

determining rates of loss of I since the ratio was determined at zero time for each run. In calculating rates of formation of II and III, it was assumed that the ratios varied in the same way as that for I.

As indicated above, material balance in runs not containing either sodium formate or sodium fluoride was poor in early stages of reaction. This is illustrated in Fig. 2 and 3 for rates of formation of products both in the presence and absence of added base. In both cases, the rate of loss of I is first order through at least 75% reaction.

Determination of H_0 .—Measurements were carried out by the usual indicator method.¹¹ The necessary value of extinction coefficient for the free base in 97.3% formic acid was obtained in

(11) Reference 6, pp. 266–271.

solutions saturated with sodium formate. For the acid form, obtained in solutions containing *p*-toluenesulfonic acid, $\epsilon \approx 0$. Calculations were made using

$$H_0 = -\log h_0 = pK_a + \log C_{B/BH^+}$$

where pK_a = indicator constants for either 4-chloro-2-nitroaniline or 4-nitrodiphenylamine, and C_B/C_{BH^+} is obtained from $\epsilon/\epsilon_B - \epsilon$ where ϵ = extinction coefficient of acidic solution and ϵ_B = extinctive coefficient for the indicator base in the solvent. Figure 4 shows the plot of $[HCl]$ vs. h_0 .

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Dehalogenation of Propargyl and Allenyl Halides. II.^{1,2}

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Reaction of lithium aluminum hydride with 3-chloro-3-methyl-1-butyne and 1-chloro-3-methyl-1,2-butadiene (I) involves two independent reactions. Displacement of chlorine by hydrogen occurred with complete acetylene-allene rearrangement to yield 3-methyl-1,2-butadiene and 3-methyl-1-butyne, respectively. Addition yielded organoaluminum derivatives which underwent further reactions; hydrolysis yielded 3-methyl-1-butene, 3-methyl-2-butene, 3-methylbutane, and 1,1-dimethylcyclopropane. The course of the addition to I was examined by deuterolysis which gave 3-methyl-1-butene-3-*d*₁, 2-methyl-2-butene-4-*d*₁, 2-methylbutane-4,4-*d*₂ (containing appreciable amounts of another dideuterio isomer), and 1,1-dimethylcyclopropane-2-*d*₁. Addition of lithium aluminum deuteride was also studied. Displacement predominated with the propargyl chloride and addition with I. Similar reactions were observed with chloroallene and bromoallene. Propargyl chloride gave mainly displacement, but propyne predominated over allene among the products. For the synthesis of allenic hydrocarbons by dehalogenation of propargyl halides, zinc-copper couple is a better reagent than lithium aluminum hydride.

It was established earlier² that dehalogenation of propargyl halides with zinc-copper couple gives the same mixture of allenic and acetylenic hydrocarbons as similar dehalogenation of the corresponding allenyl halides. Dehalogenation with lithium aluminum hydride gave very different results.^{2,4} Tertiary propargyl halides, $RR'CX\equiv CH$, gave allenic hydrocarbons, $RR'C=C=CH_2$, which appeared to contain no more than traces of the acetylenic isomers. The corresponding allenyl chloride gave mainly olefins and saturated hydrocarbons; small amounts of acetylenic hydrocarbons were also formed. Allenic hydrocarbons were not found, but small amounts would have escaped detection. 1-Bromo-3-methyl-1,2-butadiene gave a hydrocarbon mixture in 70% yield distributed as follows: 61% 3-methyl-1-butyne, 36% isopentane, 3% olefinic material (mainly 3-methyl-1-butene). Both bromoallene and propargyl bromide gave mainly propyne in this dehalogenation.

Gas-liquid chromatography has made possible a more exact study of lithium aluminum hydride dehalogenation of these halides. This paper presents the results with 1-chloro-3-methyl-1,2-butadiene (I) (Table I), 3-chloro-3-methyl-1-butyne (Table II), and with three-carbon halides (Table III).

(1) This paper is taken in part from the Ph.D. thesis of R. D. Wilcox, U.C.I.A., 1962. Part of the material was presented at the XIXth International Congress of Pure and Applied Chemistry, London, July, 1963 (Abstracts of the Congress, A, p. 23). The research was supported largely by a contract with the Office of Ordnance Research, U. S. Army.

(2) For Part I, see T. L. Jacobs, E. G. Teach, and D. Weiss, *J. Am. Chem. Soc.*, **77**, 6254 (1955). References to earlier work on dehalogenation of substituted propargyl halides are given there.

(3) U. S. Rubber Co. Fellow, 1959–1960.

(4) T. L. Jacobs and W. L. Petty, *J. Org. Chem.*, **28**, 1360 (1963).

Results and Discussion

Reactions of halides with lithium aluminum hydride were carried out in two ways. Method A involved addition of the halide to the hydride suspension at room temperature or below followed by heating to 100°. Method B involved addition at the reaction temperature which was maintained throughout the reaction period. Acid hydrolysis gave mixtures of hydrocarbons which were separated by g.l.c. and the components identified by retention times (comparison with authentic specimens) and by infrared and mass spectra. The course of the reaction with I was followed by hydrolysis of reaction mixtures with deuterium oxide and by use of lithium aluminum deuteride.

The complex mixtures of products are believed to result from two independent reactions: the first is displacement of the halogen by hydride; the second involves addition of the reagent to the propargyl or allenyl halide system. The latter forms organoaluminum compounds which mainly react further and eventually yield, by hydrolysis, olefins and saturated hydrocarbons. Further complications are introduced by reduction of at least one of the displacement products (3-methyl-1-butyne) by hydride species produced in the reaction mixture.

The displacement reaction is unique because it involves complete acetylene-allene rearrangement with both 3-chloro-3-methyl-1-butyne and 1-chloro-3-methyl-1,2-butadiene; the propargyl chloride yields only dimethylallene and the allenyl chloride yields only 3-methyl-1-butyne. As would be expected, displacement is more important with the more reactive chloride

