half-wave potentials were practically identical. The same was true of the tetrahydro compounds. Considerable differences were observed for the dihydro compounds in that half-wave potentials of -1.36 to -1.52 v. *vs.* S.C.E. were found for the dihydro form of different molecules containing pteridines, indicating that the ease of reduction of the dihydropteridine varied with the over-all structure of the molecule.

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BOUND BROOK, NEW JERSEY

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Hydrogen Exchange and Isomerization of Saturated Hydrocarbons with Sulfuric Acid

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Isomerization and hydrogen exchange reactions of saturated hydrocarbons with sulfuric acid have been studied using deuterium as a tracer and the mass spectrometer as the analytical tool. These reactions are interpreted as occurring by means of an ionic chain. The reactions observed are considered to be the reactions of the ions. The probability that an ion will isomerize or will undergo hydrogen exchange is determined by the rates of such reactions relative to the rate of reconversion of the ion to the hydrocarbon. Only isoparaffins (defined as saturated hydrocarbons with tertiary carbon atoms) undergo any observable reaction, and only isoparaffins are formed as a result of isomerization. The isoparaffin products invariably contain methyl groups attached to the tertiary carbon. The hydrogen atoms exchanging with sulfuric acid always include at least those attached to carbon atoms adjacent to the tertiary carbon. The exchange of others more distant from the tertiary carbon appears to result from isomerization of the ion, and the pattern of such exchange depends upon the molecular structure and, to some extent, upon reaction conditions. With certain isoparaffins all but one of the hydrogen atoms in the molecule invariably exchange with acid, and a study of the mass spectrum of the C_nHD_{2n+1} species furnishes a direct method for the determination of the relative rate of production from the activated state of all isomers, including the species with the same carbon skeleton as the reactant. Results of this work provide an explanation for the facts that only isoparaffins react and only isoparaffins are produced in the sulfuric acid-catalyzed alkylation reaction. The results also demonstrate that the carbonium ions are true intermediates with finite lifetimes, and that their mode of reaction depends upon the degree of their activation.

This is the second of two papers presenting the results of studies of the reactions of alkanes and cycloalkanes in the presence of concentrated sulfuric acid. In the previous paper[2a] it was shown that isobutane exchanges its primary hydrogens[2b] with sulfuric acid by means of an ionic chain reaction. The exchange of primary hydrogens is believed to occur during the residence of the hydrocarbon as an ion[3] in the sulfuric acid. The chain propagating reaction, which is rate-determining in the steady state, is the transfer of a tertiary hydride ion[4] from the hydrocarbon to the ion, regenerating a hydrocarbon molecule and producing a new ion. In order to account for the kinetics, a slow chain initiating reaction (oxidation by sulfuric acid) was postulated, as well as a chain terminating reaction that produces non-volatile, non-reactive products.

This paper describes studies of the reactions of various C_5–C_7 alkanes and cycloalkanes by methods similar to those employed in the studies of the isobutane reactions. It is shown that these new observations fit the same general model that describes the behavior of isobutane with the additional feature that the more complex carbonium ions are able to undergo certain skeletal rearrangements as well as hydrogen exchange reactions. The interrelationship of the reactions of the ions in sulfuric acid have been studied in detail.

Discussion

The experiments described in Tables I–IV are of four types: (1) The reactions of paraffins (and cycloparaffins) with sulfuric acid-d_2, (2) the reactions of paraffins with sulfuric acid, (3) the reactions of various monodeutero-2-methylpentanes with sulfuric acid, and (4) the reactions of isopentane with sulfuric acid-d_2 under various reaction conditions. For the most part, conditions were chosen such that only a small fraction of the molecules underwent reaction. This assures that

[1] Deceased, July 5, 1950.

[2] (a) J. W. Otvos, D. P. Stevenson, C. D. Wagner and O. Beeck, THIS JOURNAL, **73**, 5741 (1951). (b) Hydrogens designated primary, tertiary, etc., designate the type of carbon atom to which they are attached.

[3] A term used to designate either the solvated ion, $R^+\cdot(H_2SO_4)_n$ or the complexed, polarized ester, $(R^+\text{-}OSO_3H^-)\cdot(HS_2O_4)_n$.

[4] Hydride ion as used here denotes a hydrogen nucleus with an electron pair. It is not an ion in the sense that it is free from the influence of the rest of the hydrocarbon molecule.

TABLE I

REACTIONS OF HYDROCARBONS WITH D_2SO_4[a]

Run no.	Hydrocarbon reactant	Time, min.	d_0	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}	d_{11}	d_{12}	d_{13}	d_{14}	d_{15}
1	Isopentane[b]	40	87			[c]	<1.0	9.2	<0.3	0.6	3.8				
2	2-Methylpentane[b,d]	40	96				<0.1	1.2	0.8	1.0		<0.1	1.0		
3	[d]	20	97					0.94	0.55	0.69			0.73		
4	3-Methylpentane[b]	40	93				0.5		<0.1	2.7	<0.1	<0.4	3.3		
5	2,3-Dimethylbutane	5	99.2										0.76	0.02	
6		15	96.5										3.48	0.08	
7		40	70.5							<0.1	<0.5	5.0	21.5	3.0	
8	2-Methylhexane[b,e]	40	99					0.11	0.08	0.11	0.19	0.24		<0.08	0.25
9		120	92.5				0.11	1.36	0.68	0.88	0.99	1.59		0.15	1.61
10	3-Ethylpentane	120	96.7						0.06			1.09			2.11
11	2,3-Dimethylpentane[f]	10	99.4												0.6
12	[f]	60	97.8												2.1
13	2,4-Dimethylpentane[f]	10	99.2												0.6
14	[f]	60	96.9												3.4
15	Trimethylbutane[f]	10	99.7												0.3
16	[f]	60	98.5												1.4
17	[f]	165	95.9												4.0
18	Methylcyclopentane[b]	40	91.5				3.3	2.2	1.6	0.9	0.5				
19		120	37	1.0	1.7	4.6	19.7	14.7	11.3	6.7	2.7				
20	Methylcyclohexane[b]	40	89.5			0.3	1.9	0.9	0.9	1.1	1.4	1.7	2.1		
21		120	51	0.4	0.7	2.0	7.7	4.3	4.8	5.7	7.0	8.2	8.1		
22	Ethylcyclopentane	120	65			0.8	0.7	1.3	4.9	5.7	6.9	7.9	7.2		
23	Cyclopentane[b]	40	100												
24	2,2-Dimethylbutane[b]	40	100												
25	n-Heptane[g]	240	100												

[a] Conditions: 25°, 0.6 millimole of hydrocarbon and 2 ml. of 95.0% acid, arc-type shaker used unless otherwise noted. No experiments were included where any observable disproportionation (intermolecular carbon transfer) occurred. [b] Amount of hydrocarbon used was 1.2 millimoles instead of 0.6 millimole. [c] Absence of data indicates definite absence of species. Possible absence is indicated by $<a$, where a is the upper limit. [d] 2-Methylpentane (a) used. [e] 2-Methylhexane (a) used [f] 93.6% acid. [g] 98.6% acid. [h] Product species sometimes consist partly of molecules rearranged skeletally (see text below).

only a negligible fraction of the molecules will have been in ionic residence[5] more than once.

Hydrogen Exchange Reactions.—Data in Table I demonstrate certain consistencies in the observed reactions of alkanes with deuterosulfuric acid: (1) Only those alkanes and cycloalkanes that have tertiary carbon atoms undergo observable reaction. (2) The maximum number of hydrogen atoms exchanged in any molecule is one less than the total. (3) The minimum number of hydrogen atoms exchanged in any molecule is equal to the number of hydrogen atoms (designated for the purposes of this paper "contiguous hydrogen atoms") attached to carbon atoms adjacent to the tertiary carbon. (4) The deuterated species[6] produced correspond to those expected from (a) the exchange of contiguous hydrogens, (b) the occasional additional exchange of hydrogens on more distant secondary carbons, and (c) the occasional additional exchange of all of the hydrogen atoms of more distant methyl groups. A necessary condition for the exchange of "distant" hydrogen atoms is the concomitant exchange of all hydrogens between the tertiary carbon and the distant hydrogens in question.

Exchange between certain paraffins and deuterosulfuric acid, was observed by Ingold, Raisin and Wilson[7] and Burwell and Gordon.[8] Results obtained by them are in general agreement with these, except that reaction with *n*-hexane reported by Ingold could not be duplicated. Burwell and Gordon observed the racemization of optically active 3-methylheptane as well as its exchange. They assumed that every ion formed causes loss of optical activity. The average number of hydrogens exchanged per molecule racemized (per ion) corresponded well with the values calculated by extrapolation from our more detailed data.

Observations (2) and (3) are predicted by the mechanism developed from the studies of the reaction of isobutane with sulfuric acid.[2a] The one hydrogen atom that is never exchanged with acid is the tertiary hydrogen atom, which is acquired from another hydrocarbon molecule by the ion during its reversion to hydrocarbon in the chain-carrying reaction. The contiguous hydrogens in heavier hydrocarbons correspond to the primary hydrogens in isobutane, and like those, would be expected to exchange with acid very rapidly during the life of the ion, so that a molecule passing through the ionic state always acquires an entirely new set of contiguous hydrogens.

Isomerization Reactions.—Data in Table II demonstrate the following: (5) Only those molecules that possess tertiary carbon atoms undergo any isomeric changes in sulfuric acid at 25°; the products of such isomerizations all possess at least one tertiary carbon atom, to which is attached one or more methyl groups. (6) Isomerization processes that do not change the degree of branching are more probable than those that change the degree of branching; the most probable type involves migration of an alkyl group along a chain. (7) The initial rates of formation of isomers in isomerization reactions bear no consistent relation to the thermodynamic stabilities of the isomeric products.

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(5) Ionic residence is defined here as the state of a molecule present in the acid phase undergoing one or more of the ionic reactions described below.

(6) The standard A.C.S. system of nomenclature for deuterium compounds is used. For instance, 2-methylpentane-4-*d* represents $CH_3CH(CH_3)CH_2CHDCH_3$. In this work this is called an "isotopic isomer," and it, along with the other four possible monodeutero-2-methylpentanes, all are considered to belong to an "isotopic species," represented by the name 2-methylpentane-d_1 (or 2-methylpentane-*d*).

(7) C. K. Ingold, C. G. Raisin and C. L. Wilson, *J. Chem. Soc.*, 1643 (1936).

(8) R. L. Burwell, Jr., and G. S. Gordon, III, THIS JOURNAL, **70**, 3128 (1948); **71**, 2355 (1949).

