIII, λ_{max} 249, 229, 221 mμ; ϵ 390, 650, 710); for comparison, *cis*- and *trans*-1-phenylbutadiene, λ_{max} 265 and 280 mμ, ϵ 14,000 and 28,300, respectively[40]; 2-phenylbutadiene, λ_{max} 279 mμ, ϵ 28,500[41]; α-methylstyrene, λ_{max} 243 mμ, ϵ 11,500.[42] The values reported[24] for an impure VIII were λ_{max} 251, 258, 266, 276 mμ; ϵ 11,000, 12,000, 11,000, 9000.

Experimental

All boiling points, freezing points, and melting points are uncorrected; the latter were determined with total immersion thermometers. The fractionating columns used were A, an electrically heated glass spiral column with total condensation, partial take-off head, 50 cm. by 1 cm. i.d.; B, an insulated tantalum-spiral column, 30 cm. by 8 mm. i.d.; C and D, vacuum jacketed, silvered columns 40 and 75 cm. long packed with hollow rings.

Infrared spectra were obtained with Perkin–Elmer 421 and 21 spectrophotometers (neat or 10% in carbon tetrachloride). Ultraviolet spectra were determined on a Cary recording spectrophotometer Model 14M (in cyclohexane). Nuclear magnetic resonance spectra were obtained with a Varian Associates analytical NMR Model A-60 (10% in carbon tetrachloride with tetramethylsilane internal standard). Raman spectra were determined on a Cary Model 81 raman spectrometer[43] (neat). The spectrum from 1900 to 2500 cm.$^{-1}$ was recorded. The spectrum below 1900 cm.$^{-1}$ was obscured by fluorescence in some of the samples.

Vapor phase chromatography was performed on the following columns constructed of $^3/_8$ or 0.5 in. copper or aluminum tubing: Q, 4.5 ft. didecyl phthalate, 30% on 80–100 mesh Chromosorb W; R, 6 ft. *m*-tricresyl phosphate, 30% on 60–80 mesh Chromosorb W; S and T, 2.5 ft. and 5 ft. Apiezon L, 10% Fluoropak; U, 10 ft. Carbowax-4000 dioleate, 15% on firebrick; V, 6 ft. 3-methyl-3-nitro-pimelonitrile, 15% on firebrick; W, 6 ft. mineral oil, 30% on Celite; X, 12 ft. squalane, 25% on Chromosorb W; Y, 1 m. SE-30 (silicone rubber gum), 5% on Fluoropak; Z, 8 ft. hyprose monostearate, 25% on firebrick.

Magnesium.—A certified report (test No. 3385, Atlas Testing Laboratories, Los Angeles, Calif.) gave: zinc, 0.001; copper, 0.001; aluminum, 0.005; iron, 0.001; silicon, 0.005; manganese, 0.01; nickel, 0.0008; chromium, nil; calcium, 0.0003; zirconium, nil; silver, nil; magnesium, remainder. The magnesium was ether washed and heated in an oven at 110° prior to use.[44]

Tetramethylallene (b.p. 87–87.5°, n^{20}D 1.4410) was supplied through the courtesy of Dr. James C. Martin of The Tennessee Eastman Co., Kingsport, Tenn. The n.m.r. spectrum showed a single peak, 8.40 τ, unsplit.

2-Methyl-3-pentyn-2-ol was synthesized from acetone and propynylmagnesium bromide[45]; yield 47% (distillation through column D, b.p. 73.5–74.5° (75 mm.), $n^{18.5}$D 1.4426 (reported n^{18}D 1.44385).[6] Analysis on column Z indicated 98% purity.

Anal. Calcd. for C$_6$H$_{10}$O: C, 73.43; H, 10.27. Found: C, 73.51; H, 10.52.

(38) D. R. Davis and J. D. Roberts, *J. Am. Chem. Soc.*, **84**, 2252 (1962).

(38a) NOTE ADDED IN PROOF.—F. C. Stehling, Humble Oil and Refining Co., has found coupling constants for methyl and hydrogen *trans* ($^{CH_3}>$C=C$<_H$) of 1.2–1.5 negative and for *cis* ($^{CH_3}>$C=C$<^H$) 0.8–1.4 negative based on eight monoolefins. We wish to thank Dr. Stehling for permission to cite these results prior to publication.

(39) J. C. Lunt and F. Sondheimer, *J. Chem. Soc.*, 2957 (1950).