TABLE I
 REACTION OF 1-CHLORO-3-METHYL-1,2-BUTADIENE WITH LITHIUM ALUMINUM HYDRIDE^a

Run	<i>t</i> , °C. ^b	Yield, % ^c	(Me) ₂ CHC≡CH	(Me) ₂ CHCH=CH ₂	(Me) ₂ C=CHCH ₃	(Me) ₂ CHCH ₂ CH ₃	(Me) ₂ C $\begin{array}{l} \diagup \text{CH}_2 \\ \diagdown \text{CH}_2 \end{array}$
In diethyl carbitol, O(CH ₂ CH ₂ OC ₂ H ₅) ₂							
1	A	73	..	19.5	16.9	52.4	11.2
2	A	70	..	23.0	20.1	44.0	12.9
3	A	79	0.2	28.1	18.9	41.1	11.7
4 ^d	A	71	^f	~41 ^f	14.1	31.9	13.0
5 ^d	A	95	0.1	29.0	23.2	35.6	11.4
6	98-103	89	0.03	25.2	18.5	43.4	12.4
7 ^e	100	86	2.8	29.6	15.9	38.3	13.3
8 ^d	100	54	0.1	17.3	26.6	37.1	16.7
9 ^d	54-55	69	22.3	33.1	35.5	5.9	3.0
	^g	11.1	98.5	..	1.2	..	0.1
	^h	57.9	7.7	39.4	42.1	7.0	3.6
10	24-25	58	24.5	32.2	42.9	0.2	0.1
11 ^d	r.t.	51	14.9	25.7	58.9	0.1	0.3
12	r.t. ⁱ	51	26.4	26.4	45.8	0.4	Trace
12 ^a	ⁱ	67	11.1	15.1	38.1	21.3	12.4
13	r.t. ^j	58	24.4	27.8	47.8
13 ^a	ⁱ	68	..	20.5	24.4	43.9	11.2
14	97-100 ^k	87	0.2	29.9	27.4	34.7	7.8
15	99-103 ^l	66	1.1	28.0	28.8	31.9	10.2
16	102-104 ^m	67	5.4	26.2	36.9	23.1	8.4
In diglyme, O(CH ₂ CH ₂ OCH ₃) ₂							
17	A ⁿ	70	15.3	27.9	40.0	8.2	8.3
18	A ^o	77	23.7	38.1	27.4	8.2	2.6
19	A ⁿ	79	14.0	13.6	51.0	11.5	9.9
20	50	35	41.5	5.1	49.5	..	3.9
21	50 ^p	52	44.8	3.7	46.3	..	5.1
22	r.t. ^q	73	37.1	22.6	32.9	..	7.2

^a 3-Methyl-1,2-butadiene was shown to be absent in all of these runs. ^b A indicates method A; a temperature range indicates method B with the temperature held throughout in the range indicated. ^c Yield of hydrocarbons. The remaining figures refer to the distribution of hydrocarbon products; where they do not add to 100 the difference represents small amounts of isoprene and 2-methyl-1-butene (see Experimental). ^d Decomposition with deuterium oxide. ^e Reaction with lithium aluminum deuteride and decomposition with water. ^f 3-Methyl-1-butyne and 3-methyl-1-butene together totaled 41.0%. ^g Before hydrolysis. ^h After hydrolysis. ⁱ An aliquot was taken after 3 hr. stirring at r.t. and yield figures determined from this. The remainder of the reaction mixture was heated at 65° (1 hr.) and 90-105° (2.5 hr.). ^j Like ⁱ but final heating at 80-90° (2 hr.), 100-105° (2 hr.), left overnight at ambient temp., and finally 100-105° (2 hr.). ^k Five-minute addition, 40-min. heating. ^l Ninety-second addition, 15-min. heating. ^m Three-minute addition, 10-min. heating. ⁿ Filtered hydride solution used. ^o Unfiltered hydride solution used. ^p The unfiltered hydride solution was added to the chloride. ^q 3-Methyl-1-butyne was shown to be absent in all of these runs. ^r In diethyl carbitol, method A. ^s In tetrahydrofuran, method A, but heating at reflux. The solvent may form an azeotrope with hydrocarbon mixture.

 TABLE II*
 REACTION OF 3-CHLORO-3-METHYL-1-BUTYNE WITH LITHIUM ALUMINUM HYDRIDE^q

Run	Yield, % ^c	(Me) ₂ C=C=CH ₂	(Me) ₂ CHCH=CH ₂	(Me) ₂ C=CHCH ₃	(Me) ₂ CHCH ₂ CH ₃	(Me) ₂ C $\begin{array}{l} \diagup \text{CH}_2 \\ \diagdown \text{CH}_2 \end{array}$
23 ^r	85	84.3	1.2	9.7	4.2	0.02
	^g	97.3	0.1	2.6	..	0.03
	^h	63.3	2.9	21.2	11.1	..
24 ^r	50	79.5	5.6	6.8	7.9	..
25 ^s	44	95.8	1.3	2.6	0.3	..

* Footnotes same as in Table I.

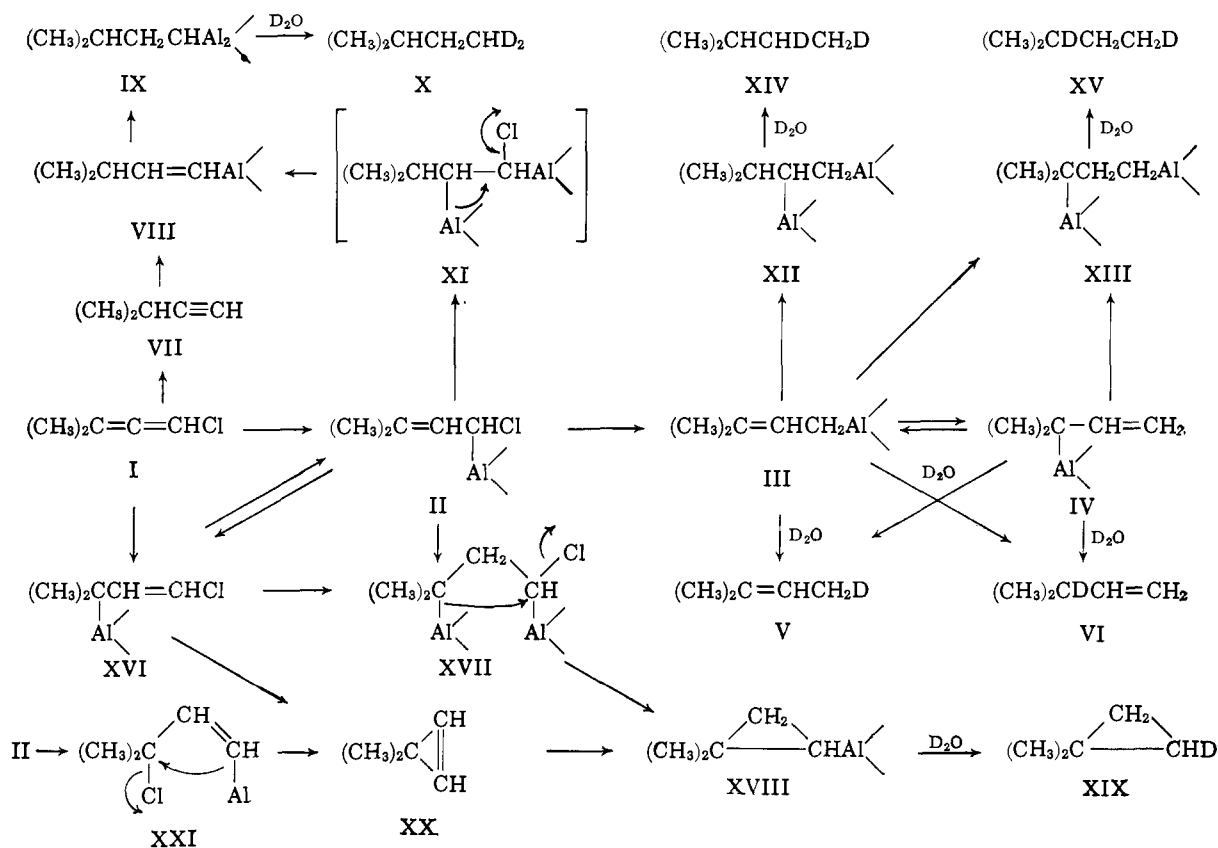
 TABLE III*
 REACTION OF PROPARGYL CHLORIDE AND HALOALLENES WITH LITHIUM ALUMINUM HYDRIDE

