Reaction of Ethyllithium with Aluminum Borohydride.—A solution of 0.403 millimole of ethyllithium in 2.0 ml. of benzene was treated with a slight excess of AlB_3H_{12}, 0.145 millimole. A white precipitate formed immediately. The reaction mixture was permitted to stand at room temperature for several hours to ensure complete reaction. The benzene and all the volatile products were distilled away from the reaction tube. The temperature was then raised to 100° and kept there for two hours in order to remove all traces of even only slightly volatile material.

The white solid remaining in the reaction tube was heated at 200° at 10^{-4} mm. without any noticeable effect. It melted at 270–275°, so there cannot be any doubt that lithium borohydride had been formed. Methyl alcohol was added to the reaction tube: 1.61 millimoles of hydrogen were obtained. The volatile products of the reaction were treated similarly, yielding 0.211 millimole of hydrogen and 0.400 millimole of ethane.

Summing up these results, it appears that a quantitative reaction between the ethyllithium and the aluminum borohydride had occurred: 0.403 millimole of ethyllithium had reacted with 0.135 millimole of $Al(BH_4)_3$ to produce 4.03 millimoles of lithium borohydride and 1.33 millimoles of triethylaluminum.[12]

Summary

1. A compound ($LiBH_4$) is formed by the action of diborane on ethyllithium. Its physical and chemical properties suggest that the compound is a salt with the structure $Li^+BH_4^-$ and the name lithium borohydride is proposed for this substance.

2. Lithium borohydride is stable to dry air, it melts at 275–280° with decomposition, and shows no evidence of volatility at temperatures at which it is undecomposed. Hydrogen chloride reacts to form hydrogen, diborane and lithium chloride. Methyl alcohol forms lithium boromethoxide, $LiB(OCH_3)_4$, and hydrogen. Trimethylamine does not react.

3. Ethyllithium undergoes what appears to be a metathetic reaction with aluminum borohydride in benzene solution: lithium borohydride is precipitated.

4. Ethyllithium adds trimethylboron (1:1 mole ratio) to form a white crystalline solid stable at ordinary temperatures. This substance $LiC_2H_5 \cdot B(CH_3)_3$ appears to be representative of a new class of compound, $M^+(BR_4^-)$.

5. The physical and chemical properties of the lithium, beryllium, and aluminum borohydrides and of diborane are compared and discussed in the light of proposed structures for the compounds.

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[12] Since no attempt was made to isolate or identify any of the products of the reaction with the exception of lithium borohydride, it is possible that the excess aluminum borohydride and the triethylaluminum were not present as such in the volatile products of the reaction. Mixtures of the compounds of the type $C_2H_5Al(BH_4)_2$ would yield the same analytical results.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Reactions of Atoms and Free Radicals in Solution. I. A Study of the Substitution of Hydrogen on an Asymmetric Carbon Atom—The Chlorination of Primary Active Amyl Chloride

BY HERBERT C. BROWN, M. S. KHARASCH AND T. H. CHAO[1]

In the light of present knowledge, it appears that the substitution and displacement reactions of organic chemistry fall into two distinct groups: reactions that proceed by means of (A) an ionic or polar mechanism, and (B) atomic or free radical intermediates.

$$\text{(A)}\quad X\!:\, + \,Y\,|\!:\!Z \longrightarrow X\!:\!Y + Z\!:$$

$$\text{or}\quad W\!:\!|\,X + Y\,|\!:\!Z \longrightarrow W\!:\!Y + X\!:\!Z$$

$$\text{(B)}\quad X\cdot + Y.\!:\!'\,Z \longrightarrow X\!:\!Y + Z\cdot$$

Reactions involving bond scissions of the type indicated in A have been studied exhaustively from the standpoint of both synthetic utilization and reaction mechanisms.[2] The hypothesis that reactions in solution may proceed by way of an atomic or free radical mechanism, as indicated in B, has not as yet been comparably developed. Indeed, until very recently, the photochemical halogenation of organic substances was the only reaction commonly accepted as belonging to that class.