(40) O. Grummitt and F. J. Christoph, *J. Am. Chem. Soc.*, **73**, 3479 (1951).

(41) I. N. Nazarov, Yu. A. Titov, and A. I. Kuznetsova, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1270 (1959).

(42) A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy," 2nd Ed., Edward Arnold, Ltd., London, 1957, p. 277.

(43) Through the courtesy of Applied Physics Corp., Arcadia, Calif.

(44) The purity of magnesium used to form Grignard reagents is of some importance; *e.g.*, copper salts cause rearrangement of halide: G. F. Hennion, J. J. Sheehan, and D. E. Maloney, *J. Am. Chem. Soc.*, **72**, 3542 (1950). The magnesium used in this study was comparatively pure; *cf.* M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice–Hall, Inc., New York, N. Y., 1954, pp. 6–8.

(45) C. D. Hurd and F. L. Cohen, *J. Am. Chem. Soc.*, **53**, 1068 (1931).

4-Chloro-4-methyl-2-pentyne (I) was prepared from 4-hydroxy-4-methyl-2-pentyne and concentrated hydrochloric acid[27] in 5.9% yield (distillation through column C), b.p. 49.5–51.5° (50 mm.), n^{20}D 1.4500[46] (reported n^{18}D 1.45118,[6] n^{20}D 1.4143[4]), f.p. −50° (reported[47] −5.1°).

Anal. Calcd. for C_6H_9Cl: C, 61.80; H, 7.78; Cl, 30.42. Found: C, 62.00; H, 7.53; Cl, 30.49.

Determination of the infrared spectrum was difficult because hydrogen chloride was given off slowly during the measurement. In addition to a strong peak at 2240 cm.$^{-1}$ there were weak peaks at 1635 and 3080 characteristic of an olefinic system. Several v.p.c. columns were employed in attempts to purify the chloride, but rearrangement occurred on all of them to produce mixtures of products. With column R clean separation into 3 components was realized. Peak 1, 33.7%, was 2-methyl-1-penten-3-yne; peaks 2 and 3, 13.8% and 52.5%, were conjugated dienes containing chlorine which was unreactive toward alcoholic silver nitrate. Peak 3 did not undergo further change when collected and chromatographed a second time. Further work will be done on these chlorides, but their conjugated dienic nature was shown by infrared, ultraviolet, and n.m.r. spectra.

Anal. Calcd. for C_6H_9Cl: C, 61.80; H, 7.78. Found: C, 62.02; H, 7.85.

Rearrangement of I.—When Compound I was heated in a sealed glass tube for 2 hr. at 100° the infrared acetylene band at 2240 cm.$^{-1}$ had almost disappeared and strong bands at 3080, 1635, and 1610 cm.$^{-1}$ had appeared.

Compound I (1.0 g.) was shaken with 0.33 g. of cuprous chloride and 0.17 g. of ammonium chloride for 5 hr. at room temperature, then vacuum transferred to yield 0.6 g. of colorless liquid; n.m.r. showed new absorptions in the 5 and 4 τ regions (vinyl hydrogens) and 7.75 to 8.10 τ (allylic hydrogens and $\overset{CH_3}{\underset{Cl}{>}}C{=}C{-}$). The infrared spectrum had bands at 2240 (s), 1968 (s), 1610 (m), 1635 (m), and 3080 (w) cm.$^{-1}$ indicative of acetylene, allene, and conjugated double bonds, respectively. Another sample was shaken for 22 hr. The infrared spectrum showed strong peaks at 1610 and 1635 cm.$^{-1}$, with weak allene and acetylene peaks. Compound I was heated as above with excess magnesium bromide for 4 hr. The n.m.r. and infrared spectra were unchanged.

4,4-Dimethyl-2-pentyne (II) was prepared from sodium *t*-butylacetylide and dimethyl sulfate[48] in 26% yield, n^{20}D 1.4077 (reported[48] n^{20}D 1.4054).

2,4-Dimethyl-1,3-pentadiene (III) was prepared from mesityl oxide and methylmagnesium bromide[49]; yield 44% (distillation through column C under nitrogen), b.p. 89–94°, n^{20}D 1.4408 (reported[49] b.p. 91.2–91.5°, n^{20}D 1.4418). This material gave a single peak on v.p.c. column Q (low boiling material responsible for the broad b.p. would have escaped detection).

Anal. Calcd. for C_7H_{12}: C, 87.50; H, 12.50. Found: C, 87.34; H, 12.61.