Compound	<i>t</i> , °C. ^b	Yield, % ^c	CH ₃ C≡CH	CH ₂ =C=CH ₂	CH ₃ CH=CH ₂	CH ₃ CH ₂ CH ₃	CH ₂ $\begin{array}{l} \diagup \text{CH}_2 \\ \diagdown \text{CH}_2 \end{array}$
HC≡CCH ₂ Cl	A	53	72.3	26.0	0.7	1.0	..
CH ₂ =C=CHCl	100	64	10.2	..	0.3	89.0	0.5
CH ₂ =C=CHBr							
Run 26	99-103	47	19.7	..	Trace	80.3	Trace
Run 27	48-52	63	96.0	0.2	2.8	1.0	..
Run 28	25-27	61	98.3	0.4	1.2	0.1	..

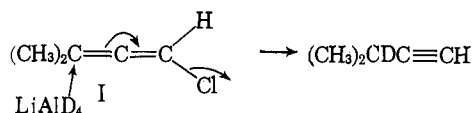
* Footnotes same as in Table I.

(propargyl) and addition with the allenyl chloride where the vinyl-type chlorine should not undergo displacement readily. Investigation of the mechanisms of these

displacement reactions has not proceeded far, but it is clear that a common intermediate is not involved. The reaction of the allenyl halide with lithium aluminum

CHART I
 THE REACTION OF LITHIUM ALUMINUM HYDRIDE WITH 1-CHLORO-3-METHYL-1,2-BUTADIENE


deuteride (run 20) yielded 3-methyl-1-butyne which was all deuterated on the tertiary carbon. This is easily explained by an $SN2'$ mechanism.



However, it is difficult to rule out deuteride attack on the halogen which might be expected to give $(\text{CH}_3)_2\text{C}-\text{C}\equiv\text{CH}$ (or a metallic derivative corresponding to this) and deuterium chloride. If the latter reacted with this intermediate before the hydrolysis step or before replacement of the acetylenic hydrogen, the product would also be 3-methyl-1-butyne-3- d_1 . $SN2'$ attack would be more hindered sterically for I than for the propargyl chloride, but models suggest that it would not be particularly difficult.

Displacement products are volatile and can be removed under reduced pressure before hydrolysis. It was shown in run 9 that the material so obtained from I was almost pure 3-methyl-1-butyne and represented about 70% of the alkyne produced in the run; products obtained before hydrolysis represented only 16% of the total hydrocarbon yield. The hydrocarbons obtained after hydrolysis were largely olefinic or saturated. One might have expected all of the 3-methyl-1-butyne to be retained in the reaction mixture as a metallic acetylide. However, the reaction of 1-hexyne with lithium aluminum hydride at 42° in ether is slow⁵ and dialkylaluminum hydrides react with 1-hexyne or phenylacet-

ylene by addition rather than by formation of an acetylide.⁶ Probably 3-methyl-1-butyne was not converted more completely to acetylide under our conditions because the reaction was slow and hydride species, less reactive toward acetylenic hydrogen, gradually replaced lithium aluminum hydride in the reaction mixture.

The addition products obtained from reaction of I with lithium aluminum hydride followed by deuterolysis were 2-methyl-2-butene-4- d_1 (V), 3-methyl-1-butyne-3- d_1 (VI), 2-methylbutane-4,4- d_2 (X), containing appreciable amounts of another deuterio isomer, and 1,1-dimethylcyclopropane-2- d_1 (XIX). All of these compounds and a number of their deuterio isomers were synthesized by standard methods and the identity of the deuterolysis products established by infrared and mass spectra comparisons. These products can be explained by the formulation in Chart I.

The formulation shows initial attack on the allenyl system by hydride hydrogen at the central carbon of I to yield mainly II which loses chlorine to yield the allylic aluminum compounds III and IV. Deuterolysis of these would yield V and VI; III and IV might be in equilibrium or either might yield both V and VI. Runs 10-13 indicate that at room temperature this represents most of the addition reaction.

Other orientations for the original addition appear less likely. Hydride attack at either terminal carbon of the allenyl system would place an aluminum atom on the center carbon; deuterolysis shows that this does not occur. The fourth possible orientation is discussed below.

(5) G. B. Smith, D. H. McDaniel, E. Biehl, and C. A. Hollingsworth, *J. Am. Chem. Soc.*, **82**, 3560 (1960).

(6) G. Wilke and H. Müller, *Ann.*, **629**, 222 (1960).

Runs 12 and 13 are especially significant for elucidation of the reaction scheme. They showed that at higher temperatures the displacement product, 3-methyl-1-butyne (VII), undergoes addition reactions. This was unexpected because we found that 3-methyl-1-butyne is not reduced by lithium aluminum hydride in diglyme at 100°. Recovery of the alkyne was high and 3-methylbutane, the only other product detected, was formed in less than 1% yield. It was reported⁷ that 1-hexyne is not reduced at 60° in dioxane, although some reduction of this alkyne occurred at 90° in a mixture of *n*-butyl ether and ethyl ether.⁸ However, dialkylaluminum hydrides add readily to 1-alkynes.⁶ The nature of the substituted aluminum hydride species present in our experiments is uncertain, but lithium chloride was observed to precipitate during reaction and these species may well be of the type RAlH_2 or R_2AlH , which add to VII producing VIII and hence IX and X. It has been shown that the rate of addition of dialkylaluminum hydrides to compounds like VIII is comparable to the rate of addition of such hydrides to 1-alkynes.⁶

The extent to which 3-methylbutane arose from VII is uncertain, but it is clear that not all of it was produced in this way because in runs 12 and 13 the decrease in VII was less than half of the increase in X; the rest of it must have come from III and IV or from chloro compounds still in the reaction mixture after the room temperature reaction. The hydrocarbon yield was higher from that portion of the reaction mixture which was held at higher temperature which suggests the chlorine-containing compounds survived the low temperature treatment. It is unlikely that unchanged I remained for it should have been possible to remove it under reduced pressure from room temperature runs before hydrolysis, and this was not observed.