However, the number of examples bids fair to increase rapidly. Specifically, the addition of hydrogen bromide,[3] mercaptans[4] and sodium bisulfite[5] to olefins, the peroxide-catalyzed chlorination of aliphatic compounds with sulfuryl chlo-

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[1] Eli Lilly Fellow, 1939–1940.

[2] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, Chapters V and VI.

[3] Kharasch and Mayo, THIS JOURNAL, **55**, 2468 (1933); Kharasch, Engelmann and Mayo, *J. Org. Chem.*, **2**, 288, 400 (1937).

[4] Kharasch, Hammond, Melof and Mayo, unpublished work; Kharasch, Read and Mayo, *Chem. and Ind.*, **57**, 752 (1938).

[5] Kharasch, May and Mayo, *J. Org. Chem.*, **3**, 175 (1938); Kharasch, Schenck and Mayo, THIS JOURNAL, **61**, 3092 (1939).

ride,[6] the photochemical sulfonation of aliphatic hydrocarbons and acids with the same reagents,[7] and the photochemical and peroxide-catalyzed carboxylation of paraffin hydrocarbons with oxalyl chloride[8] have been shown to have characteristics commonly ascribed to chain reactions, and probably proceed through atomic and free radical intermediates.[9]

In spite of these recent developments, knowledge of the chemical properties of atoms and free radicals in solution and of the reaction mechanisms involving these reactive intermediates is extremely meager. Therefore, this Laboratory has undertaken a series of investigations of the chemical properties of atoms and free radicals in solution and of the stereochemical aspects of reactions involving these intermediates.

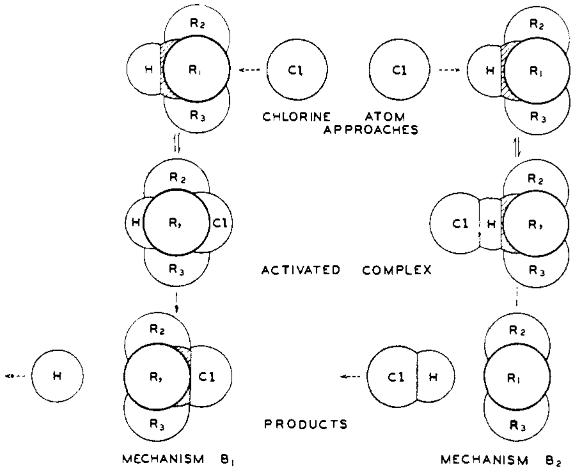


Fig. 1.—Possible mechanisms for the reaction of a chlorine atom with a hydrocarbon. In the above diagram the free radical (Mechanism B_2) has been represented as planar. The argument is not affected if the free radical retains a pyramidal configuration in which the carbon atom undergoes rapid oscillation through the plane of the three substituents.

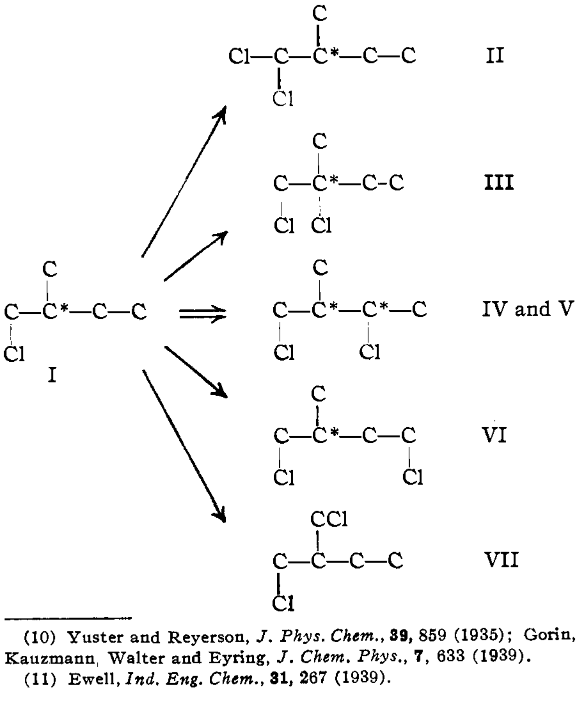
One of the oldest and simplest of the atomic reactions is the photochemical (or peroxide-catalyzed) chlorination of a hydrocarbon. Yet no experimental evidence is available to permit a choice to be made between the two possible mechanisms, B_1 and B_2, which have been suggested for this reaction.