TABLE II

ISOMERIZATION OF HYDROCARBONS IN SULFURIC ACID[a]

Run no.	Hydrocarbon reactant	Acid concn., %	Reaction time, min.	Products, mole %[b] 2-Me alkane	3-Me alkane	2,3-Di-Me alkane	2,4-Di-Me alkane
26	2-Methylpentane[c]	93.7	150		1.5		
27		93.7	330		5.3	[e]	
28		94.1	60		0.4		
29		94.1	120		1.7		
30		94.1	240		5.6		
31		95.8	60		4.0		
32		95.8	150		14.4		
33		95.8	180		16.3		
34		95.8	315		19.6		
35	No agitation	95.8	180		1.0		
36	Horizontal shaking	95.8	90		2.2		
37	Horizontal shaking	95.8	180		12.6		
38	0°, horizontal shaking	95.8	90		0.0		
39	0°, horizontal shaking	95.8	255		0.2		
40	3-Methylpentane[d]	93.7	150	12.4		0.0	
41		93.7	360	21.7		1.4	
42		95.8	60	19.1		0.7	
43		95.8	150	45.7		0.8	
44		95.8	360	56.1		2.1	
45		96.2	40	3.6		0.0	
46		96.2	90	14.8		0.5	
47		96.2	180	38.8		0.0	
48		96.2	360	57.6		2.0	
49	0°. horizontal shaking	95.8	90	3.9		<0.1	
50	0°. horizontal shaking	95.8	255	4.5		<0.1	
51	2,3-Dimethylbutane	93.7	150	0.1	0.3		
52		93.7	360	11.5[f]	5.0		
53		95.8	60	0.6	0.3		
54		96.2	40	1.5	0.6		
55		96.2	90	3.3	1.3		
56	2-Methylhexane	95.8	60		1.1		
57		95.8	150		4.1		
58		95.8	360		12.9		
59	2,3-Dimethylpentane	94.1	90	0.3	0.1	(0.3)[g]	3.8
60		94.1	240	1.1	0.5	(2.4)[g]	6.5
61	2,4-Dimethylpentane	94.1	90	1.2	0.4	4.2	(3.6)[g]
62		94.1	240	2.1	1.2	8.1	(6.3)[g]
63	Trimethylbutane	94.1	90	0.3	0.1	0.6	0.4
64		94.1	240	0.4	0.2	1.0	1.6
				Methylcyclohexane		1,3-Dimethylcyclopentane	
65	*cis*-1,2-Dimethylcyclopentane	94.1	60	< 0.4		0.7–3.2	
66		94.1	120	< 0.8		1.7–7.0	
67		94.1	240	< 1.1		3.1–9.9	
68	Ethylcyclopentane	94.1	100	30			
69		94.1	240	50			

[a] Conditions: 25°, 0.6 millimole of hydrocarbon, 2 ml. of H_2SO_4, and arc-type shaker used unless otherwise noted. [b] Products given are those expected without intermolecular transfer of carbon atoms. [c] 2-Methylpentane (a) preparation used, except in runs 28, 29 and 30. [d] 3-Methylpentane (a) preparation used, which contained 3.6% 2-methylpentane. [e] <1.3% 2,3-dimethylbutane formed in all cases; <0.4% formed in cases where <10% 3-methylpentane was formed. [f] Analyses complicated by disproportionation products. More severe conditions (longer time or higher acid concentration) than those shown gave disproportionation to such an extent that analysis was impossible. [g] 2,2-Dimethylpentane and/or trimethylbutane.

Neopentyl and neohexyl ions, postulated as generated from certain alcohols and amines by mild reagents,[9] readily rearrange to form tertiary alkyl derivatives. The inertness in sulfuric acid of paraffins without tertiary carbon atoms must be ascribed to difficulty of ion formation rather than to lack of reactivity of the ion. Gordon and Burwell[8] could not induce hydrogen exchange or isomerization of *n*-octane in the presence of an isoparaffin reacting in sulfuric acid. Further demonstration of this fact is given below.

Examination of the data in Tables I and II shows that under similar conditions the number of molecules undergoing hydrogen exchange is always roughly equal to, or greater than the number of similar molecules isomerizing. Since isobutane exchanges all of its primary (contiguous) hydrogen atoms many times during ionic residence, it is reasonable to believe that all ions of any iso-

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[9] M. Freund and F. Lenze, *Ber.*, **24**, 2150 (1891).

TABLE III

REACTIONS OF DEUTERO-2-METHYLPENTANES IN H_2SO_4[a]

Run no.	Hydrocarbon reactant	Acid concn., %	Time, hr.	Product[b] composition, mole %			
				2-MP-d_1	2-MP-d_0	3-MP-d_0	3-MP-d
	2-Methylpentane		0		100.0	0.0	
28		94.1	1		99.6	0.4	
29		94.1	2		98.3	1.7	
30		94.1	4		94.4	5.6	
	2-Methylpentane-2-*d*		0	73.5	26.5	0.0	[c]
70		90.2	1	73.5	26.5	.0	0.0
71		92.2	1	72.6	26.0	.5	0.9
72[d]		94.1	1	71.0	25.5	1.0	2.5
73		94.1	2	70.0	25.2	1.3	3.7
74		94.1	4	68.5	24.6	1.9	5.0
	2-Methylpentane-4-*d*		0	81.0	19.0	0.0	[e]
75		90.2	1	79.7	20.3	.0	<0.2
76		92.2	1	78.0	21.7	.3	< .2
77[d]		94.1	1	72.3	25.2	2.6	< .2
78		94.1	2	69.2	26.4	4.4	< .2
79		94.1	4	51.1	37.6	11.3	< .2
	2-Methylpentane-5-*d*		0	76.2	23.8	0.0	[f]
80		94.1	2	72.1	25.8	1.3	0.8
81		94.1	4	65.3	29.0	3.7	2.1

[a] Conditions: 25°, 0.6 millimole of alkane, 2 ml. of acid, arc-type shaker. [b] 2-MP- and 3-MP represent 2-methylpentane and 3-methylpentane. [c] Deuterated 3-methylpentane was analyzed to be either 3-methylpentane-3-*d* or 3-methyl-*d*-pentane. [d] Average of two runs performed under identical conditions. [e] Figures given are upper limits to concentrations of any monodeutero-3-methylpentane. [f] From the analysis the species could consist of either 3-methylpentane-2-*d* or 3-methylpentane-1-*d* or both.

TABLE IV

EFFECT OF CONDITIONS ON REACTION OF ISOPENTANE WITH D_2SO_4

Run no.	Reaction conditions[a]	Deuterated species found, mole %								$\frac{d_9 + d_{10} + d_{11}}{\Sigma d_n}$
		d_0	d_5	d_6	d_7	d_8	d_9	d_{10}	d_{11}	
82	30'	89.5			0.6	6.75	0.1	0.2	2.64	0.29
83	360', no agitation	93.6			0.6	2.84	.2	0.4	2.36	.46
84	60', 95% acid	48	0.3	0.8	4.3	28.7	.6	3.3	13.8	.34
85	60', 91% acid	89		0.1	0.2	5.45	< .1	0.8	4.75	.49
86	60', horizontal shaking	73	0.1	0.4	1.4	14.9	.3	1.3	8.8	.38
87	60', 0°, horizontal shaking	97.5		0.1	0.1	1.8	< .1	0.1	0.43	.21

25°, 0.6 millimole of isopentane and 2 ml. of 93.6% acid, arc-type shaker used unless otherwise noted.

paraffin exchange all of the contiguous hydrogen atoms similarly. Further, it seems likely that ions will vary in their tendency to isomerize during ionic residence, so that in some instances an ion may not have time to isomerize. Hydrogen exchange without isomerization has been observed, but isomerization without hydrogen exchange has never been observed in sulfuric acid.[10]

The reason for the exclusive production of isoparaffins by isomerization in sulfuric acid must lie either in (1) low stability of non-tertiary ions compared to that of tertiary ions or (2) high activation energy for the production of non-tertiary ions from tertiary ions. Secondary ions, if formed, should readily abstract a tertiary hydrogen in a hydrogen transfer reaction, on the basis of the expected relative affinities of secondary and tertiary carbonium ions for a hydride ion. The effect of (2) is difficult to assess; however, calculation of (1) from energy data shows that a tertiary carbonium ion should be more stable than a secondary carbonium ion by the order of 10–15 kcal./mole at 25°, assuming similar solvation energies for the two ion types.

In view of the considerations stated above it is clear that reaction paths leading to all the isomers of a system are not equally accessible. Therefore it is not surprising that the rates of formation of isomers from a given isoalkane are not in the ratio of their equilibrium concentrations. It is only when the isomerization of the ions is rapid compared to the rate of the chain-carrying step and when the ions all participate with the same specific rate in the chain-carrying reaction that one obtains a product distribution representative of the equilibrium concentrations of the ions (barring, of course, a fortuitous combination of rate constants). If, further, this equilibrium distribution of ions is like that of the isoalkanes themselves then the product distribution will represent the thermodynamic equilibrium among the isomers.

Nature of the Chain Propagation Reaction.—That the chain propagation reaction consists exclusively of transfer of a tertiary hydride to a tertiary carbon atom of a tertiary carbonium ion is demonstrated by the reaction of 2-methylpentane-2-*d* with sulfuric acid. The only product was 3-methylpentane-3-*d*, and there was no detectable loss of deuterium to the acid although approxi-

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[10] Isomerization without hydrogen exchange between acid and hydrocarbon is possible with solid or semi-solid catalysts, however. This has been observed with *n*-butane over aluminum chloride-alumina (C. D. Wagner, O. Beeck, J. W. Otvos and D. P. Stevenson, *J. Chem. Phys.*, **17**, 419 (1949)).

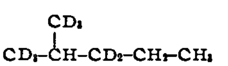
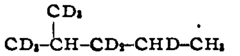
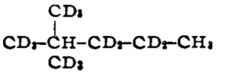
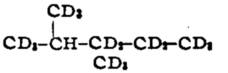
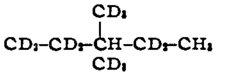
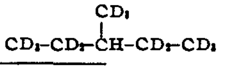
mately 30% of the molecules had undergone hydrogen exchange.[11] Loss of deuterium to the acid would result from any of the following, either directly or as a consequence of a subsequent ionic residence: abstraction of a secondary hydrogen by a tertiary carbonium ion, a tertiary hydrogen by a secondary carbonium ion, or intramolecular shift of a secondary hydrogen to the tertiary carbon, followed by chain transfer involving the resulting secondary carbonium ion.

Relation between Hydrogen Exchange and Isomerization.—If it is assumed that a hydrogen must be "contiguous" in order to exchange with acid, the exchange of "distant" hydrogens could be explained by migrations of hydrogens along the chain. Such migrations would produce either secondary or primary carbonium ions. However, since secondary (primary) carbonium ions are of negligible importance from the standpoint of the chain-carrying reaction, they are undoubtedly insignificant also in providing structures from which distant hydrogen exchange can occur. It seems reasonable to postulate, therefore, that exchange of distant hydrogens results from concerted movement of an alkyl group and hydrogens in such a way that the charge remains at the tertiary position, thus making new sets of hydrogens "contiguous" at some time during the life of the ion. Supporting evidence for this point of view will be presented in the following discussions of the behavior of the individual hydrocarbons.