Experiments designed to show the nature of II have not been completed. However, organoaluminum compounds of the type $\text{R}_2\text{AlCH}_2\text{X}$ have been examined recently.⁹ These compounds are very unstable, but are stabilized by diethyl ether and as etherates first decompose at 100°. Furthermore, the addition of a second $>\text{Al-H}$ compound to II might be a slow reaction because olefins with internal double bonds react at one-hundredth the time with dialkylaluminum hydrides as do terminal olefins¹⁰ and disubstituted acetylenes add only one molecule of dialkylaluminum hydride even at 90°. Thus, II might have persisted in the reaction mixture and given VIII *via* XI or by some other route (*e.g.*, $\text{S}_{\text{N}}2'$ displacement of the chlorine in II).

In run 13 some 3-methylbutane must have come from III and IV because more was produced than can be accounted for by disappearance of VII plus increased hydrocarbon yield. The direction of addition of $\text{H-Al}<$ species to III is not easy to predict, but either XII or XIII would yield a dideuterio-2-methylbutane different from X (*i.e.*, XIV or XV); IV would be expected to yield XIII. Meager evidence presented in the Experimental part favors XIV over XV as the chief contaminant of X, but small amounts of any of the

other dideuterio-2-methylbutanes could have been present. It seems probable that most of the 3-methylbutane which did not arise from VII in run 13 was produced from III and IV because no simple route from III or IV to 1,1-dimethylcyclopropane (XIX) appears probable and much of the chloro compound remaining after room temperature reaction must have gone to XIX.

Compound XIX was the least expected product encountered in this work. It was shown to be monodeuterated on the ring. Runs 12 and 13 showed that it was formed in major amounts only at higher temperatures; XVII is a likely precursor of XVIII and hence of XIX because cyclopropane formation occurs readily from $\text{R}_2\text{Al-C-C-X}$.^{9,11} Compound XVII might be produced from II or part of the original addition to I might have given XVI, which has a vinyl chlorine that would probably not have been lost at room temperature; at higher temperatures XVI could yield XVII. The increase in yield between the low and high temperature portions of runs 12 and 13 was more than enough to account for all of the XIX produced. Compounds II and XVI are allylic isomers that might be in equilibrium.

An alternative path to XIX involves 3,3-dimethylcyclopropene XX which might react rapidly with an $>\text{AlH}$ species to yield XVIII and hence XIX; XX might be formed by an internal displacement on XVI, but this seems unlikely because vinyl chlorines are not readily displaced. Allylic rearrangement of II might yield XXI; this is a tertiary allylic chloride rather than primary (a type known to yield cyclopropenes⁹), but it seems probable that XX would be formed readily from it.

It was hoped that experiments with lithium aluminum deuteride would distinguish between the various paths to 1,1-dimethylcyclopropane because either route through XVII would give the 2,2- d_2 -isomer. Any XX formed would have a vinyl deuterium and addition of lithium aluminum deuteride to this would give a mixture of dideuterio isomers (2,2 plus *cis*- and *trans*-2,3). Unfortunately, the dimethylcyclopropane- d_2 obtained showed a broad n.m.r. peak which appeared to contain much unresolved fine structure. This may indicate a mixture of dideuterio isomers, but the result is not certain.

Although in runs 12 and 13 part of the 2-methylbutane was formed from 3-methyl-1-butyne, it is unlikely that much of this saturated hydrocarbon was produced in this way in the 100° runs of Table I where the relative amounts of displacement and addition would be expected to be different. Run 12 showed that VII is not converted rapidly to IX because only 56% of the moderate amount formed at room temperature was destroyed after 1 hr. at 65° and 2.5 hr. at 90–105°; VII was removed completely only after 6 hr. at the higher temperature (run 13). Runs 14, 15, and 16 were carried out for short periods at around 100° followed by rapid cooling to quench the reaction. Almost no VII was found when the heating time was 40 min., and only 5% when the time of addition plus reaction was 13 min. These experiments indicate that at 100° the amount of addition relative to displacement is considerably higher. Since X is the principal 3-

(7) W. J. Bailey and C. R. Pfeifer, *J. Org. Chem.*, **20**, 1337 (1955).

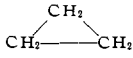
(8) G. B. Smith, D. H. McDaniel, E. Biehl, and C. A. Hollingsworth, *J. Am. Chem. Soc.*, **82**, 3560 (1960).

(9) H. Hoberg, *Ann.*, **656**, 1 (1962).

(10) K. Ziegler, H. G. Gellert, H. Martin, K. Nagel, and J. Schneider, *ibid.*, **589**, 91 (1954).

(11) P. Binger and R. Köster, *Tetrahedron Letters*, 156 (1961).

TABLE IV
REACTIONS OF ALLYLIC CHLORIDES WITH LITHIUM ALUMINUM HYDRIDE IN DIETHYL CARBITOL AT $\sim 100^\circ$

Allylic chloride	Yield, ^a %	Proportions of hydrocarbons produced—		
		$(\text{CH}_3)_2\text{C}=\text{CHCH}_3$	$(\text{CH}_3)_2\text{CHCH}=\text{CH}_2$	$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$
$(\text{CH}_3)_2\text{CClCH}=\text{CH}_2^b$	82	79.6	14.3	0.1
$(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{Cl}^c$	89	97.8	1.8	0.04
		$\text{CH}_3\text{CH}=\text{CH}$	$\text{CH}_3\text{CH}_2\text{CH}_3$	
$\text{CH}_2=\text{CHCH}_2\text{Cl}$	23	90.4	9.6	0.01
	73	99.0	1.0	0.02

^a Yield of hydrocarbons. ^b A trace of 2-methyl-1-butene and 6% isoprene were also obtained. ^c 2-Methyl-1-butene (0.4%) was also obtained.

methyl-1-butane- d_2 in 100° runs, the route $\text{II} \rightarrow \text{XI} \rightarrow \text{VIII} \rightarrow \text{IX}$ appears to be the most probable one for its formation.

Experiments with lithium aluminum deuteride confirmed the formulation in Chart I; however, none of the deuterated hydrocarbons in this series was synthesized for comparison so the results are less certain. Mass spectra showed the proper number of deuterium atoms for each product. Infrared and n.m.r. spectra established the structure of 2-methyl-2-butene-3,4- d_2 for the product corresponding to V and supported the structure 3-methyl-1-butene-1,2- d_2 for the product corresponding to VI. It was not possible to deduce the positions of deuterium atoms from the infrared spectrum of the 2-methylbutane- d_3 .

A number of experiments was carried out in diglyme, a considerably better solvent than diethyl carbitol for lithium aluminum hydride. The same products were obtained, but the proportions were different. The scatter in relative proportions was considerable in most runs under comparable conditions with either solvent and no attempt was made to interpret the trends that are suggested by the figures in Table I. Higher proportions of 3-methyl-1-butyne were always observed in diglyme but this might be due to increase of displacement relative to addition or to slower removal of the alkyne by further addition. Filtered solutions (runs 17 and 19) appeared to behave about the same as unfiltered (run 18); in most runs part of the reagent was present as a suspension. In parallel experiments (runs 20 and 21) addition of lithium aluminum hydride solution to the chloride was compared with the more usual addition of chloride to hydride; the proportions of products were very similar.