Mechanism B_1	Mechanism B_2
$Cl_2 \rightleftarrows 2Cl\cdot$	$Cl_2 \rightleftarrows 2Cl\cdot$
$Cl\cdot + RH \longrightarrow RCl + H\cdot$	$Cl\cdot + RH \longrightarrow R\cdot + HCl$
$H\cdot + Cl_2 \longrightarrow HCl + Cl\cdot$	$R\cdot + Cl_2 \longrightarrow RCl + Cl\cdot$

It is true that mechanism B_2 might be expected to have the lower activation energy,[10] and would appear, on that basis, the more probable. It would be unjustifiable, however, to reject mechanism B_1 on *a priori* grounds until more definite information is available concerning the actual mechanics of the approach of the chlorine atom to the hydrocarbon molecule. The two possible methods of approach of a chlorine atom to the asymmetric carbon atom of an optically active hydrocarbon in a direction collinear with the tertiary carbon-to-hydrogen bond are illustrated in Fig. 1.[11]

The substitution of chlorine for hydrogen on the asymmetric carbon atom of an optically active compound by mechanism B_1 would result in Walden inversion with retention of optical activity. The reaction according to mechanism B_2 should yield an inactive (*dl*) product if a free radical with an appreciable half-life period is formed. The question thus posed was attacked experimentally through a study of the photochemical and peroxide-catalyzed chlorination of primary active amyl chloride [(+)1-chloro-2-methylbutane].

The introduction of a second atom of chlorine into active amyl chloride (I) makes possible six isomers (II–VII).



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(6) Kharasch and Brown, THIS JOURNAL, **61**, 2142, 3432 (1939); **62**, 925 (1940).

(7) Kharasch and Read, *ibid.*, **61**, 3089 (1939); Kharasch, Chao and Brown, *ibid.*, **62**, 2393 (1940).

(8) Kharasch and Brown, *ibid.*, **62**, 454 (1940); Kharasch, Kane and Brown, unpublished work.

(9) For a recent review of the peroxide effect, see Smith, *Ann. Rept.*, **36**, 219 (1939).

(10) Yuster and Reyerson, *J. Phys. Chem.*, **39**, 859 (1935); Gorin, Kauzmann, Walter and Eyring, *J. Chem. Phys.*, **7**, 633 (1939).

(11) Ewell, *Ind. Eng. Chem.*, **31**, 267 (1939).

TABLE I

PHYSICAL CONSTANTS OF (+)1-CHLORO-2-METHYLBUTANE AND ITS DICHLORO DERIVATIVES[a]

	B. p. °C.	at mm.	$[\alpha]_D$	n_D	d_4
1-Chloro-2-methylbutane (I)	*100.45*	*760*^{b}	*+1.68*^{20b}	*1.4124*^{20b}	*0.8875*^{20b}
	43	100	+1.65^{23}	1.4123$^{23.5}$	*0.8852*^{20c}
	(100	760)			0.8855^{20}
1,2-Dichloro-2-methylbutane	*133–135*^{d}				*1.0785*^{d}
(III)	71.5	100	+0.05^{23}	1.4432$^{23.5}$	1.0766^{20}
	(133.5	760)			
1,1-Dichloro-2-methylbutane	76 ± 2	100			
(II)	(138 ± 2	760)	(+2.2^{23})^e	(1.439$^{23.5}$)^e	(1.083^{20})^e
1,3-Dichloro-2-methylbutane (−)	*53–54*	*19*^{f}		The closeness of boiling points of these isomers prevented their separation and the determination of their constants. The values for $[\alpha]_D$ listed for IV and V were merely the highest obtained for fractions rich in these isomers and are not to be considered as values for the pure compounds.	
(IV)	(*156–157*	*760*)^f			
	89.2	100	−7.05^{23}		
	(153	760)			
1,3-Dichloro-2-methylbutane (+)	*53–54*	*19*^{f}			
(V)	(*156–157*	*760*)^f			
	91	100	+5.70^{23}		
	(155	760)			
1-Chloro-2-chloromethylbutane	89–91	100			
(VII)	(153–155	760)			
1,4-Dichloro-2-methylbutane	*50*	*12*^{g}	*+9.73*^{21g}		*1.103*^{21g}
(VI)	*170–172*^{h}				
	101–102	100	*−9.7*^{23}	1.4562^{21}	1.1003$^{24.5}$
	(168–169	760)			