2-Methylpentane.—2-Methylpentane was selected as the compound for intensive study by means of deuterium-containing isotopic isomers because it is the simplest compound in which isomerization could be related to distant exchange. The isomerization reaction is relatively clean-cut; 3-methylpentane is the only isomer produced at a significant rate in sulfuric acid (Table II, experiments 26–37). From data obtained in experiments with 2-methylpentane-2-*d*, -4-*d* and -5-*d* (Table III, experiments 70–81) one may estimate that the initial products of reaction (produced with essentially only one ionic residence per reacting molecule) of 2-methylpentane with D_2SO_4 are those shown in Table V.

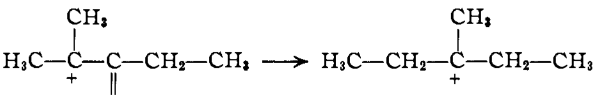
TABLE V

PRODUCTS OF REACTION OF 2-METHYLPENTANE WITH SULFURIC ACID-d_2

Product	Relative amount
 $CD_3\text{-}\overset{CD_3}{CH}\text{-}CD_2\text{-}CH_2\text{-}CH_3$	1.0
 $CD_3\text{-}\overset{CD_3}{CH}\text{-}CD_2\text{-}CHD\text{-}CH_3$	0.8
 $CD_3\text{-}\overset{CD_3}{CH}\text{-}CD_2\text{-}CD_2\text{-}CH_3$	0.7
 $CD_3\text{-}\overset{CD_3}{CH}\text{-}CD_2\text{-}CD_2\text{-}CD_3$	0.8
 $CD_3\text{-}CD_2\text{-}\overset{CD_3}{CH}\text{-}CD_2\text{-}CH_3$	0.3
 $CD_3\text{-}CD_2\text{-}\overset{CD_3}{CH}\text{-}CD_2\text{-}CD_3$	0.3

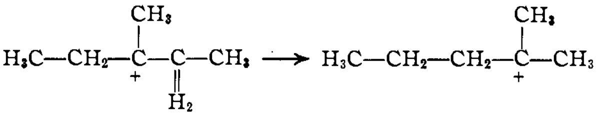
This analysis is based upon the following qualitative reasoning; the semi-quantitative estimates of relative concentrations are then readily made from the data: (1) When 3-methylpentane was formed from 2-methylpentane-4-*d* in sulfuric acid, the deuterium was always lost from the hydrocarbon. It is inferred from this that the 3-methylpentane formed possesses at least ten new hydrogen atoms. The -d_8 and -d_9 species obtained in the reaction of 2-methylpentane with deuterosulfuric acid must then have the 2-methylpentane configuration. (2) Experiments with 2-methylpentane-5-*d* confirm that 3-methylpentane can sometimes be produced (about half the time) without disturbing the hydrogen atoms on the originally distant methyl group (the product then possessing ten new hydrogen atoms), but that the remainder of the 3-methylpentane produced contains thirteen new hydrogen atoms. (3) With both 2-methylpentane-4-*d* and 2-methylpentane-5-*d* in sulfuric acid, 2-methylpentane-d_0 was produced. By using the rate of formation of 3-methylpentane as a parameter, it is found that deuterium loss from the -4-*d* compound occurs about twice as fast as that from the -5-*d* compound, consistent with the production of 2-methylpentane with only nine or ten new hydrogen atoms as well as with thirteen new hydrogen atoms.

This result is substantially in accord with the following picture: all ions produced from 2-methylpentane exchange all eight of the contiguous hydrogen atoms many times with the acid. With a fraction of the ions, sufficient energy is available for skeletal rearrangement, expressed in an over-all sense



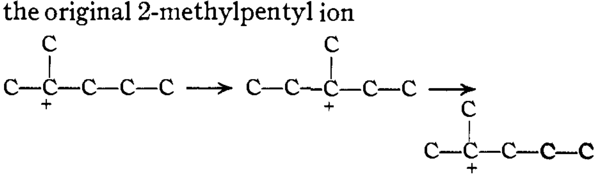
$$H_3C-\underset{+}{\overset{CH_3}{C}}-\underset{H_2}{\overset{}{C}}-CH_2-CH_3 \longrightarrow H_3C-CH_2-\underset{+}{\overset{CH_3}{C}}-CH_2-CH_3$$

Hydride transfer to form 3-methylpentane at this stage gives, with D_2SO_4, 3-methylpentane-d_{10}. Further migration of the methyl to the next carbon atom



$$H_3C-CH_2-\underset{+}{\overset{CH_3}{C}}-\underset{H_2}{C}-CH_3 \longrightarrow H_3C-CH_2-CH_2-\underset{+}{\overset{CH_3}{C}}-CH_3$$

gives 2-methylpentane-d_{13}.[12] When this stage is reached, any rearrangement gives ultimately either 2-methylpentane-d_{13} or 3-methylpentane-d_{13}. If an initially-formed 3-methylpentyl ion reverts to the original 2-methylpentyl ion



$$C-\underset{+}{\overset{C}{C}}-C-C-C \longrightarrow C-C-\underset{+}{\overset{C}{C}}-C-C \longrightarrow C-\underset{+}{\overset{C}{C}}-C-C-C$$

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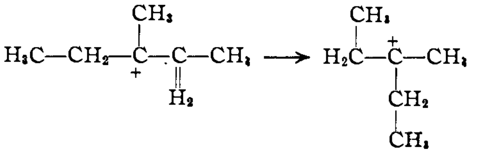
(11) From Table V it is apparent that the number of ions formed is approximately six times the number of 3-methylpentane molecules produced.

(12) Movement of the left-hand ethyl group in the same manner:



$$H_3C-CH_2-\underset{+}{\overset{CH_3}{C}}-\underset{H_2}{C}-CH_3 \longrightarrow H_2\overset{CH_3}{C}-\underset{CH_2CH_3}{\overset{+}{C}}-CH_3$$

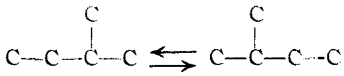
followed by chain transfer gives 3-methylpentane-d_{11}.

(in terms of particular carbon atoms in a given molecule) followed by hydride transfer to form the 2-methylpentane hydrocarbon, we can assume that hydrogens exchanged during the existence of the 3-methylpentyl ion will cause the 2-methylpentane-d_{10}, $CD_3-CHCD_3-CD_2-CD_2-CH_3$, to be produced. The formation of 2-methylpentane-d_9 cannot be explained in terms of this simple picture (see below).

The behavior of the ion thus appears to be the following: the mean time required for unit skeletal rearrangements of the ions is of the same magnitude as the period of ionic residence; only a few such shifts take place. Contiguous hydrogen exchange is very rapid compared to these shifts, particularly where primary hydrogens are involved, and isotopic equilibrium between such hydrogen atoms and the solvent hydrogens is always reached.

3-Methylpentane.—The only species produced are the -d_7, -d_{10} and -d_{13}. The mass spectrum of the -d_{13} species is essentially identical with that produced from 2-methylpentane, and corresponds to a 2:1 mixture of 2-methylpentane-d_{13} and 3-methylpentane-d_{13}. This behavior is consistent with the picture that such extensive exchange results from many isomerizations of the ion; the composition of the product then bears no relation to the reactant, but depends only upon the relative probability of formation of the isomers from the mixture of isomeric ions. The -d_7 species must retain the 3-methylpentane configuration (see below).

Isopentane.—The isomerization in isopentane, ordinarily undetectable



$$C-C-\overset{C}{\overset{|}{C}}-C \rightleftarrows C-\overset{C}{\overset{|}{C}}-C-C$$

could conceivably be observed using isotopic carbon. However, the isomerization is also observable using deuterium. Isopentane molecules exchange either eight or eleven hydrogen atoms with acid (experiment 1, Table I). The -d_8 species is undoubtedly unrearranged skeletally, while the -d_{11} species results from skeletal isomerization. The ratio $(\text{-}d_8)/((\text{-}d_8) + (\text{-}d_{11}))$ should be a measure of the fraction of the ions that undergo no isomerization during ionic residence.

2,3-Dimethylbutane.—This compound is known to be easily oxidized by oxygen or bromine, and it is thus not unexpected that the formation of ions by oxidation with sulfuric acid would be relatively easy. The chain-carrying step should also be facilitated by the presence of two tertiary hydrogen atoms. The rate of the hydrogen exchange reaction in terms of molecules was found to be much larger than with any other acyclic hydrocarbon tested, in agreement with the above views. The dimethylpentanes are also active in this respect, undergoing faster hydrogen exchange than the other heptanes. Since precautions were taken to remove all olefins from the dimethylbutane sample, the greater reactivity of these compounds cannot be ascribed to the presence of impurities. It is interesting that the formation of monomethylpentanes from 2,3-dimethylbutane as well as the reverse reaction, the formation of 2,3-dimethylbutane from monomethylpentanes, is slow[13] in comparison with interconversion of the monomethylpentanes. This shows that there is no simple relationship between the rate of isomerization of a carbonium ion and its stability. In discussions of reactions involving molecular rearrangements it has been often implied that the rearranged product is the exclusively observed product because the initially formed carbonium ion is unstable with respect to its isomers and thus rapidly isomerizes. The above recorded observations of the behavior of the three isohexylcarbonium ions in sulfuric acid show the existence of activation barriers in the interconversions, and therefore the rate of isomerization of a carbonium ion to form another ion is a specific function of the ionic structures and the environment.

With 2,3-dimethylbutane all hydrogen atoms but one exchange with acid when any exchange. At first glance, it seems that the rule of contiguous exchange is not applicable here. However, it is not unexpected that the charge on the ion should oscillate very rapidly between the tertiary carbon atoms (with the remaining tertiary hydrogen atom occupying an intermediate position), so that all methyl groups are, in effect, equivalent. The chain-carrying step supplies a hydride to one of the tertiary carbons at random, regenerating 2,3-dimethylbutane as the -d_{13} species if D_2SO_4 is used. A second entry of such a molecule into ionic residence permits the -d_{14} species to be produced if a molecule donates its tertiary deuterium atom to the ion already possessing thirteen deuterium atoms, and this effect is noted at higher conversions.

The straightforward initial reaction furnishes an unexpectedly simple method for determining the isotopic purity of deuterosulfuric acid. It is inherently very sensitive. If the acid is nearly 100% isotopically pure the mole fraction of 2,3-dimethylbutane-d_{12} will be approximately 13 times the atom fraction of H in the deuterosulfuric acid. Neglecting small isotope effects, the relationship between the -d_{13}/-d_{12} mole fraction ratio and isotopic purity is given by

$$\frac{d_{13}}{d_{12}} = \frac{x^{13}}{13x^{12}(1 - x)} = \frac{x}{13(1 - x)}$$

where $x = D/D + H$, D and H representing relative numbers of deuterium and hydrogen atoms in the acid. In experiments 5 and 6, the upper limits for the -d_{12} species mole fraction were 0.002 and 0.005, respectively. Calculations on this basis gave $99.5^{+}\%$ as the lower limit for the isotopic purity of the D_2SO_4 in terms of D and H.