The allylic isomers 3-chloro-3-methyl-1-butene and 1-chloro-3-methyl-2-butene were dehalogenated with lithium aluminum hydride to see if cyclopropane derivatives were formed, but none could be detected. However, with allyl chloride very small amounts of cyclopropane were found. Table IV summarizes the results. These experiments show that displacement occurs almost to the exclusion of addition with these active halides.

The 3-carbon halides behaved quite differently from the 5-carbon. Displacement of halogen was much more important than addition and gave propyne as the main product from both acetylenic and allenic halides. With propargyl chloride the propyne:allene ratio was 2.1:1 (with the bromide it was >50)². With bromoallene the propyne:allene ratio was even larger if the temperature was not above 50° , but at 100° the main product was propane; chloroallene gave even more propane at 100° . Experiments designed to show whether propane

arose by addition to the propyne produced have not yet been performed. These results suggest that the haloallenes react by an $\text{SN}2'$ process but that an ordinary $\text{SN}2$ process is more important with propargyl chloride or bromide. Other mechanisms have not been ruled out however.

In order to compare the zinc-copper couple with lithium aluminum hydride as a reagent for dehalogenation of substituted propargyl halides, the former was employed with 3-chloro-3-methyl-1-butyne as described previously² and the hydrocarbons (80% yield) analyzed by g.l.c. The product consisted of 98.8% 3-methyl-1,2-butadiene, 0.3% 3-methyl-1-butyne, 0.8% 3-methyl-1-buten-3-yne, and 0.1% isoprene (presumably from impurity in the starting chloride).

Synthesis of aliphatic allenic hydrocarbons by the classical method¹² is somewhat tedious and dehalogenation of substituted propargyl halides $\text{RR}'\text{CXC}\equiv\text{CR}''$ (R , R' , and $\text{R}'' = \text{H}$ or alkyl) is potentially much simpler. To be useful it is necessary that rearrangement be the principal reaction and that other products be readily removable. From the information available it appears that the method is mainly useful with tertiary and secondary propargyl halides, $\text{RR}'\text{CXC}\equiv\text{CH}$ and $\text{RHCXC}\equiv\text{CH}$, and that zinc-copper couple is the reagent of choice. With 3-chloro-3-methyl-1-butyne it gives an excellent yield of 3-methyl-1,2-butadiene and the impurities have acetylenic hydrogens so that removal by acetylide formation is practical. By contrast, lithium aluminum hydride gives olefins and saturated hydrocarbons as impurities; these may be very difficult to remove. For example, 3-methyl-1,2-butadiene boils at 40° and 2-methyl-2-butene at 38.5° (other C_6H_{10} isomers boil lower and should be removable by careful distillation). Run 25, Table II, indicates that tetrahydrofuran is a superior solvent for this dehalogenation because it yields lower percentages of olefins and isopentane. This solvent was originally chosen by Bailey and Pfeifer¹³ for this reaction. We found, however, that several per cent of tetrahydrofuran remained in the 3-methyl-1,2-butadiene even after careful fractional distillation through a 3-ft. center-rod column; possibly an azeotropic mixture is formed by these compounds. 3-Bromo-3-methyl-1-butyne gave a very high yield of 3-methyl-1,2-butadiene with lithium aluminum hydride, but the pure starting bromide was not obtained in good yield.⁴ Possibly triphenyl phosphite dibromide¹⁴ would yield such tertiary propargyl bromides in good yield. Both zinc-copper couple

(12) M. Bouis, *Bull. soc. chim. France*, [4] **41**, 1160 (1927); *Ann. chim.*, [10] **9**, 402 (1928).

(13) W. J. Bailey and C. R. Pfeifer, *J. Org. Chem.*, **20**, 95 (1955).

(14) D. K. Black, S. R. Landor, A. N. Patel, and P. F. Whiter, *Tetrahedron Letters*, No. **8**, 483 (1963).

and lithium aluminum hydride gave mixtures of an allene and an acetylene with secondary propargyl halides, $\text{RCHXC}\equiv\text{CH}$ ^{2,15,16}; the ratio of allenic to acetylenic product was always larger with the former than with the latter.

Other reagents for dehalogenation may well prove to be superior to either of those discussed above. One which has been examined to some extent is formation and hydrolysis of Grignard reagents; however, this does not appear to be more promising.

Experimental

Infrared spectra were obtained on a Perkin-Elmer Model 21 spectrophotometer or a Beckman IR-4 (lithium fluoride optics); n.m.r. spectra were generally determined on a 40-Mc. instrument (carbon tetrachloride solutions, usually 5-7%) but a few were obtained on a Varian A-60. Mass spectra were obtained on a Consolidated Electrodynamic instrument, Model 21-621, equipped with an isotope ratio accessory and a 4-cycle logarithmic recorder; a few were obtained on a Model 21-620. Cracking patterns in the form of relative intensities at each mass number (most intense peak as standard) for the hydrocarbons and deuterated hydrocarbons involved are available in the original thesis.¹⁷

Vapor phase chromatograms were obtained on an apparatus assembled from standard parts but arranged for temperature control of columns. The probable error in determinations was estimated to be less than $\pm 0.7\%$ in most cases.

Reaction of 1-Chloro-3-methyl-1,2-butadiene (I) with Lithium Aluminum Hydride.—Compound I was synthesized as reported earlier.^{2,18} The following are typical examples of the reduction methods used.

Method A; Run 2.—Lithium aluminum hydride (4.6 g., 0.121 mole) was ground to a powder (caution) and added to 100 ml. of dry diethyl carbitol in a 250-ml. three-necked flask. The flask was equipped with an addition funnel, stirrer, and a condenser which was connected to a Dry Ice trap. The reaction vessel was cooled in ice, and 10.8 g. (0.105 mole) of I was added dropwise during a period of 0.5 hr. (With larger runs it was sometimes observed that the reaction was very exothermic during the addition stage.) The system was then heated on a steam bath for 3 hr., with stirring. The pressure on the system was reduced to 100 mm. in order to collect any volatile materials in the trap. However, only a drop or two of material was observed. The trap was replaced by a clean one, and the reaction mixture hydrolyzed with 100 ml. of 1.5 *N* hydrochloric acid. The reaction vessel was again cooled with ice, the pressure was reduced, and the volatile products collected in the Dry Ice trap along with a small amount of water; yield 4.8 g., 69.9%.

Attempts were made to isolate volatile material before hydrolysis only in runs 1, 2, 9, and 23.