No reaction was observed when 2.0 g. of II and 2.3 g. of powdered maleic anhydride were shaken or stirred at room temperature. The reaction mixture became homogeneous after 1 hr. at 60°, but the product was a gelatinous mass from which no pure adduct could be isolated.

2-Methyl-1-penten-3-yne (IV) was prepared in 53% yield (crude) by dehydration of 2-methyl-3-pentyn-2-ol with potassium bisulfate[50]; g.l.c. on column X showed that this product was 80–85% pure. Redistillation through a short column gave material, b.p. 82–84°, of greater than 99% purity (g.l.c.) but recovery was only 40%; a yellow polymeric liquid remained as a residue from the distillation. A sample collected from g.l.c. showed n^{22}D 1.4488. The boiling point and refractive index agree with those reported[51] for a sample prepared by methylation of 2-methyl-1-buten-3-yne but not with those reported[45] earlier

(46) The index of refraction increased as the chloride stood at room temperature; n^{20}D 1.4500 was obtained from a freshly distilled sample, not allowed to stand over 15 min. One sample was observed to increase 0.0027 unit in 30 min., probably attributed to elimination of hydrochloric acid.

(47) Reference 31. The freezing point was incorrectly transcribed from Dr. E. Spinner's thesis (which reads −51°) to the published article. We are indebted to Dr. G. Baddeley of the Manchester College of Science and Technology for supplying the correct value.

(48) A. I. Zakharova, *Zh. Obshch. Khim.,* **23**, 1572 (1950).

(49) R. Jacquemain, *Compt. rend.,* **215**, 200 (1942).

(50) A. Arai and I. Ichikizaki, *Bull. Chem. Soc. Japan,* **35**, No. 1, **45** (1962).

(51) C. W. Kruse and R. P. Kleinschmidt, *J. Am. Chem. Soc.,* **83**, 216 (1961).

for a sample obtained by dehydration of 2-methyl-3-pentyn-2-ol. Our sample absorbed oxygen rapidly as reported by Kruse and Kleinschmidt[51] and gave unsatisfactory analytical results.

Anal. Calcd. for C_6H_8: C, 89.94; H, 10.06. Found: C, 87.60; H, 9.61, for a sample collected from v.p.c.

The infrared spectrum (Table II) showed bands in agreement with those reported[51] and the structure was confirmed by n.m.r. It seems probable that the refractive index reported earlier[45] was obtained on material which had been exposed to air for some time.

A sample of IV turned to a yellow solid at room temperature when allowed to stand in the dark but not tightly sealed.

Coupling Reactions. General Procedure.—The Grignard reagent was prepared in ether under nitrogen in the usual fashion. A Teflon stirrer was used and the flask was flame dried under nitrogen flow. A crystal of iodine was added to initiate reaction. The reagent was transferred under nitrogen through a double layer of ether-washed glass wool to a second 3-necked flask; it was then stirred rapidly as compound I was added dropwise (0.5 mole of I was added for each mole of Grignard reagent). The reaction mixture became slightly warm.

Stirring was continued for varying time after addition was complete and the reaction mixture allowed to stand before decomposition by slow addition with stirring of iced ammonium chloride solution. The organic layer was separated and dried over Drierite; it was then analyzed by g.l.c. The ether was next removed by distillation (distillate checked for purity) and the residual liquid investigated.

Coupling with Methylmagnesium Bromide.—Compound I (68.0 g., 0.58 mole) was added to 370 ml. of 2.44 M solution of Grignard reagent during 1.5 hr. Stirring was continued for 1 hr. and the reaction mixture allowed to stand 3 hr.; g.l.c. on columns Q, W, and X showed 3 components in addition to ether. Removal of ether left 43 g. of product (77% if calculated as C_7H_{12}); g.l.c. (column X) showed no change in relative amounts of the 3 components. These components in order of increasing retention were shown to be: peak 1, 65%, 4-4-dimethyl-2-pentyne (II); peak 2, 11%, 2-methyl-1-penten-3-yne (IV); peak 3, 24%, 2,4-dimethyl-1,3-pentadiene (III). The percentages were corrected by standardization of the column with authentic compounds and the peaks were shown to be augmented by the authentic compounds on columns Q, W, and X. 2,4-Dimethyl-2,3-pentadiene (V), when mixed with the coupling product, formed a new peak between peaks 2 and 3 on columns Q and X. A g.l.c. on the coupling product taken 7 months later showed no change in the relative amounts of the components. Peaks 1 and 3 were collected and heated for 1 hr. at 95° in sealed tubes; no rearrangement was observed. The infrared and n.m.r. spectra of the mixture contained only those absorptions found in the individual spectra of the three components (excepting three small high-field absorptions which may have been due to telomers), and the two n.m.r. absorptions corresponding to peak 1 constituted over 50% of the total area. No absorption at 8.40 τ (tetramethylallene) was present.