[a] Values reported in literature are indicated by italics. Values calculated from experimental data are indicated by parentheses. [b] Brauns, *J. Research Natl. Bur. Standards*, **18**, 315 (1937). [c] Whitmore and Olewine, THIS JOURNAL, **60**, 2570 (1938). [d] Chalmers, *Trans. Roy. Soc. Can.*, [3] **22**, Sec. III, 69 (1928). [e] These values have been calculated from the constants of fraction No. 7 on the basis that it consists of 60:40 mixture of III and II as indicated by hydrolysis experiments (Fig. 3). [f] Tischtschenko, *J. Gen. Chem.* (U. S. S. R.), **6**, [68], 1116 (1936). [g] Braun and Jostes, *Ber.*, **59B**, 1091 (1926). [h] Perkin, *Chem. Zentr.*, **83**, II, 1210 (1912).

For the purpose of the present investigation it was, of course, essential to isolate the 1,2-dichloro derivative (III), and to establish whether or not optical activity had been retained. It was found possible to separate this isomer from the others by careful fractionation (fractions 2–4, Fig. 2). The optical inactivity of the product[12] indicates that the substitution of hydrogen by chlorine in aliphatic hydrocarbons by a reaction of the atomic type proceeds through mechanism B_2.

The study of the other products formed in the chlorination was not without interest. Of the six possible dichloro derivatives, four (III, VI, and an inactive mixture of IV and V) have been previously described, and their reported boiling points (Table I) correspond fairly well with the three plateaus in the rectification curve (Fig. 2). The other isomers (II and VII) have not been reported.

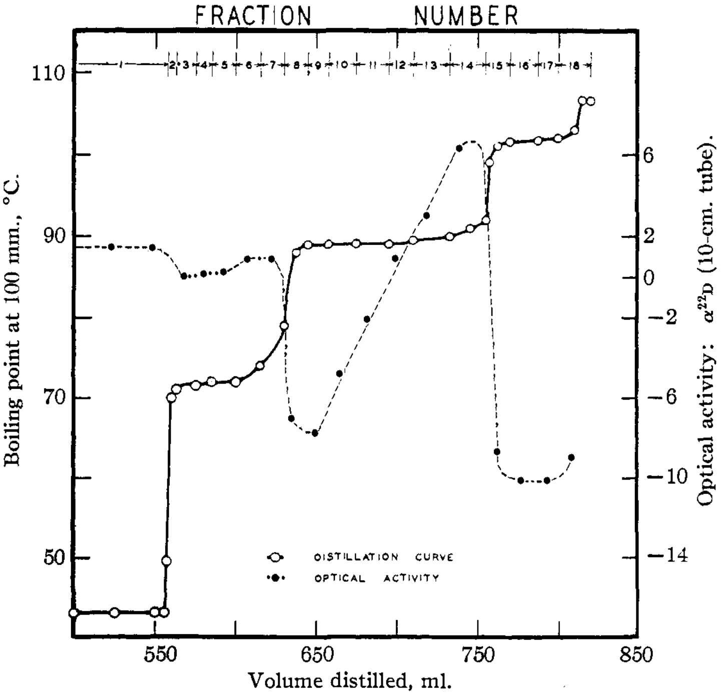

Fig. 2.—Distillation curve of product obtained by the chlorination of primary active amyl chloride with sulfuryl chloride and peroxides at 80°.