Method B; Run 6.—Lithium aluminum hydride (1.28 g., 0.0348 mole) was wrapped in heavy aluminum foil and crushed with a hammer. The powdered hydride was added to 25 ml. of dry diethyl carbitol in a 100-ml. four-necked flask. The flask was equipped with an addition funnel, stirring motor, serum cap, and Dry Ice condenser. The glassware was baked out in an oven at 170° for several hours, and was allowed to cool in a vacuum desiccator before assembly. The reduction was carried out under an atmosphere of dry nitrogen. Compound I (3.0 g., 0.0293 mole) was dissolved in 10 ml. of dry diethyl carbitol, and added to the reaction mixture dropwise during the period of 0.5 hr. The reaction flask was heated with an oil bath which was maintained between 98-103° during the period of addition and for the subsequent 3-hr. reaction time. The oil bath was removed and the reaction flask allowed to cool to room temperature. Hydrolysis was accomplished by the addition of 4 ml. of 3% hydrochloric acid dropwise through the serum cap. The volatile products were driven into the Dry Ice trap by heating the reaction vessel with an open flame. In this manner some water and diethyl

carbitol were collected along with the desired product. In the usual procedure 25 ml. of *n*-decane was added to the trap contents. The trap was cooled sufficiently to freeze the water, and the *n*-decane and products removed by means of a micro eyedropper. The solution was distilled through a very small simple distillation apparatus. The chilled hydrocarbons were transferred to a vial with a micro eyedropper, and weighed; yield 1.82 g., 88.8%.

A number of liquid phases for g.l.c. were examined for their ability to separate the mixture of hydrocarbons. A 15-ft. tetraiso-butylene column (25% on 60-80 mesh Chromosorb W) was most convenient for the 5-carbon series. An 8-ft. didecyl phthalate column (25% on 60-80 mesh, acid-washed firebrick) was also useful. With these columns any mixture of hydrocarbons in the iso-5-carbon system can be determined. A 20-ft. dimethyl sulfolane column (30% on 60-80 mesh, acid-washed firebrick) worked well except that 1,1-dimethylcyclopropane and 3-methyl-1-butene were not separated. This column was the most effective of those tried for separation of the three carbon compounds: g.l.c. separation of all of these hydrocarbons was done at room temperature.

No 3-methyl-1,2-butadiene was detected in any of the dehalogenations of I. As little as 0.1% could have been detected in most instances. Small amounts of isoprene and 2-methyl-1-butene were found in some runs. These were believed to result from impurities which developed in I on storage. Freshly distilled samples of this chloride usually gave neither hydrocarbon.

In runs 4, 5, 8, 9, and 11 the reaction mixture was outgassed under vacuum before hydrolysis, which was carried out by addition of 2 *N* deuterium chloride in deuterium oxide. Lithium aluminum deuteride (97% pure) was used in runs 7 and 22.

The results of all runs with I are recorded in Table I.

Compounds for Comparison with Reaction Products.—The following were obtained from the Phillips Petroleum Co.: isoprene (polymerization grade), 2-methyl-1-butene (pure grade), and 2-methyl-2-butene (pure grade). 2-Methylbutane was prepared by catalytic hydrogenation of isoprene; g.l.c. showed the sample to be essentially 100% pure.

3-Methyl-1-butyne was prepared from 3-methyl-1-butene (Matheson) by addition of bromine and dehydrobromination with sodamide in liquid ammonia. 2-Methyl-1-buten-3-yne was prepared by sulfuric acid dehydration of 2-methyl-3-butyne-2-ol (Air Reduction Chemical Co.). 1,1-Dimethylcyclopropane was prepared from isobutylene (Matheson) with iodomethylenezinc iodide.¹⁹

The reactions of 3-chloro-3-methyl-1-butyne, propargyl chloride, chloroallene, and bromoallene with lithium aluminum hydride were carried out as for I. Results are recorded in Tables II and III. The 20-ft. dimethyl sulfolane column was used for g.l.c. analysis of the products in the 3-carbon system. 3-Chloro-3-methyl-1-butyne is more stable to storage than I; the impurity observed in g.l.c. analysis of the reaction products was 2-methyl-1-butene and probably resulted from impurity not removed from the starting material.

Propargyl chloride was obtained as a gift from the General Aniline and Film Corp. It was converted to chloroallene by rearrangement on solid potassium hydroxide with shaking.²⁰ Purification was accomplished by g.l.c. (6-ft. preparative didecyl phthalate column) although later work has shown that careful fractional distillation gives pure material. Bromoallene was prepared similarly from propargyl bromide (General Aniline and Film Corp.), but the cuprous bromide rearrangement²¹ is better for this compound. Propyne was obtained from the Air Reduction Chemical Co., cyclopropane from Matheson, and propane and propylene from Phillips (reagent grade). Allene was supplied by R. N. Johnson.¹⁶

Synthesis of the various deuterated olefins and saturated hydrocarbons needed for comparison with products of the lithium aluminum hydride reactions was accomplished by conventional procedures. The methods used and the properties of the products are detailed below.

1-Chloro-3-methyl-2-butene and 3-chloro-3-methyl-1-butene were prepared by addition of hydrogen chloride to isoprene at -78°. Careful fractional distillation at reduced pressure through a 5-ft. column filled with tantalum Heli-Pac gave 3-

(15) J. H. Wotiz, *J. Am. Chem. Soc.*, **73**, 693 (1951).

(16) T. L. Jacobs and R. N. Johnson, *ibid.*, **82**, 6397 (1960).

(17) "Dehalogenation Reactions of Propargyl and Allenyl Halides," R. D. Wilcox, Ph.D. Dissertation, University of California, Los Angeles, Calif., Jan., 1962.

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

(19) H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959).

(20) The details of this rearrangement will be published shortly.

(21) T. L. Jacobs and W. F. Brill, *J. Am. Chem. Soc.*, **75**, 1314 (1953).

chloro-3-methyl-1-butene, b.p. 32.5° (129 mm.), and 1-chloro-3-methyl-2-butene, b.p. 61.5–61.9° (129 mm.), in agreement with earlier values.²² The tertiary isomer contained small amounts of isoprene which did no harm for present uses. This survived the reaction with lithium aluminum hydride and was detected among the products reported in Table IV.

2-Methyl-2-butene-4-*d*₁ (V) and 3-Methyl-1-butene-3-*d*₁ (VI).—3-Chloro-3-methyl-1-butene was allowed to react with magnesium in tetrahydrofuran in the cyclic reactor²³ and the Grignard reagent decomposed with deuterium oxide. Distillation gave a mixture of the desired olefins which was freed from solvent (Hyprose monostearate column) and separated (tetraisobutylene column) by g.l.c. The mass and infrared spectra of V and VI were the same as samples from runs 5 and 11. In the infrared V had C–D bands at 2209 and 2169 cm.⁻¹; VI had bands at 2170, 2138, and 2098 cm.⁻¹.

2-Methyl-2-butene-3-*d*₁ and 3-Methyl-1-butene-2-*d*₁.—3-Methyl-2-butanone (Eastman white label) was found to be quite impure and was purified through the semicarbazone. Reduction with lithium aluminum deuteride (20% excess) in ether under nitrogen gave 3-methyl-2-butanol-2-*d*₁ which was converted to a tosylate with *p*-toluenesulfonyl chloride in pyridine. The crude product solidified when cooled to –16° and was recrystallized from pentane. The undeuterated tosylate was reported²⁴ to melt at 20.1–20.8°; a m.p. was not taken on the deuterio isomer but it did not melt in an Abderhalden drying pistol under reduced pressure at 19°. The material was left for 4 hr. at reduced pressure; longer evacuation sometimes gave desotylation.