The 3 components were collected from column Q and examined: peak 1, n^{20}D 1.4071, n^{25}D 1.4044, gave infrared and n.m.r. spectra identical with authentic II. A Raman spectrum showed no bands from 1900 to 2248 cm.$^{-1}$, then 2 bands [2248 (s) and 2355 (0.7 the intensity of the other)] in the acetylene region; these bands agree with literature values for disubstituted acetylenes.[35]

Anal. Calcd. for C_7H_{12}: C, 87.50; H, 12.50. Found: C, 87.29; H, 12.67.

Peak 2: the infrared and n.m.r. spectra were in agreement with authentic spectra of IV.

Peak 3, n^{20}D 1.4414, gave a positive test with bromine in carbon tetrachloride and a negative test with alcoholic silver nitrite. Infrared, ultraviolet, and n.m.r. spectra were identical with spectra of authentic III.

Anal. Calcd. for C_7H_{12}: C, 87.50; H, 12.50. Found: C, 87.31; H, 12.73.

A second coupling of 4.0 g. (0.034 mole) of I with 37 ml. of 1.6 M methylmagnesium bromide was carried out with 0.27 g. (0.0027 mole) of V present, addition time 12 min., stirring 1 hr., standing 3 hr.; g.l.c. on column X gave less III (see Table I) and allowed separation of V which was unchanged (comparison with authentic sample by g.l.c.).

Coupling with Phenylmagnesium Bromide.—Compound I (45 g., 0.39 mole) was added to 500 ml. of 1.39 M solution of phenylmagnesium bromide during 40 min. (stirring 45 min., standing 3 days); the yield of crude product was 77%. Small amounts of lower-boiling compounds were separated on columns

Q, R, or X; these products were shown to be ether, benzene, and 2-methyl-1-penten-3-yne. Chlorobenzene was shown to be absent which indicated that Grignard reagent–halogen exchange to form the organometallic derivative of I had not occurred. Bromobenzene was also absent. Columns T, U, and Y were examined for separation of the main components, but only T was satisfactory. A shorter Apiezon column (S) was less satisfactory, but did permit easy recovery and identification of biphenyl, a minor component of the mixture. The remaining material was separated on column T at 155° into 3 pure compounds: peak 1, 56%, 4-methyl-4-phenyl-2-pentyne (VI); peak 2, 41%, 4-methyl-2-phenyl-1,3-pentadiene (VII); and peak 3, 3%, 2-methyl-4-phenyl-1,3-pentadiene (VIII).

Peak 1, n^{20}D 1.5200, had infrared bands at 3020–3080, 1700–2000, 1595, and 1490 cm.$^{-1}$ characteristic of monosubstituted benzenes. There was no band in the 2240 cm.$^{-1}$ region characteristic of C≡C, but a Raman spectrum showed three such bands: 2240 (s), 2272 (0.9 of s), and 2312 (0.4 of s) cm.$^{-1}$. The ultraviolet spectrum had no maximum in the region examined, but a shoulder was present at 216 mμ. The n.m.r. spectrum (Table II) was that expected for structure VI.

Anal. Calcd. for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.04; H. 9.18.

Peak 2, n^{20}D 1.5448 (reported[22] n^{20}D 1.547), was characterized by infrared, ultraviolet, and n.m.r. spectra.

Anal. Calcd. for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.26; H, 9.08.

Peak 3, n^{20}D 1.5610, was characterized by infrared, ultraviolet, and n.m.r. spectra.

Anal. Calcd. for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.04; H, 8.98.

Compound VI (Peak I) was collected from column T and added to a solution of phenylmagnesium bromide of the same concentration as used for coupling. The mixture was refluxed for 10 hr., allowed to stand overnight, and treated with iced ammonium chloride solution; g.l.c. showed that VI had survived with no formation of VII or VIII. Compound VI was also sealed in glass under nitrogen and heated at 100° for 7 days. G.l.c. showed no change.