2-Methylhexane.—2-Methylhexane isomerizes to form 3-methylhexane, as expected (experiments 56–58). The mass spectrum of the highly deuterated species produced by action of D_2SO_4 (experiments 8 and 9) may be interpreted on the basis that a mixture of deuterated 2-methylhexane and 3-methylhexane is produced (see section below,

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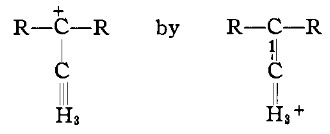
[13] Evering and Waugh (Preprints, Petroleum Division, American Chemical Society Meeting, April, 1948, p. 75) found that the methylpentanes are readily interconvertible in the presence of aluminum chloride, but that interconversions between them and 2,3-dimethylbutane are slow. Any isomerization results in a change in the degree of branching, and such a process appears to be much less probable than the migration of an alkyl group along a chain.

Mass Spectrometric Analyses). The species of lower deuteration ($-d_8$ and $-d_9$) are assumed to be entirely 2-methylhexane, by analogy with the 2-methylpentane behavior. Production of other isoheptanes was not noted at this degree of conversion.

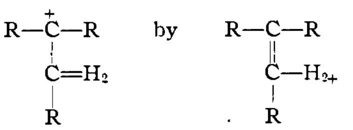
3-Ethylpentane.—When 3-ethylpentane was treated with D_2SO_4 (experiment 10) the only products formed were very highly deuterated heptanes ($-d_{12}$ and $-d_{16}$, with perhaps a trace of $-d_9$). The mass spectra of the deuterated species could not be interpreted as being those of deuterated 3-ethylpentanes; instead, the molecules that had undergone hydrogen exchange had, as far as could be determined, all been isomerized to a mixture of other heptanes. This result supports the theory that exchange of many hydrogens per molecule requires extensive carbon skeleton isomerization.

This behavior is similar to that observed with ethylcyclopentane, described below. Ions without contiguous methyl groups either isomerize very rapidly, or the period of ionic residence is longer than usual, since isomerization always occurs. The greater electron release potentiality of a methyl than of a methylene group results in more resonance stabilization of the structure



$$\begin{array}{c} R-\overset{+}{C}-R \\ | \\ C \\ \equiv \\ H_3 \end{array} \quad \text{by} \quad \begin{array}{c} R-C-R \\ \| \\ C \\ \| \\ H_3{}^{+} \end{array}$$

than of the structure



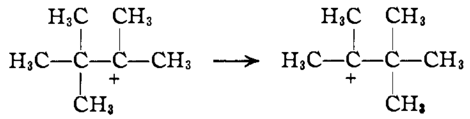
$$\begin{array}{c} R-\overset{+}{C}-R \\ | \\ C{=}H_2 \\ | \\ R \end{array} \quad \text{by} \quad \begin{array}{c} R-C-R \\ \| \\ C-H_2{}^{+} \\ | \\ R \end{array}$$

Thus it would be expected that methylalkyl ions should be more stable than ions with no methyl group attached to the tertiary carbon. However, stability is not the only criterion for ease of isomerization (see above under 2,3-dimethylbutane). Steric hindrance for the chain-carrying step may appreciably increase ionic residence.

Dimethylpentanes.—As would be expected from the observations on the methylpentanes, 2,3- and 2,4-dimethylpentanes are readily interconvertible. However, the apparent rates of conversion to other isomers, the methylhexanes and trimethylbutane, are greater than would have been expected from the rate of formation of methylpentanes from 2,3-dimethylbutane (see experiments 59–62). The formation of trimethylbutane from the dimethylpentanes took place at rates comparable ($^1/_3$–$^3/_4$) with their rate of interconversion.

From the absence of detectable isotopic species with fewer than fifteen deuterium atoms in the products of the reaction with deuterosulfuric acid (experiments 11–14), it follows that many isomerization processes occur during each ionic residence. Many isomerizations per ionic residence would further require the same distribution of product structures in the deuteroheptane from either 2,4- or 2,3-dimethylpentane. Such is the case (see section below, Mass Spectrometric Analyses). If ion isomerization is rapid compared to hydride transfer, then processes having smaller probability for occurrence may become increasingly important. This seems to be true in the heptanes; the real differences in probability for isomerization processes that do and those that do not change the degree of branching may be masked by the fact that equilibrium for the faster process is reached and ionic residence is long enough to permit less likely processes to take place.

Trimethylbutane.—The reactions involving this compound are particularly interesting. If the ion in D_2SO_4 were converted to the parent molecule without rearrangement, a product species with only six deuterium atoms would be expected. However, all molecules undergoing hydrogen exchange are observed to acquire fifteen deuterium atoms, and among these are a considerable number with the trimethylbutane structure. This may be explained by the transformation

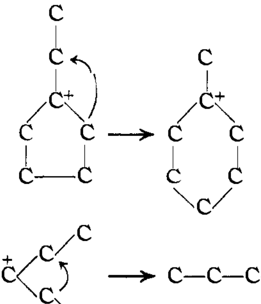


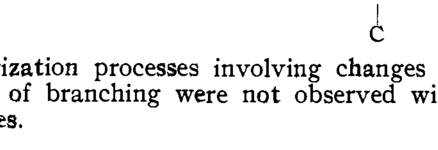
$$H_3C-\overset{H_3C}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{+}{C}}-CH_3 \longrightarrow H_3C-\overset{H_3C}{\underset{+}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$$

which may be very fast, since it requires no concomitant migration of hydrogen atoms.

Tertiary Alicylic Hydrocarbons.—The reactions of methylcyclopentane, methylcyclohexane, ethylcyclopentane and *cis*-1,2-dimethylcyclopentane were studied (experiments 65–69, 18–22). Methylcyclopentane and methylcyclohexane gave no evidence of skeletal rearrangement; the expected methyl migration around the ring is of course undetectable. The presence of highly deuterated products as well as the expected $-d_7$ species produced by contiguous exchange is consistent with the picture that some, but not extensive, methyl migration takes place. Conversion of *cis*-1,2-dimethylcyclopentane to 1,3-dimethylcyclopentanes confirms the fact that methyl migration around the ring does occur.

With ethylcyclopentane the only isomerization product observed is methylcyclohexane, and the isomerization proceeds at a rapid rate. This and 3-ethylpentane are the only cases studied where the original ion is not converted to a hydrocarbon of the same structure. It is also apparent that the migrating group cannot be a methyl. The simplest pictures for the isomerizations of these carbon skeletons are

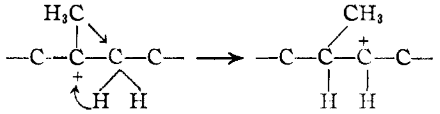




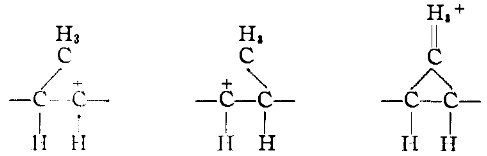
Isomerization processes involving changes in the degree of branching were not observed with the cyclanes.

The comparison of the mass spectra of deuterated methylcyclohexane and ethylcyclopentane (experiments 21, 22) shows they are substantially identical except that from ethylcyclopentane species low in deuterium are lacking; this is expected, since with this compound skeletal isomerization invariably takes place.

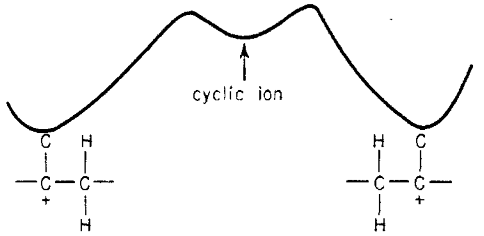
The Intermediate Transition State.—The nature of the isomerization of a carbonium ion in sulfuric acid is of some interest. The concept of a cyclic intermediate is attractive. It could be formed in a single step by concerted movement of a methyl and hydrogen attached to adjacent carbons



The cyclic ion, stabilized by contributions from several resonance structures, particularly when the migrating group is methyl

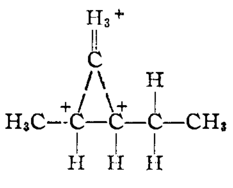


is visualized as a true intermediate with finite lifetime. The potential energy diagram representing the ion isomerization may be represented

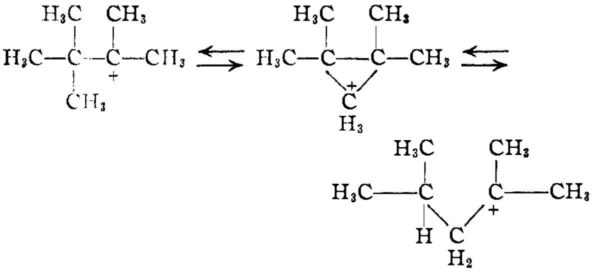


Reversion to the original ion or conversion to an isomeric ion requires the above concerted process in reverse.

The exchange of the non-contiguous hydrogens does not quite fit the simple picture of exchange of distant hydrogens by the process of migration of alkyl groups to make them contiguous. Such distant secondary hydrogens do not exchange in pairs; often only one of the two attached to a secondary carbon has been found to exchange. In 2-methylpentane we know the -d_9 species produced in D_2SO_4 must have the 2-methylpentane structure. The cyclic intermediate offers a possible explanation for the production of this species. In this intermediate there is a partial positive charge on the center carbon of the chain which may permit the secondary hydrogens to exchange at a low rate. Reversion of the carbon skeleton to the original 2-methylpentane structure then must take place frequently after one hydrogen but before both hydrogens have exchanged. Conversion of the intermediate to the 3-methylpentyl ion of course produces ultimately either a -d_{10} or -d_{13} species of the 2-methylpentane or 3-methylpentane configuration.



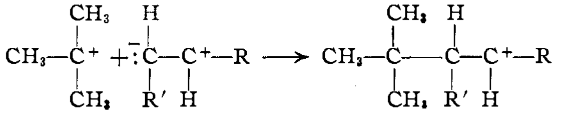
The isomerization reactions involving trimethylbutane are not easy to explain in terms of single-step Wagner–Meerwein shifts.[14] With acyclic ions, such isomerizations require migration of an alkyl group to a carbon more distant than the adjacent one, rearrangement of the migrating group to offer a different point of attachment, or participation of primary carbonium ions. The concept of a cyclic intermediate permits a simpler solution



Intramolecular migration of one hydrogen atom to an adjacent carbon must take place concomitantly.

The cyclic intermediate may also play a part in determining the course of isomerization of an ion. In particular, it would be expected to aid migration of an alkyl group along a chain, for the resonance structures of the ion are similar. As a factor in aiding the formation or removal of a tertiary carbon it should be less effective, for in intermediate ions in these processes the resonance structures are less equivalent.