*Anal.*²⁵ Calcd. for C₁₁H₁₇DSO₃: C, 59.20; H, 7.86; excess D, 5.56 atom %. Found: C, 59.25; H, 7.50; excess D, 5.37 atom % (corresponds to 96.6% of theor. deuterium content; lithium aluminum deuteride contained about 97% of theory).

The tosylate was heated in 2,6-lutidine to give an 83% yield of olefins which were separated by g.l.c. Relative magnitudes of the mass spectral peaks in the parent ion region indicated that deuteration was as complete as in the starting tosylate. Cracking patterns were clearly different from those of V and VI. The infrared spectra were also different; the C–D spectrum of 3-methyl-1-butene-2-*d*₁ was characterized by a sharp peak at 2222 cm.⁻¹ and that of 2-methyl-2-butene-3-*d*₁ by one at 2228 cm.⁻¹.

2-Methylbutane-4,4-*d*₂ (X).—Commercial isovaleraldehyde was contaminated by large amounts of two alcohols. A purified sample²⁶ was reduced with lithium aluminum deuteride (97%) in ether to yield 3-methyl-1-butanol-1-*d*₁ which was purified on a Beckman Megachrom column (liquid phase, polyethylene glycol-400). The alcohol had C–D absorption in the infrared at 2164 cm.⁻¹ and C–H at 2960, 2935, and 2880 cm.⁻¹.

The deuterated alcohol was converted to a tosylate (an oil) by *p*-toluenesulfonyl chloride in pyridine and the tosylate was reduced with lithium aluminum deuteride in tetrahydrofuran after careful drying with molecular sieve. The product was partially freed from solvent by distillation, the rest of the solvent was removed by g.l.c. (Hyprose monostearate column), and further purification effected on a tetraisobutylene column. The mass spectrum of X was similar to that of the deuterated 2-methylbutane from run 8, but not identical. The infrared spectra of the two samples were very similar; synthetic: C–D, 2210, 2182, 2126; C–H, 2965, 2935, 2907, 2872, 2858 cm.⁻¹; run 8: C–D, 2214, 2175, 2125; C–H, 2960, 2930, 2907, 2872, 2858 cm.⁻¹.

The 2-methylbutane-*d*₂ from run 8 was photobrominated²⁷ in carbon disulfide (Pyrex flask, illumination with a pair of 200-watt clear tungsten bulbs placed 1 in. from the reaction vessel), solvent removed, and the product dehydrobrominated with excess 2,6-lutidine (short reaction period with shaking); the olefins were isolated by distillation. 2,6-Lutidine was removed from product by g.l.c. (Hyprose monostearate column) and the olefins were

separated on the tetraisobutylene column. The only products that appeared on the chromatogram were 2-methyl-2-butene, 2-methyl-1-butene, and a trace of the starting 2-methylbutane.

The mass spectrum of the 2-methyl-1-butene indicated a molecular weight of 72 (dideuterated product), but the rest of this product was accidentally lost. The 2-methyl-2-butene also showed a molecular weight of 72, but a small amount of monodeuterated material may also have been present. The following infrared bands were observed: 3060 w, 3043 w, 2977, 2930, 2920, 2887, 2860, 2225 w, 2192 w, 2170 w, and 2141 cm.⁻¹. The band at 2225 lies close to the 2228 band of 2-methyl-2-butene-3-*d*₁ and the 2222 band of 3-methyl-1-butene-2-*d*₁. This can be attributed to the presence of deuterium on the double bond and would not be expected from an olefin derived in this way from either X or XV. However, this band is very weak in the 2-methyl-2-butene from the photobromination sequence but strong and sharp in the other olefins cited.

The n.m.r. spectrum showed a vinyl hydrogen and a methyl peak split by about 5 c.p.s. (at 60 Mc.). The sample was unfortunately too dilute to observe fine structure in the vinyl hydrogen or to obtain an accurate vinyl hydrogen:methyl hydrogen ratio.

These experiments show that X is the main 2-methylbutane-*d*₂, but do not give conclusive evidence on the nature of the isomeric contaminants. The weak infrared band at 2225 cm.⁻¹ favors 2-methylbutane-3,4-*d*₂ (XIV) as one of these.

Other 2-methylbutane-*d*₂ isomers were synthesized in an attempt to learn more about the contaminants.

2-Methylbutane-3,4-*d*₂ (XIV) was prepared by reduction of 1,2-dibromo-3-methylbutane with lithium aluminum deuteride in diethyl carbitol. 3-Methyl-1-butene was the main product along with 2-methyl-2-butene and the desired dideuterioalkane. The latter was isolated by g.l.c. (tetraisobutylene column). Although the cracking pattern was somewhat like that of X and of 2-methylbutane-*d*₂ from run 8 it exhibited enough differences to indicate that XIV was not the major component in the latter. The C–D bands in the infrared were observed at 2170, 2140, and 2132 cm.⁻¹. These were of low intensity compared with isomeric 2-methylbutane-*d*₂ isomers. Thus XIV is the isomer which would be hardest to detect in a mixture containing mainly 2-methylbutane-4,4-*d*₂.

2-Methylbutane-2,4-*d*₂ (XV) was prepared by deuterolysis of the Grignard reagent from 2-chloro-2-methylbutane-4-*d*₁ in tetrahydrofuran; the chloride was prepared by addition of hydrogen chloride to V and was purified by g.l.c. (Hyprose monostearate column). Compound XV was separated from solvent and purified by g.l.c. Its cracking pattern and infrared spectrum were different from those of the 2-methylbutane-*d*₂ from run 8. Characteristic C–D peaks in the infrared were observed at 2170, 2138, and 2109 cm.⁻¹. The 2138 band should have been especially easy to detect had XV been present in more than very small amounts in the 2-methylbutane-*d*₂ from run 8.

2-Methylbutane-3,3-*d*₂ was prepared from the tosylate of 3-methyl-2-butanol-2-*d*₁ (described above) by reaction with lithium aluminum deuteride in tetrahydrofuran. Traces of pentane from recrystallization of the tosylate were present because the tosylate could not be left under reduced pressure long enough; these were removed by solution of the tosylate in cyclohexane and evaporation of the solution to dryness at reduced pressure (done twice). Removal of all of the pentane was necessary because it contained small amounts of 2-methylbutane that could not be removed later. The pure tosylate was finally dissolved in tetrahydrofuran and dried for a day with molecular sieve (stirring). The solution was shown to be free from 2-methylbutane by g.l.c.; g.l.c. purification of the 2-methylbutane-3,3-*d*₂ as for the other isomers gave pure material for which the mass and infrared spectra were different from those of the isomer from run 8. The characteristic C–D frequencies in the infrared were found at 2203, 2170, and 2101 cm.⁻¹.