The crude coupling product mixture was distilled under reduced pressure through column B to yield the products shown in

TABLE III

Fraction	B.p., °C.	Mm.	Wt., g.	n^{20}D
1	65–80	6	2.1	1.5290
2	80–82	6	4.0	1.5274
3	82	6	1.7	1.5314
4	76	2	1.3	1.5469

Table III. Fraction 4 had an index of refraction close to that reported by Zakharova[6] for the main product of the coupling reaction. Column T separated fraction 4 into 40% VI, 33% VII, and 27% VIII.

Coupling with Isopropylmagnesium Bromide.—Compound I (45 g., 0.39 mole) was added slowly dropwise to 450 ml. of 1.7 *M* isopropylmagnesium bromide. Stirring was continued for 1.5 hr. after addition was complete and the mixture was warmed slightly on a steam bath during this time; it was then treated with iced ammonium chloride solution. Isopropyl bromide used for preparation of the Grignard reagent was shown to be pure by g.l.c. on column Q. The apparatus for the coupling was pro-

vided with a −70° trap on the exit tube to collect any propene or propane that might be produced as the result of reducing action of the Grignard reagent or of reaction of the reagent with hydrogen chloride from elimination from I; this trap contained no more than 2 drops of liquid at the end of the reaction, so these side reactions were relatively unimportant. Much of the ether was removed through a short distilling column and the residue examined by n.m.r. and infrared. It was then separated by g.l.c. on column Q at 156° and gave 3 peaks in addition to 22% of ether. The yield of crude product, corrected for ether content, was 70% calculated as C_9H_{16}. The first peak (probably a mixture), 22% of total area of all 3 peaks, showed bands in the infrared and n.m.r. which were not present in spectra of the unchromatographed product. Peak 2, 27% (XI), and peak 3, 51% (X), were primary products of the coupling. All of the bands in the infrared and n.m.r. spectra of crude coupling product could be accounted for by X, XI, and ether. The area ratio of peak 2 to peak 3 was 35:65. From area ratios of the n.m.r. peaks corresponding to X and XI in the crude coupling product these two compounds were present in 40:60 ratio. Apparently the material in peak 1 was formed from X and XI on the column. Isopropyl bromide, isopropyl chloride, 4-chloro-4-methyl-2-pentyne (I), and I which had been treated with aqueous ammonium chloride were found not to be components of the mixture by g.l.c. comparison with coupling product.

Distillation of the coupling product through column A gave extensive polymerization and 26 g. of brown viscous material remained as a residue even after heating to 90° (10 mm.). A series of lower boiling fractions (total 1 g.) were obtained, and each showed varying amounts of several peaks with retention times near that of peak 1 above. The infrared spectra of these fractions showed large carbonyl and hydroxyl bands as well as very weak bands at 2240 and 1960 cm.$^{-1}$. The fractions were unsaturated to bromine in carbon tetrachloride. The principal distillate, b.p. 56.5–57.5° (55 mm.), 6.4 g., consisted of X and XI, but the amount of the allene was greatly reduced relative to X.

The coupling of I with isopropylmagnesium bromide was repeated with 8 g. of I and 1.80 *M* Grignard reagent (no gas trap used). Ether and low-boiling material were removed on a rotary evaporator and the reaction mixture was not heated during work-up. The crude product showed only X and XI by infrared and n.m.r.; g.l.c. on column U gave XI and X as peaks 1 and 2 in the ratio 36:64. There were also two smaller peaks at long retention times whose infrared spectra showed carbonyl absorption with no double bond, triple bond, or allene bands. The material included in these g.l.c. fractions appears to have been formed during chromatography.

Pure samples of X and XI were isolated from the various g.l.c. experiments and examined.

Peak 2 (column U) or peak 1 (column U), n^{25}D 1.4383, was shown by n.m.r. and infrared spectra (Table II) to be 2,4,5-trimethyl-2,3-hexadiene (XI).

Anal. Calcd. for C_9H_{16}: C, 87.02; H, 12.98. Found: C, 87.11; H, 13.26.

Peak 3 (column Q) or peak 2 (column U), n^{20}D 1.4320, n^{25}D 1.4312, was shown by n.m.r. and infrared spectra (Table II) to be 4,4,5-trimethyl-2-hexyne, (X). The Raman spectrum had no bands between 1900 and 2243 cm.$^{-1}$; a strong band at 2243 and one half as strong at 2298 were characteristic of C≡C.

Anal. Calcd. for C_9H_{16}: C, 87.02; H, 12.98. Found: C, 86.97; H, 13.26.