Implications with Respect to the Alkylation Mechanism.—Several conclusions from this work aid in extending and clarifying the concepts of the carbonium ion mechanism of alkylation[15] particularly with respect to the properties of the carbonium ions involved. We may represent the coupling reaction as follows, using *t*-butyl ion



$$CH_3-\overset{CH_3}{\underset{CH_3}{C^+}} + \overset{H}{\underset{R'}{\bar{:}C}}-\underset{H}{C^+}-R \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{H}{\underset{R'}{C}}-\underset{H}{C^+}-R$$

with the olefin written in its polar form. The slowness of conversion of olefin to carbonium ion[2a] assures the presence of a finite concentration of olefin in the acid. We know from work reported above that (1) only tertiary carbonium ions receive hydride ions to regenerate hydrocarbon in a chain-carrying step, and (2) the rate of isomerization of branched ions is roughly similar to or faster than the rate of the chain-carrying step. Therefore, where R′ is H, isomerization always occurs to form a tertiary ion, which may then react to form an isoparaffin. Whether R′ is or is not H, the variety of the isomerizations that are possible during ionic residence produces the variety of isoparaffin products.

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[14] See Table II. Also, V. I. Komarewsky and W. E. Ruther, THIS JOURNAL, **72**, 5501 (1950).

[15] P. O. Bartlett, F. E. Condon and A. Schneider, *ibid.*, **66**, 1531 (1944); L. Schmerling, *ibid.*, **67**, 1778 (1945); **68**, 275 (1946); H. S. Bloch, H. Pines and L. Schmerling, *ibid.*, **68**, 153 (1946).

If the ion is highly branched, dealkylation or disproportionation will be favored, and conditions favorable to long ion residence would provide an additional tendency to produce such side reactions. It is to be noted that with stronger acids, such as moist aluminum chloride, chain-carrying steps involving secondary carbonium ions and secondary hydrogens may be possible, so that a greater variety of products would be expected to result.

Effects of Reaction Conditions.—It was shown in the previous paper[2a] that the addition of isobutylene to an isobutane–sulfuric acid system eliminated the initial induction period and increased the overall rate of the hydrogen exchange reaction by a factor proportional to a fractional power of the initial olefin concentration. This effect was presumably due to an increase in the concentration of carbonium ions and a resulting increase in the number of ionic chains at any instant.

When 2-methylpentane containing 1% 2-methyl-2-butene was shaken with 2 ml. of 95.8% sulfuric acid in the usual manner, the interconversion reaction to 3-methylpentane reached approximate equilibrium in less than 70 minutes (24% 3-methylpentane). A small amount of 2,3-dimethylbutane was also formed, and there was some evidence of disproportionation. Gordon and Burwell[8] found that added butylenes increased the rate of racemization of optically active 3-methylheptane. An increase in the number of ionic chains would be expected to increase the rate of all reactions dependent upon the existence of ions.

Molecular Weight.—It is evident from Tables I and II that for a given type of compound, such as $(CH_3)_2CHR$, where R is a *n*-alkyl group of any size, the rates of isomerization and hydrogen exchange, in terms of numbers of molecules undergoing these reactions per unit time, decrease significantly with increasing molecular weight. Thus, for example, experiments 1, 2 and 8 show 1% 2-methylhexane, 4% 2-methylpentane and 13% isopentane undergoing some type of hydrogen exchange under the same experimental conditions in 95% D_2SO_4. Experiments 31 and 56 show 1.1% 2-methylhexane and 4.0% 2-methylpentane isomerizing in 96% H_2SO_4 under identical conditions. Burwell[8] found the same qualitative effect on the hydrogen exchange reaction. The reason for this effect is not clear, since solubility, ease of polarization by acid, and ability to transfer the tertiary hydride or to be oxidized are characteristics which all may influence the rate of ion formation. This effect is not so noticeable in the cyclane series; methylcyclopentane and methylcyclohexane undergo the hydrogen exchange reaction at roughly equal rates.

Agitation and Hydrocarbon–Acid Ratio.—There is a strong effect of degree of agitation on the rate of isomerization as shown in experiments 33 and 35, Table II. This is expected in a heterogeneous system where a rate-determining step is the entrance of the reactant into the reaction zone. In line with this, one expects with a given rate of agitation and amount of acid that the total conversion will be approximately constant, so that the percentage conversion will be inversely proportional to the amount of hydrocarbon used. This was proved to be the case in a special run made parallel with No. 33, Table II, differing from it only in that the volume ratio of hydrocarbon to acid was 1:1 instead of 0.07:2. The per cent. isomerization was approximately 1% instead of 16.3%.

The concept that "distant" hydrogen exchange is due to isomerization makes it possible to estimate the fraction of the molecules that isomerize during their residence as ions. Thus, with isopentane the ratio of species $(d_9 + d_{10} + d_{11})/\Sigma d_n$[16] gives the ratio of the number of molecules undergoing at least one carbon atom rearrangement to the total number passing through at least one ionic residence. According to the postulated mechanism, one should be able to increase the chance of isomerization of an ion by decreasing the degree of agitation, since the termination of the life of the ion to regenerate the hydrocarbon depends upon contact with a hydrocarbon molecule, probably at the interface. This is demonstrated to be the case in experiments 82 and 83, Table IV, where the ratio is 0.29 with agitation and 0.46 without agitation. An alternative explanation for this result is the concept that the ion reacts with hydrocarbon molecules in solution, and that rate of interchange of hydrocarbon molecules between phases is decreased in the absence of agitation so that molecules once they are in solution tend to return to the ionic state several times before they leave the catalyst phase. The experimental result may be due to either or both of these experimentally indistinguishable interpretations.

Acid Concentration.—The rates of isomerization and hydrogen exchange are very sensitive to acid concentration. This was previously noted with respect to isobutane hydrogen exchange.[2a] Experiments 84 and 85 (Table IV) represent an attempt to explore the effect of acid concentration on the probability that a carbonium ion will isomerize during its lifetime. It was found that although the fraction of isopentane molecules reacting with D_2SO_4 was much smaller in dilute acid, the proportion of -d_{11} species in the product was much higher. This may be interpreted on the basis of longer ionic residence; there is greater probability of isomerization if the ionic residence period is longer, assuming no significant effect of acid concentration on the activation energy of isomerization. In more dilute acid the chain transfer steps are undoubtedly more difficult because of poorer polarization of isoparaffin and probably lower solubility of isoparaffin in the acid. The chains will be fewer in number and their rate of propagation slower.

Temperature.—Experiments 38, 39, 49 and 50, Table II, and 87, Table IV, were performed at 0°. Isomerization and hydrogen exchange reactions are very slow at that temperature. In the hydrogen exchange experiment with isopentane, run No. 87, the -d_{11}/-d_n ratio was much lower (0.21 *vs.* 0.38) than at room temperature (run No. 90). It is clear that with increasing temperature more ions are formed per unit time and the probability for isomerization of those ions is increased. This probability is determined by the relationship be-

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(16) Species other than -d_1 and -d_{11} are produced when the depth of conversion is great enough to cause significant isotopic dilution of the acid.

tween the rate of isomerization of the ion and the rate of reversion of the ion to the hydrocarbon.

Burwell and Gordon[8] found that chlorosulfonic acid at −78° could catalyze racemization of (+)-3-methylheptane without isomerization and with little hydrogen exchange. This result is consistent with the results with isopentane reported above. Increased viscosity of the acid at that temperature may cause very much decreased rate of hydrogen exchange between ion and acid. That mobility of the catalyst is essential for this exchange is indicated by the lack of exchange between isobutane and water-promoted aluminum chloride on alumina.[10] Although the chain transfer reaction occurs over that catalyst, hydrogen exchange with catalyst appears to be absent.

Experimental

Experimental Materials.—The hydrocarbons used are the following: cyclopentane Phillips Research Grade, refractionated; isopentane Phillips Research Grade; 2-methylpentane NBS[17]-204a ((a) Phillips Research Grade, specially treated,[18] mass spectrum indistinguishable from that of the NBS sample); 3-methylpentane NBS–205a ((a) Phillips Pure Grade, specially treated,[18] mass spectrum discloses presence of 3.6% 2-methylpentane); 2,3-dimethylbutane Phillips Research Grade, specially treated[18]; 2,2-dimethylbutane Phillips Research Grade; *n*-heptane Westvaco Chlorine Products material, b.p. 98.43°; 2-methylhexane NBS–223 ((a) commercial material distilled through 20 plates, at a reflux ratio of 25:1, b.p. 90.3°); 2,3-dimethylpentane NBS–227; 2,4-dimethylpentane NBS–228; 3-ethylpentane NBS–225; trimethylbutane NBS–222; methylcyclohexane, purified by distillation, $n^{20}_{\rm D}$ 1.4229; ethylcyclopentane NBS–266; *cis*-1,2-dimethylcyclopentane from fractional distillation of *cis-trans* mixture, purity estimated from distillation curve to be 99.9%; 2,3,3-trimethylpentane NBS–244; 2,2,4-trimethylpentane plant material, purified with silica gel for use as a solvent for spectroscopy; 2-methyl-2-butene NBS–286; 2-methylpentane-2-*d* synthesized (see subsequent section), contained 26.5% ordinary 2-methylpentane; 2-methylpentane-4-*d* synthesized, contained 19.0% ordinary 2-methylpentane; 2-methylpentane-5-*d* synthesized, contained 23.8% ordinary 2-methylpentane; sulfuric acid-d_2 was prepared by the distillation of SO_3 into D_2O.[1a]

Procedure.—For each experiment, 2 ml. of the acid was pipetted into a glass tube, sealed at one end, 10 mm. o.d. × 200 mm. long. The tube was constricted about 150 mm. from its closed end, attached to a vacuum system by a rubber tube, and evacuated. The hydrocarbon (0.6 millimole, measured as gas pressure in a known volume) was distilled into the tube. The distillation was carried out by cooling only a part of the tube above the acid, since freezing of the acid would result in tube breakage. A rubber stopper and short glass cylinder were used to hold the liquid nitrogen. The tube was sealed and was then shaken along its axis (by a shaking machine) in an arc of 35°, 21.5 cm. from the pivot point, 235 times per minute. At the end of the shaking period the tube was broken open and the hydrocarbon was distilled into a trap in liquid nitrogen and then into a sample tube for mass spectrometric analysis. When compounds of widely different boiling point might be formed by disproportionation or dealkylation, as with the heptanes and octanes, the entire sample was distilled into a liter bulb attached by a Kovar seal to a metal valve (no grease). The liter volume was sufficient for complete vaporization at 25°, so that the sample removed for mass spectrometric analysis was representative.

In certain cases runs were made at low temperature with the samples enclosed in a jar containing ice. The jar was shaken along its axis (and the axis of the reaction tubes) in a reciprocal horizontal motion, 200 oscillations per minute, with an amplitude of 15 cm.

Mass Spectrometric Analyses.—The mass spectrometric analyses of the products from reacting systems containing no excess deuterium were carried out by standard methods, involving no assumptions whose validity was not subject to direct test. Suitable sets of simultaneous equations involving mass spectral intensities and concentrations were solved for the concentrations of probable reaction products and the uniqueness of each resultant solution was checked by comparing calculated and observed mass spectral intensities of ions not used in the sets of simultaneous equations.