2-Methylbutane-2,3-*d*₂ was prepared by deuterolysis of the Grignard reagent from 2-chloro-2-methylbutane-3-*d*₁ in tetrahydrofuran. The chloride was prepared by addition of deuterium chloride to 2-methyl-2-butene. After the usual purification the product was found to have infrared and mass spectra very different from those of the 2-methylbutane-*d*₂ from run 8. Characteristic C–D frequencies were found at 2165, 2147, and 2120 cm.⁻¹.

(22) W. G. Young, S. Winstein, and H. L. Goering, *ibid.*, **73**, 1958 (1951), and references cited there.

(23) The cyclic reactor was a modification of that described by D. C. Rowlands, K. W. Greenlee, and C. E. Boord, Abstracts, 117th National Meeting of the American Chemical Society, Philadelphia, Pa., 1950, p. 81.

(24) S. Winstein and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1120 (1952).

(25) Deuterium analyses by J. Nemeth, Urbana, Ill.

(26) We wish to thank Mr. H. White of the Dow Chemical Co. for donating this material.

(27) G. A. Russell and H. C. Brown, *J. Am. Chem. Soc.*, **77**, 4025 (1955); G. A. Russell, *ibid.*, **80**, 4987 (1958). We are indebted to Professor K. Wiberg, who suggested photobromination for the degradation of the 2-methylbutane.

1,1-Dimethylcyclopropane-2- d_1 (XIX) was not synthesized independently. The infrared spectrum of XIX from run 5 showed C-D bands at 2251 and 2269 cm^{-1} and C-H bands at 3059, 3021, 2994, 2941, 2924, 2880, and 2864 cm^{-1} . The stronger C-D band (2251) is related to the 3021 C-H band by the approximate relationship $\nu_{\text{H}} = 1.35\nu_{\text{D}}$.²⁸ Both of these bands may arise from the ring $>\text{C}<_{\text{D}}^{\text{H}}$ system since the C-H band does not appear in the spectrum of 1,1-dimethylcyclopropane (C-H

bands at 3063, 2994, 2941, 2924, 2909, 2880, and 2864 cm^{-1} ; of these the peaks at 3063 and 2994 appear to be characteristic of cyclopropane compounds). The observed C-D bands are at sufficiently high frequencies to exclude saturated carbon atoms other than methylene in cyclopropane rings as a location for observed deuterium.

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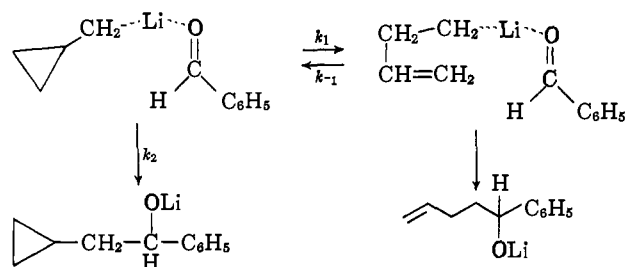
Preparation and Properties of Cyclopropylcarbinylithium¹

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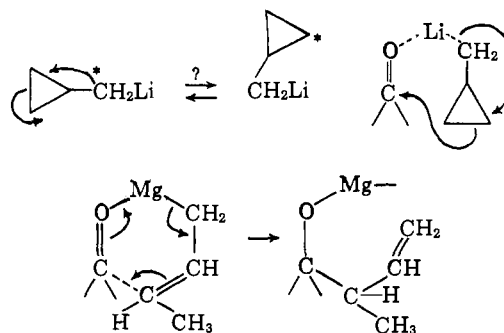
The title compound has been prepared by the lithium-halogen exchange reaction at -70° and subjected to reaction with a number of electrophilic reagents. Cyclopropylcarbinylithium- $\alpha,\alpha\text{-}d_2$ was also generated and found not to undergo isotopic scrambling.

In the course of studies on the organolithium-induced isomerization of benzyl alkyl ethers³ (the Wittig rearrangement) we observed that benzyl cyclopropylcarbinyl ether underwent isomerization mainly to phenylcyclopropylcarbinylcarbinol. This result was of interest since the accepted mechanism^{3,4} of the Wittig rearrangement involves cleavage and recombination, with the migrating group ejected as a carbanion (complexed by lithium ion with the benzaldehyde). Since attempts to generate the cyclopropylcarbinyl anion independent of electrophilic trapping reagents (see below) invariably lead to products containing the allylcarbinyl structure, we needed independent evidence that the unrearranged anion had at least sufficient stability to react intramolecularly with benzaldehyde in the Wittig intermediate at a rate somewhat faster than isomerization ($k_2 > k_1$). Since $k_1 \gg k_{-1}$, k_2 must be very large, for all indications suggest a very



low barrier for cyclopropylcarbinyl to allylcarbinyl interconversion (see below). We have succeeded in preparing cyclopropylcarbinylithium (I) by the low temperature metal-halogen exchange reaction in ether,¹ thus confirming the stability of this species under sufficiently mild conditions, which are comparable to those under which optically-active 2-octyllithium undergoes extensive racemization.⁵ Our initial observations have been extended and here we report conditions even more

suitable for rapid generation of cyclopropylcarbinylithium and its reactions with various electrophilic species to give unrearranged cyclopropylcarbinyl-containing derivatives. In addition, experiments bearing on the question of isotope scrambling of the labeled anion have been carried out. This isomerization could be involved in the collapse of the Wittig intermediate from benzyl cyclopropylcarbinyl ether, by analogy with the formation of α -methylallyl products from the butenyl Grignard reagent.⁶



First, it is worthwhile to review previous studies of carbanionoid cyclopropylcarbinyl systems. Roberts and Mazur⁷ found that products derived from the Grignard reagent of cyclopropylcarbinyl bromide had the allylcarbinyl structure; furthermore, n.m.r. studies of the freshly-prepared Grignard reagent⁸ showed $\geq 99\%$ of the rearranged reagent. Even when the Grignard reagent was generated in the presence of benzoic acid, to trap the initially-formed anion as soon as it is formed, only 6% of methylcyclopropane was isolated, as compared with 92% of 1-butene.⁹ It is also of interest that the deamination of cyclopropylcarbinylamine by either difluoramine or the action of hydroxylamine-O-sulfonic acid in base on the *p*-toluenesulfonyl derivative (Nickon-Sinz reaction) gives exclusively 1-butene,¹⁰ in spite of the fact that the latter procedure

(1) A preliminary communication on this subject has appeared: P. T. Lansbury and V. A. Pattison, *J. Am. Chem. Soc.*, **85**, 1886 (1963).

(2) (a) Alfred P. Sloan Foundation Fellow; (b) supported by a grant from the U. S. Army Research Office (Durham); (c) participant in NSF Research Participation Program for College Chemistry Teachers, summer, 1963.

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