Examination of the properties of each of the

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(12) The slight activity exhibited by these fractions (+0.05, +0.18, +0.22; Fig. 2) is due to small quantities of the active 1,1-dichloro isomer (II).

fractions obtained in the distillation has led the authors to the following conclusions: 1. The first plateau in the fractionation curve corresponds to inactive (*dl*)1,2-dichloro-2-methylbutane (III) with gradually increasing amounts of the active (+)1,1-dichloro isomer (II). 2. The second plateau represents the two diameric 1,3-dichloro-2-methylbutanes (IV and V) and the inactive 1-chloro-2-chloromethylbutane (VII). It is interesting that these diastereoisomers could be partially separated by distillation. 3. The third plateau represents the pure (−)1,4-dichloro derivative (VI). The identity of this substance was established definitely by its physical constants. The rotation exhibited by this substance (after refractionation of fractions 15–18), $[\alpha]^{20}_{\mathrm{D}}$ −9.7, indicated that it must be the enantiomorph of the known (+)1,4-dichloro-2-methylbutane, $[\alpha]^{20}_{\mathrm{D}}$ +9.73, prepared previously from (+)*d*-β-methyladipic acid.[13]

The presence of the 1,2-dichloro isomer (III) in these fractions, 2–6, was confirmed by a comparison of the hydrolysis of these fractions with that of 1,2-dichloro-2-methylpropane in 80% alcohol.[14] As shown in Fig. 3, the hydrolysis of both substances proceeds as a first-order reaction with velocities of the same order of magnitude. In both cases, hydrolysis appears to involve chiefly the tertiary chlorine atom, since the reaction practically ceases after 50% of the total halogen has been hydrolyzed.

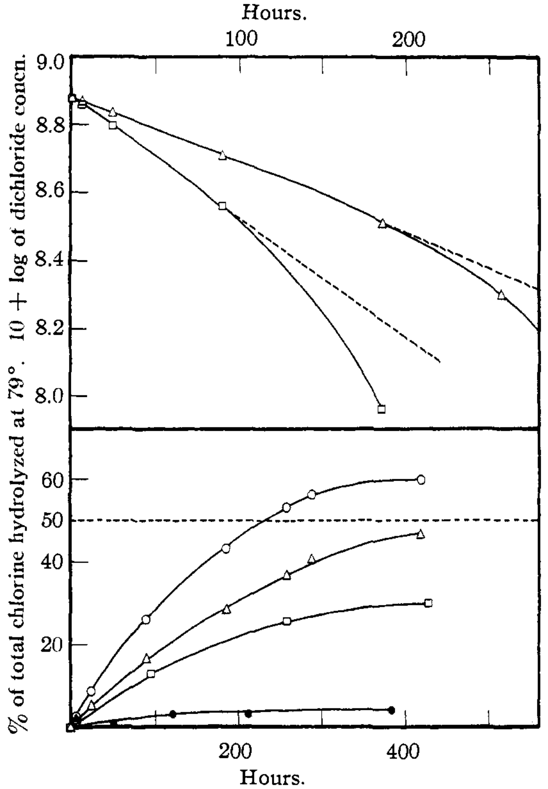

Fig. 3.—Hydrolysis of dichloro derivatives in 80% alcohol: O, 1,2-dichloro-2-methylbutane; △, 1,2-dichloro-2-methylpropane; □, fraction no. 7 (mixture of 1,2-dichloro- and 1,1-dichloro-2-methylbutane); ●, 1,1-dichloroethane.

The conclusion that the slight optical activity exhibited by these fractions is due to varying amounts of the active 1,1-dichloro isomer (II) is supported by the observation that the activity of the more volatile fractions decreases with the efficiency of the fractionation, although the total activity of all the fractions is not altered (*i. e.*, no racemization of an active product occurs in the process of fractionation). Furthermore, it may be observed that the quantity of halogen hydrolyzed in a given time (*i. e.*, tertiary halogen possible only in the 1,2-dichloro isomer) is less for the sample of higher optical activity (curve O, Fig. 3).