The purities of the preparations of 2-methylpentane-2-*d*, -4-*d*, and -5-*d* were determined by means of the methods developed in connection with the problem of assaying the preparations of the C_1–C_4 monodeutero paraffins.[19] The use of 7.0 ev. (uncor.) ionizing electrons permits the direct determination of both C_6H_{12} and C_6H_{14} content of $C_6H_{13}D$ preparations. For the estimation of C_6H_{12} from the specific intensity of the ion $m/q = 84$ in the 7.0 ev. mass spectrum, the sensitivity of 2-methyl-2-pentene was used. For the estimation of the C_6H_{14} content it was assumed that the sensitivities of the C_6H_{14} and $C_6H_{13}D$ at m/q equal to 86 and 87, respectively, are equal.

The mass spectra of 2-methylpentane-2-*d*, -4-*d* and -5-*d* were calculated from the mass spectra of the preparation by correction for the 2-methylpentane-d_0 content determined as above outlined. These mass spectra are shown in Table VI. There are also shown in Table VI the measured mass spectra of 3-methylpentane-d_0 and the estimated mass spectra of the 3-methylpentanes-*d* used in interpreting the mass spectra of the products of reactions of the 2-methylpentanes-*d* with ordinary sulfuric acid. From the results of the experiments with both methylpentanes and ordinary sulfuric acid it was concluded that the production of 2,3-dimethylbutanes in the reaction between 2-methylpentanes-*d* and ordinary sulfuric acid could be neglected. The concentrations of 2-methylpentane-d_0 and -d_1 in the reaction products were calculated from the specific intensities of the ions $m/q = 72$ and 71 since these (along with $m/q = 70$) are least subject to interference from 3-methylpentanes. The specific intensities of the ions $m/q = 58$ and 56 were then corrected for 2-methylpentane contributions and the residual specific intensities were used to calculate the con-

Table VI

Mass Spectra of the Methylpentanes and Certain Monodeutero-methylpentanes

75 ev. 65° Magnetic Scan (Westinghouse Mass Spectrometer)

	2-Methylpentanes				3-Methylpentanes		
m/*q*	-d_0-	-2-*d*	-4-*d*	-5-*d*	-d_0-	-3-*d*[a]	-4-*d* and -5-*d*
88		2.68	2.48	2.54			
87	2.47	42.1	40.1	39.8	2.07	34.7	33.0
86	39.8	1.77	3.62	4.05	32.8	1.23	2.55
85	3.90	1.75	0.25	0.08	2.85	1.23	0.20
84	0.16	0.08	0.02	0.02	0.06		
73		5.70	5.70	6.00			
72	5.68	106.0	108.0	112.2	0.86	16.0	16.0
71	106.5	30.3	27.2	31.4	16.0	4.8	4.8
70	29.1	4.2	4.0	1.7	4.76		
69	1.99	0.95	0.47				
58	1.69	25.4	7.57[b]	6.96[b]	10.3	244	122
57	39.5	13.5	36.0	44.0	244	222	233
56	19.0	15.2	24.3	23.2	222	13.7	120
55	14.7	5.74	5.45	7.0	13.7		

[a] The 3-methylpentane-*d* mass spectra are estimated. [b] The 58/57 ratio provides a check on the isomeric purity of the preparations. While the synthetic route would not be expected to lead to shifts in the substituent position (where the OH is on a carbon not adjacent to the tertiary), the substantial absence of deuterium in the C_4 ion fragment for the -4-*d* and -5-*d* furnishes further evidence on this point.

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(17) Samples designated NBS were obtained from the National Bureau of Standards.

(18) Treated by shaking 100 ml. for 30 minutes with 25 cc. of mercuric sulfate–sulfuric acid reagent (228 g. of mercuric sulfate dissolved in 690 ml. of 22% sulfuric acid and diluted to one liter). It was then washed with sodium bicarbonate solution, dried, distilled from potassium hydroxide pellets, and passed through a 40-cm. column of 200 mesh silica gel. Refractive indices of the 2-methylpentane and 2,3-dimethylbutane so treated checked the indices of the NBS samples to ±0.00005.

(19) D. P. Stevenson and C. D. Wagner, This Journal, **72**, 5612 (1950).

centrations of 3-methylpentanes. The quality of the analysis so obtained was checked by comparing the observed intensities of the ions of $m/q = 87$, 86, 70 and 57 with those calculated from the composition and the mass spectra of the components. In the case of the reaction of 2-methylpentane-2-*d* an additional check on $m/q = 43$ was made in order to test further the validity of the assumption of negligible concentrations of 2,3-dimethylbutanes in the product.

There are shown in Table VII typical examples of calculated and observed intensities for the mass spectra of the products of various experiments.

TABLE VII

COMPARISON OF CALCULATED AND OBSERVED SPECIFIC INTENSITIES IN MASS SPECTRA OF PRODUCTS OF REACTIONS[a] OF 2-METHYLPENTANES-*d* WITH SULFURIC ACID

	2MP-4-*d*,[b] 1 hr.	2MP-4-*d*, 2 hr.	2MP-5-*d*, 2 hr.	2MP-5-*d*, 4 hr.
87 (calcd.)	28.9	26.8	27.7	25.0
87 (obsd.)	29.2	26.9	28.0	25.2
86 (calcd.)	12.80	13.91	12.78	14.18
86 (obsd.)	12.89	14.11	12.85	13.96
70 (calcd.)	10.18	10.63	8.36	8.93
70 (obsd.)	9.96	10.52	8.39	8.86
57 (calcd.)	41.5	44.8	44.3	49.5
57 (obsd.)	41.8	45.4	44.2	49.0

[a] See Table III for description of experiments and results of analyses. [b] MP, methylpentane.

The qualitative identification of the products resulting from the reactions of the various hydrocarbons with deuterosulfuric acid was accomplished by noting in the mass spectra of the products the ions of greater molecular weight than that of the initial hydrocarbon. The fact that C_4 and heavier alkanes and cyclanes have in their mass spectra virtually no ions, $C_nH_{m-2}^+$ - - -C_n^+, where the hydrocarbon is C_nH_m, renders this qualitative identification of the empirical formulas of the new species formed straight forward. The quantitative estimates of the quantities of $C_nH_{m-k}D_k$ formed from C_nH_m, were made by first correcting the mass spectra in the "heavy mass region" ($m/q > 12\,n + m \sim C_nH_m$) for natural C^{13} contributions by the formula

$$i'_m = i^{\circ}_m - 0.0101n \times i^{\circ}_{m-1}$$

where i' and i° are corrected and observed intensities, respectively, and the subscript indicates the molecular weight (m/q) of the ion. Each i'_m was then corrected for the contribution to this intensity from the substance of one higher molecular weight by the formula

$$i''_m = i'_m - \rho i'_{m+1}$$

where ρ was taken equal to the ratio $C_nH_{m-1}^+/C_nH_m^+$ characteristic of the mass spectrum of C_nH_m. The justification for such a choice of the second correction is given in the following paragraph.

From the studies of the mass spectra of the monodeutero-isobutanes and 2-methylpentanes it was apparent that the ions $C_nH_{m-1}^+$ are largely formed from $C_nH_m^+$ by loss of the tertiary hydrogen. Further, all the exchange experiments are only consistent with the view that regardless of the extent of exchange in an isoparaffin, the tertiary hydrogen is preserved. Thus the $C_nH_{m-k}D_k$ each will contain a tertiary hydrogen (protium) and give rise to an ion $C_nH_{m-k-1}D_k$ in their mass spectra. The above referred to studies have also shown that substitution of D for H other than tertiary H tends to increase the relative probability of the isoparaffin ion dissociating its tertiary H. Hence we expect $C_nH_{m-k-1}D_k^+/C_nH_{m-k}D_k^+ \geqslant C_nH_{m-1}^+/C_nH_m^+$. The equality sign must be included because for an isoparaffin having both secondary and tertiary hydrogen there is a finite probability of the formation of $C_nH_{m-1}^+$ from $C_nH_m^+$ through dissociation of a secondary hydrogen and thus the substitution of D's for secondary H's will tend to compensate for the isotope effect in increasing the dissociation probability of the tertiary H. The contribution of $C_nH_{m-k}D_k$ to ions of two less m/q through the dissociation of a secondary D from the molecule ion can be neglected because of the markedly lower dissociation probability of C–D than of an equivalent C–H bond.

The concentrations of the various $C_nH_{m-k}D_k$ isotopic species in the product were calculated from the corresponding i''_m with the assumptions that all sensitivities were equal and equal to the parent ion sensitivity of the hydrocarbon being studied. Exceptions to this method of calculation were made in those cases where it was quite clear that the $C_nH_{m-k}D_k$ species (actually restricted to completely deuterated molecules, C_nHD_{2n+1}) was composed of very different carbon structures from that of the original C_nH_m. The criterion of the extent of isomerization that accompanied exchange in a particular reaction was the comparison of the ratios $C_{n-1}H_{2n-1}^+/C_nH_{2n+2}^+$ with $C_{n-1}HD_{2n-2}^+/C_nHD_{2n+1}^+$, characteristic of the mass spectra of original isoparaffin and product.

This analytical procedure is illustrated in Table VIII where the original data and the successive steps in a typical

TABLE VIII

THE ANALYSIS OF THE REACTION PRODUCT FROM 2-METHYLPENTANE AND D_2SO_4 (95%) AFTER 20 MINUTES

m/q	i_m°	C^{13} correction	i'_m	Heavier species correction	i''_m	
100	0.02	− 0.02	= 0.00			
99	.29	− .00	= .29		0.29 ÷ 0.374 = 0.78%	C_6HD_{13}
98	.05	− .00	= .05	− 0.03	.02 ÷ .374 = .05%	$C_6H_2D_{12}$
97	.02	− .02	= .00		.00 ÷ .374 = .00%	$C_6H_3D_{11}$
96	.29	− .02	= .27		.27 ÷ .374 = .72%	$C_6H_4D_{10}$
95	.27	− .03	= .24	− .03	.24 ÷ .374 = .64%	$C_6H_5D_9$
94	.40	− .00	= .40	− .02	.38 ÷ .374 = 1.02%	$C_6H_6D_8$
93	.07	− .00	= .07	− .04	.03 ÷ .374 = 0.08%	$C_6H_2D_7$
92	.00				——	
91	.00				3.29	
90	.00					
89	.00					
88	.00					
87	2.35					
86	37.5	÷ .398	= 94.3% C_6H_{14} (2-Methylpentane)			
85	3.82					
84	0.15				81/99 = 0.65/0.29 = 2.24	
83	.01					
82	.03					
81	.65				71/86 = 106.5/37.5 = 2.70	
80	.07				Hence 3-me-d_3-pentane-d_{10}/2-me-d_3-pentane-d_{10} $\backsimeq$ 1/2	
71	101.0					
64	3.52	÷ 1.90	= 1.9% SO_2			

calculation are shown. The example is that of the product from the reaction of 2-methylpentane with D_2SO_4 (95%), 25 minutes contact at 25°. In the first column of Table VIII are shown the m/q of the ions and in the second column there are the observed specific intensities of the ions in the mass spectra of the product. The absence of detectable intensity for ions $88 \leqq m/q \leqq 92$ indicates that no $C_6H_{12}D_2$, $C_6H_{11}D_3$, $C_6H_{10}D_4$, $C_6H_9D_5$ or $C_6H_8D_6$ was formed. The third column shows the quantities, $0.061 \times i_{m-1}$ and the fourth column the first corrected intensities, i'_m. The fifth column shows $0.102\, i'_m$ and the sixth column the second corrected intensities i''_m. The 81/99 ratio of the product, 2.24 (representing the reciprocal of the relative probabilities for producing undissociated ions and those lacking one methyl group) is considerably less than the 71/86 ratio of 2-methylpentane. If the C_6HD_{13} were all 2-methylpentane-d_{13} the 81/99 ratio would be expected to be equal to or greater than the 71/86 ratio of 2-methylpentane-d_0 since in both isobutane-d_9 and isopentane-d_{11} the 49/67 and 65/83 ratios are greater than the 43/58 and 57/72 ratios characteristic of isobutane-d_0 and isopentane-d_0, respectively (see below). Since the 71/86 ratio of 3-methylpentane is but 0.50 and other experiments showed the 2- and 3-methylpentane to be interconvertible in the presence of sulfuric acid, it is concluded that the C_6HD_{13} is about a 2:1 mixture of the 2- and 3-isomers of methylpentane. The sensitivity used to calculate the concentration of $C_6H_{14-n}D_n$ shown in the eighth column from the i''_m, $0.374\ (\%)^{-1}$, was taken as the weighted (2:1) average of the sensitivities of 2-methylpentane-d_0 and 3-methylpentane-d_0 of Table VII.

Since the 71/86 ratio of the product agrees with that of 2-methylpentane-d_0 it is concluded that the C_6H_{14} in the product contains essentially no isomerized and unexchanged 2-methylpentane, and therefore the 2-methylpentane-d_0 sensitivity was used to calculate the concentration of C_6H_{14}. The ion of $m/q = 64$ was interpreted as due to sulfur dioxide and calculated accordingly since $m/q = 64$ is not expected to occur in the mass spectra of the deuterohexanes and does not occur in the mass spectra of 2-methylpentane.

As was mentioned above, the ratios $C_{n-1}HD_{2n-2}^+/C_nHD_{2n+1}^+$ and $C_{n-1}H_{2n-1}^+/C_nH_{2n+2}^+$ characteristic of the mass spectra of the reaction products and the initial hydrocarbon (and its isomers) were compared as a guide to the probable nature of the structure of the product. In the case of the products resulting from the reaction of the various heptanes with D_2SO_4 the mass spectral ratio $C_5HD_{10}^+/C_7HD_{15}^+$ was compared with $C_5H_{11}^+/C_7H_{16}^+$ in addition to the comparison of the $C_6HD_{12}^+/C_7HD_{15}^+$ and $C_6H_{13}^+/C_7H_{16}^+$ to obtain further information. The experimental data are given in Tables IX and X and their interpretation discussed in the following paragraphs.

TABLE IX

MASS SPECTRAL DATA PERTAINING TO THE STRUCTURE OF C_nHD_{2n+1} FORMED FROM C_nH_{2n+2} AND D_2SO_4

Isoparaffin	$\frac{C_{n-1}H_{2n-1}^+}{C_nH_{2n+2}^+}$	$\frac{C_{n-1}HD_{2n-2}^+}{C_nHD_{2n+1}^+}$
Isobutane	15.3	17.0
Isopentane	3.08	3.68
2-Methylpentane	2.87	2.22
3-Methylpentane	0.50	2.34
2,3-Dimethylbutane	1.68	1.70
Methylcyclopentane	1.14	1.52
Methylcyclohexane	1.37	1.69
Ethylcyclopentane	0.22	1.69

TABLE X

MASS SPECTRAL DATA PERTAINING TO THE STRUCTURE OF C_7HD_{15} FORMED FROM VARIOUS C_7H_{16} AND D_2SO_4

Heptane	$\frac{C_6H_{13}^+}{C_7H_{16}^+}$	$\frac{C_5H_{11}^+}{C_7H_{16}^+}$	$\frac{C_6HD_{12}^+}{C_7HD_{15}^+}$	$\frac{C_4HD_{10}^+}{C_7HD_{15}^+}$
2-Methylhexane	2.65	0.13	2.02	1.83
3-Methylhexane	0.33	3.05	..	..
3-Ethylpentane	0.044	4.69	2.53	1.05
2,3-Dimethylpentane	0.61	3.32	1.88	1.67
2,4-Dimethylpentane	3.12	0.15	1.73	1.58
Trimethylbutane	120	0.11	5.26	1.09

Inasmuch as isobutane, isopentane and methylcyclopentane do not isomerize in ordinary sulfuric acid, and neither isobutane nor 2-methylpentane exchange their tertiary hydrogens with sulfuric acid, the compounds C_4HD_9, C_5HD_{11}, and C_6HD_{11} formed from isobutane, isopentane and methylcyclopentane, respectively, in their reactions with D_2SO_4 may be assumed to have unchanged structures and tertiary protium atoms.

Thus the $C_{n-1}HD_{2n-2}^+/C_nHD_{2n+1}^+$ ratios characteristic of the mass spectra of their products provide a guide to magnitude of the isotope effects on the dissociation probabilities of molecule ions to be expected from the replacement of $2n + 1$ protium atoms by deuterium atoms in an isoparaffin. It will be noted, Table IX, that in each case cited, the isotope effect is that of increasing the dissociation probability of the molecule-ion.

In view of the foregoing remarks it is quite certain that the products C_6HD_{13} and C_7HD_{15} resulting from 2-methylpentane and 2-methylhexane, respectively, contain isomer(s) in addition to the 2-methylalkanes, since in both cases the $C_{n-1}HD_{2n-2}^+/C_nHD_{2n+1}^+$ ratios in the mass spectra are considerably smaller than the $C_{n-1}H_{2n-1}^+/C_nH_{2n+2}^+$ ratios of the initial hydrocarbons. The decreases are in the direction expected to accompany the formation of the 3-methyl isomers, in agreement with the findings in the experiments on these substances with ordinary sulfuric acid. The $C_{n-1}HD_{2n-2}^+/C_nHD_{2n+1}^+$ ratio characteristic of the mass spectrum of the C_6HD_{13} from 3-methylpentane is greater than the $C_{n-1}H_{2n-1}^+/C_nH_{2n+2}^+$ ratio characteristic of 3-methylpentane by much more than can be accounted for by isotope effect, hence we conclude that this C_6HD_{13} contains a large concentration of the 2-methyl isomer. The essential equality of the $C_{n-1}HD_{2n-2}^+/C_nHD_{2n+1}^+$ ratios, characteristic of the mass spectra of the C_6HD_{13} produced from both 2-methylpentane and 3-methylpentane is best accounted for by the conclusion that the C_6HD_{13} produced is an equilibrium mixture of the 2-methyl and 3-methyl isomers. If isotope effects are neglected, because their magnitudes in these cases are unknown, the data in Table VI lead to 2.12 as the value expected for the $C_{n-1}HD_{2n-2}^+/C_nHD_{2n+1}^+$ ratio characteristic of the mass spectrum of the equilibrium mixture (2-methylpentane = 71.2% m, 3-methylpentane = 28.8%m) of methylpentanes. This calculated value is in reasonable agreement with that observed, 2.22–2.34, and the deviation is in the direction to be expected from the neglect of isotope effects. It seems then that the equilibrium mixture of carbonium ions in sulfuric acid in this case has roughly the same composition as the equilibrium mixture of parent hydrocarbons. A similar calculation of the expected $C_{n-1}HD_{2n-2}^+/C_nHD_{2n+1}^+$ ratio in the mass spectrum of an equilibrium mixture of the 2-methyl and 3-methyl isomers of C_7HD_{15} (2-methyl = 53.3% and 3-methyl = 46.7%) leads to 1.74 which again deviates from the observed, 2.02, in the manner to be expected from the neglect of isotope effects. In the case of the product from 2-methylhexane the very large value of $C_5HD_{10}^+/C_7HD_{15}^+$ confirms the formation of the 3-methyl isomer. The calculated value of this ratio for an equilibrium mixture is 1.29, and the deviation is again in the right direction.

The thermodynamic stability of methylcyclohexane relative to that of its cyclopentyl isomers precludes the possibility that the C_7HD_{13} formed from this substance is other than methylcyclohexane-d_{13}. The relative magnitudes of $C_{n-1}HD_{2n-4}/C_nD_{2n-1}^+$ and $C_{n-1}H_{2n-3}^+/C_nH_{2n}^+$ characteristic of the mass spectra of product and initial hydrocarbon are comparable with those observed in other cases where no isomerization would be expected, namely, isobutane, isopentane and methylcyclopentane. The equality of the $C_{n-1}HD_{2n-4}^+/C_nHD_{2n-1}^+$ ratios of the mass spectra of the C_7HD_{13} from ethylcyclopentane and methylcyclohexane is conclusive evidence that the isomerization of ethylcyclopentane in sulfuric acid gives methylcyclohexane exclusively.

The studies of the reaction of 2,3-dimethylbutane in ordinary sulfuric acid showed the isomerization of this substance to be very slow; thus the C_6HD_{13}, formed in the reaction with D_2SO_4 may be taken to be exclusively 2,3-dimethylbutane. The equality of $C_{n-1}HD_{2n-2}^+/C_nHD_{2n+1}^+$ and $C_{n-1}H_{2n-1}^+/C_nH_{2n+2}^+$ of product and initial hydrocarbon indicates the absence of isotope effect. This absence of isotope effect on the dissociation probability of 2,3-dimethylbutane molecule-ions provides substantiation of assumptions made in the interpretation of the mass spectra of the products of reaction of the dimethylpentanes and D_2SO_4.

The essential equality of the $C_6HD_{12}^+/C_7HD_{15}^+$ and $C_5HD_{10}^+/C_7HD_{15}^+$ ratios characteristic of the mass spectra of the C_7HD_{15} formed from both 2,3- and 2,4-dimethylpentane indicates the C_7HD_{15}'s to have essentially the same isomer distributions. Since the experiments in ordinary sulfuric acid with this pair of isomers indicated the initial reactions to be primarily methyl group shifts it seems reasonable to assume the C_7HD_{15} to be primarily a mixture of the 2,3- and 2,4-dimethylpentanes. In view of the finding that the methylpentanes and methylhexane give C_nHD_{2n+1} which are approximately equilibrium mixtures of the 2- and 3-isomers one would expect the same to obtain for the 2,3- and 2,4-dimethylpentane-d_{15}'s. However, the equilibrium ratio, 2,3-/2,4- equals 3.7, and the 97/115 and 81/115 ratios calculated for concentrations corresponding to equilibrium are 1.04 and 2.47, respectively. These are incompatible with the observed 1.8 ± 0.1 and 1.6 ± 0.1. If the ratio of 2,3 to 2,4-dimethylpentane is assumed to be 0.83 the 97/115 and 81/115 ratios are calculated to be 1.80 and 1.56, respectively, in good agreement with the observed values.