The chlorination of primary active amyl chloride (I) was also carried out photochemically with gaseous chlorine, great care being taken to prevent racemization during the isolation of the product. Since the results substantially support the conclusions already reached, they need be described but briefly (see experimental part).

An incidental product of the present investigation may be of some general interest. It has been shown that if the assumption be made that (+)2-methyltetramethylene glycol (IX) has the same configuration as (+)primary active amyl alcohol (VIII), then the configuration of the latter can be related to that of (+)methylsuccinic acid, *d*(+)β-methyladipic acid (X), (+)citronellal and a host of other natural products.[15] The fact that the (−)1,4-dichloro-2-methylbutane (VI) obtained in this investigation from the (−) primary active amyl alcohol (XII) found in fusel oil is the enantiomorph of the (+)1,4-dichloro derivative (XI) previously prepared from *d*-(+)β-methyladipic acid (X) supports the argument.

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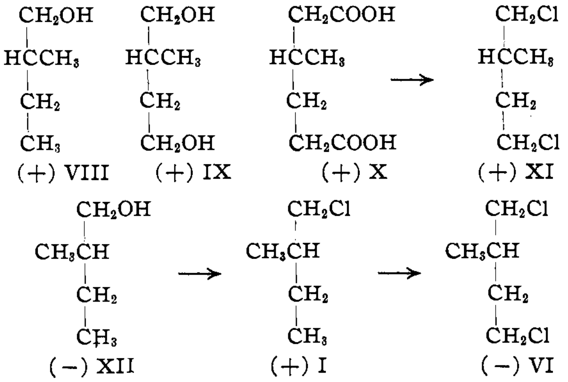
[13] Braun and Jostes, *Ber.*, **59**, 1091 (1926).

[14] Because the 1,2-dichloro derivative proved to be suprisingly inert, the simple method of analysis for tertiary halogen (Michael and Leupold, *Ann.*, **379**, 287 (1911)) could not be applied. The inertness of 1,2-dichloro derivatives of this type may be judged from the fact that the hydrolysis of 1,2-dichloro-2-methylpropane in 80% alcohol is slower than the hydrolysis of 2-chloro-2-methylpropane by a factor of approximately 4000.

[15] Freudenberg, "Stereochemie," Franz Deuticke, Leipzig, 1933, pp. 680–681.



Experimental Part

Primary Active Amyl Chloride.—One liter of active amyl alcohol (97%) was isolated by the fractionation of 20 liters of fusel oil containing 15.6% of active material.[16] The alcohol was transformed into the chloride (82% yield) by treatment with thionyl chloride and pyridine.[17]

Peroxide-Catalyzed Chlorination.—Active 1-chloro-2-methylbutane (I) was chlorinated with sulfuryl chloride in the presence of benzoyl peroxide.[6] A ratio of 10 moles of amyl chloride to 1 mole of sulfuryl chloride was used in order to minimize the formation of polychlorinated derivatives. By several repetitions of the process, a total of 2.65 moles of the monochloride was transformed to the dichloride. The mixture of products was then carefully fractionated under reduced pressure (100 mm.). The last portion (*i. e.*, the hold-up) was transferred to a smaller column for fractionation. The results are tabulated in Table II and illustrated graphically in Fig. 2.

Photochemical Chlorination.—One part of chlorine was dissolved in 10 parts of the active chloride, and the mixture was illuminated at 0° for eight hours, when the reaction appeared to be complete. Most of the excess monochloride was removed as rapidly as possible under reduced pressure below room temperature, and a portion of the product was placed in a 40-cm. tube. No change in optical activity was observed over a period of seventy-two hours at room temperature. Heating of the product in a sealed tube at 100° for ten hours with or without hydrogen chloride did not appreciably affect the rotation. Fractionation of the material yielded the same mixture of isomers obtained previously in the peroxide-catalyzed chlorination of the active chloride with sulfuryl chloride. These results appear to eliminate the possibility that an active 1,2-dichloro derivative (III) is formed at one stage of the reaction but is racemized in the process of isolation.

TABLE II

DISTILLATION OF THE PRODUCT OBTAINED BY THE CHLORINATION OF PRIMARY ACTIVE AMYL CHLORIDE

Fraction	B. p. (100 mm.) °C.	Vol., cc.	Optical activity $\alpha^{23}D$ (10 cm. tube)	$n^{23.5}D$	d_4
1	43–43	555	+ 1.43	1.4123	0.8855^{20}
2	43–71	8	....	1.4355	
3	71–71.5	12	+ 0.05	1.4432	1.0766^{20}
4	71.5–72	9.5	+ .18	1.4430	
5	72–72	15	+ .22	1.4429	
6	72–74	16	+ .87	1.4422	
7	74–79	13.5	+ .89	1.4417	1.0790^{20}
8	79–89	15	− 7.00	1.4467	
9	89–89	14	− 7.68	1.4481	$1.0898^{24.5}$
10	89–89.2	16	− 5.20	1.4483	
11	89.2–89.2	17	− 2.10	1.4488	
12	89.2–89.5	18	+ 0.95	1.4494	$1.0897^{24.5}$
13	89.5–90	23	+ 3.00	1.4489	
14	90–92	22	+ 6.21	1.4491	$1.0909^{24.5}$
15	92–101.5	15	− 8.69	1.4532	
16	101.5–101.7	19.5	−10.10	1.4540	
17	101.7–102	12.5	−10.15	1.4542	$1.1046^{24.5}$
18	102–107	19	− 9.00	1.4568	

Hydrolysis of the 1,2-Dichloro Derivatives.—Samples of the alkyl chlorides were introduced into a volumetric flask, and sufficient 80% alcohol was added to make 100 ml. of solution. Five-milliliter fractions were sealed in small glass capsules and heated in a bath at 79°. The extent of hydrolysis was followed by titration of the hydrochloric acid formed with 0.02 *N* sodium hydroxide, and checked in several instances by analysis for chloride ion. The results are summarized in Table III and illustrated in Fig. 3.

TABLE III

COMPARISON OF FIRST ORDER RATE CONSTANTS FOR THE HYDROLYSIS OF TERTIARY CHLORIDES IN 80% ALCOHOL AT 79°

Compound	*K* (hr.$^{-1}$)
t-Butyl chloride	17.4[a]
1,2-Dichloro-2-methylpropane	4.4×10^{-3}
1,2-Dichloro-2-methylbutane	8.2×10^{-3}

[a] Calculated from the equation $\ln K = 35.56 - (23{,}060/RT)$, Hughes, *J. Chem. Soc.*, 255 (1935).

Summary

A careful study of the chlorination of primary active amyl chloride ((+)1-chloro-2-methylbutane) was undertaken to obtain information on the mechanism involved in the substitution of hydrogen by an atomic process.

The isolation of inactive 1,2-dichloro-2-methylbutane indicates that the reaction proceeds through a mechanism involving the transitory existence of a free radical ($RH + Cl\cdot \longrightarrow R\cdot + HCl$).

In the course of this study the diastereoisomers, (±)1,3-dichloro-2-methylbutane, were partially separated by fractionation, and pure (−)1,4-dichloro-2-methylbutane was isolated. This substance must be the enantiomorph of the known (+)1,4-dichloro-2-methylbutane prepared previously from *d*(+)β-methyladipic acid. The arguments used in relating the configuration of *d*(+)β-methyl-adipic acid and (+)active amyl alcohol are thereby supported.

The hydrolysis of 1,2-dichloro-2-methylpropane and 1,2-dichloro-2-methylbutane in 80% alcohol has been studied and the rate constants determined.

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(16) The column (2.3 m. × 18 mm., packed with single-turn glass helices) was constructed by Professor W. G. Brown of the department. Its efficiency (based upon the separation of active amyl alcohol from fusel oil) is estimated at 75 theoretical plates.

(17) Clark and Streight, *Trans. Roy. Soc. Can.*, **23**, 77 (1929).