If it is assumed that the C_7HD_{15} formed from the dimethylpentane is a mixture of dimethylpentanes in their equilibrium ratio (2,3-/2,4- = 3.7) plus trimethylbutane, there is no relative concentration of dimethylpentanes and trimethylbutane compatible with the observed ratio, $C_6HD_{12}^+/C_7HD_{15}^+$ and $C_5HD_{10}^+/C_7HD_{15}^+$.

The ratios $C_6HD_{12}^+/C_7HD_{15}^+$ and $C_5HD_{10}^+/C_7HD_{15}^+$ characteristic of the mass spectrum of the C_7HD_{15} formed from trimethylbutane clearly indicate this C_7HD_{15} to be a mixture of isomers. If the mixture is assumed to have only trimethylbutane, 2,4- and 2,3-dimethylpentanes in the ratio 3:3:1 the mass spectral ratios are calculated to be $C_6HD_{12}^+/C_7HD_{15}^+ = 5.30$ and $C_5HD_{10}^+/C_7HD_{15}^+ = 0.95$ in quite reasonable agreement with the observed values.

The mass spectrum of the C_7HD_{15} formed from 3-ethylpentane clearly indicates 3-ethylpentane-d_{15} to be a minor product. The magnitude of $C_5HD_{12}^+/C_7HD_{15}^+$ shows one or all of the following isomers, 2-methylhexane-d_{15}, 2,4-dimethylpentane-d_{15} and trimethylbutane-d_{15}, to have been formed in significant quantity. Similarly the finite value of $C_5HD_{10}^+/C_7HD_{15}^+$ indicates the presence of one or all of the following isomers, 3-ethylpentane-d_{15}, 3-methylhexane-d_{15} and 2,3-dimethylpentane-d_{15}. The relative magnitudes of the ratios $C_6HD_{12}^+/C_7HD_{15}^+$ and $C_5HD_{10}^+/C_7HD_{15}^+$ in the mass spectrum of this product indicate the relative concentrations of the two groups of isomers (2-MH + 2,4-DMP + 2,2,3-TMB):(3-EP + 3-MH + 2,3-DMP), to be between 2.0:1 and 2.5:1.

Syntheses of the Monodeutero-2-methylpentanes.—These compounds were prepared by treatment of the appropriate Grignard reagent with 99.8% deuterium oxide (obtained from Stuart Oxygen Company under allocation by the Atomic Energy Commission). The halides were prepared by the reactions

$$n\text{-PrMgBr} \xrightarrow[\text{H}^+]{\text{Me}_2\text{CO}} \text{Me}_2\text{C(OH)Pr} \xrightarrow[\text{concd.}]{\text{HCl}} \text{Me}_2\text{CClPr} \quad (1)$$

$$\text{Me}_2\text{CHCH}_2\text{CHOHMe} \xrightarrow{\text{PBr}_3} \text{Me}_2\text{CHCH}_2\text{CHBrMe} \quad (2)$$

$$\text{Me}_2\text{CHCH}_2\text{MgCl} \xrightarrow[\substack{\text{oxide,}\\ \text{H}^+}]{\text{ethylene}} \text{Me}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{\text{PBr}_3} \text{Me}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{Br} \quad (3)$$

The following are the details of the syntheses.

2-Methylpentane-2-*d*.—Grignard reagent was prepared in a three-neck round-bottom 500-ml. flask using 18 ml. (200 millimoles) of *n*-propyl bromide (Eastman Kodak Company white label grade, fractionated in a 60 bubble plate column at 50:1 reflux ration, b.p. 70.74°) 4.9 g. of magnesium turnings and 50 ml. of ether. Then a solution of 25 ml. of acetone in 30 ml. of ether was added slowly with stirring. The mixture was thoroughly cooled in ice and 20 ml. of concentrated hydrochloric acid in 40 ml. of water was added slowly with stirring. The ether phase was separated, washed and dried, and the ether was removed by distillation. To the alcohol residue was added 350 ml. of concd. hydrochloric acid. The mixture was shaken and allowed to separate. The upper phase was dried over calcium chloride, distilled through phosphorus pentoxide, and fractionally distilled. The product distilling at 111–112° amounted to 12.8 g., or 106 millimoles.

Grignard reagent was prepared in a conventional apparatus under nitrogen by the slow addition of 12.8 ml. of the hexyl chloride in 40 ml. of dry ether to 2.6 g. of magnesium. The dropping funnel was replaced by a rubber policeman, and the mercury-seal stirrer by a stainless steel rod inserted through a rubber stopper. With the mixture cooled in ice, 6.5 ml. of deuterium oxide (99.8% D) was added in portions as a spray from a fine hypodermic needle, which was inserted into the system through the rubber policeman. The manual stirrer was used occasionally to stir the mixture and to break up the aggregates of basic salt around the D_2O droplets. After the mixture was allowed to stand at room temperature for two hours, all of the volatile materials in the system were distilled under vacuum into a cold trap. The distillate was shaken with Ascarite and fractionated in a Podbielniak-type column. The fraction boiling between 58 and 70° amounted to 6.8 g., corresponding to a 74% yield of hydrocarbon. Mass spectrometric analysis, however, disclosed that the material contained 0.3% ethyl ether, 23% 2-methylpentenes and 18–25% ordinary 2-methylpentane.

The distillation was repeated with a small forecut removed to eliminate the ether. Then 2.35 g. of bromine was distilled into the sample cooled in liquid air. The mixture was warmed to −10° and shaken. The bromine reacted completely almost immediately, leaving a colorless solution. The volatile, unbrominated materials were removed by distillation on the vacuum system until the vapor pressure of the residue at room temperature was less than 2 mm.

The distillate, which according to the first analysis should contain less than 1% olefin after treatment with the amount of bromine used, was found by mass spectrometric analysis to contain $< 0.46\%$ olefin. It was treated with 0.3 g. of bromine plus one drop of water at room temperature for 15 minutes. In this treatment, the bromine color did not disappear, and the excess bromine and any hydrogen bromide or alkyl bromides were removed by treatment of the mixture with 5 ml. of redistilled ethanolamine at room temperature. For removal of any ammonia produced in this reaction, and any residual ether, the sample was then shaken with one ml. of 70% sulfuric acid at 0°. Mass spectrometric analysis then showed no impurities except ordinary 2-methylpentane, present to the extent of 26.5%.

The alkylene dibromide residue from the initial bromination was refluxed for three hours with 3 g. of zinc dust and 10 ml. of *n*-butyl alcohol. The volatile products were fractionally distilled to isolate the hexenes. By infrared spectrophotometry the mixture was found to consist of 72% 2-methyl-1-pentene and 28% 2-methyl-2-pentene.[20] It is doubtful that any trace of other olefins was present.

2-Methylpentane-4-*d*.—Methylisobutylcarbinol was carefully purified by distilling it through an 80-plate column at a reflux ratio of 25:1, b.p. 132.0, n^{20}_D 1.4114. Twenty grams of the alcohol was placed in a three-neck flask containing a thermometer and a dropping funnel. Eight ml. of phosphorus tribromide was added slowly, with swirling and cooling in a bath at −78°, so that the temperature of the mixture was maintained between −20 and 0°. After the addition, the mixture was left overnight at room temperature. The phosphorous acid was removed from the alkyl bromide by distilling the bromide under 25 mm. pressure at 40–50°. The distillate was washed with 85% sulfuric acid at 0°, then with a small amount of sodium bicarbonate solution and dried with potassium carbonate. The product amounted to 18 g.

The bromide was converted to the Grignard reagent using 2.65 g. of magnesium turnings and 40 ml. of ether. The deuteroalkane was prepared and isolated as described above for 2-methylpentane-2-*d*. The volatile product was found by mass spectrometric analysis to contain 6.7% olefin and approximately 19% ordinary 2-methylpentane. The olefin was removed as described above for 2-methylpentane-2-*d*, using 1.0 g. of bromine and one drop of water at room tem-

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(20) It seems apparent that a randomly-selected "contiguous" hydrogen atom is transferred from one alkyl moiety to the tertiary carbon of another, producing alkane and alkene. This side reaction may be a free radical disproportionation or a reaction of a carbanion with the alkyl bromide (*cf*. Condon, THIS JOURNAL, **73**, 4677 (1951)).

perature for 15 minutes. The final product contained 19.6% ordinary 2-methylpentane.[21]

2-Methylpentane-5-*d*.—Grignard reagent was prepared, using 10.4 ml. (100 millimoles) of isobutyl chloride (Eastman Kodak Company isobutyl chloride, fractionated in a 30-plate column, b.p. 69.2°, $n^{20}D$ 1.39811), 30 ml. of ether, 2.5 g. of magnesium turnings and a dry nitrogen atmosphere. At the completion of the reaction the condenser was replaced by a condenser at −30°, and the dropping funnel by a gas inlet tube ending above the surface of the liquid. An iron–constantan thermocouple was inserted directly into the mixture by passage through the condenser. With slow stirring, ethylene oxide (105 millimoles) was introduced at a rate of about 50 ml./min. (indicated by a rotameter between the flask containing the liquid ethylene oxide and the reaction flask). The temperature was maintained below 10° until the addition of reagent was completed, at which time the mixture was refluxed for 30 minutes.

Benzene (30 ml.) was added and the mixture was distilled with stirring until the temperature of the distilling vapor rose to 65°. At that point the condenser was shifted so that the mixture was refluxed for 45 minutes. It was then cooled in ice and ice-water (30 ml.) was added.

After the mixture had stood overnight, it was cooled in ice and a cold solution of 5 ml. of concentrated sulfuric acid in 30 ml. of water was added with stirring. Ether was added and the upper layer was separated, washed with sodium bicarbonate solution, dried and fractionated until the boiling point of the distillate reached 125°.

The hexanol residue was cooled to −30° and 2 ml. of phosphorus tribromide added in portions with stirring. The temperature was allowed to rise to 25° over a period of 48 hours. The product was distilled on the vacuum system twice, and hydrogen bromide was removed by evacuation at 0° until the vapor pressure was less than 10 mm. Any traces remaining were eliminated by distillation through ascarite. The distillate was taken up in ether, washed with sodium bicarbonate solution, and dried with anhydrous potassium carbonate.

The solution was converted to the deuterohydrocarbon in a manner similar to that used for 2-methylpentane-2-*d* above, except that 0.5 g. of magnesium turnings were used. The product distilled from 70% H_2SO_4 was found by mass spectrometric analysis to contain 4.8% benzene, 10.7% ether, 1.7% hexylene, 64% deuteroalkane and 20% ordinary 2-methylpentane. It was treated with 0.2 ml. of bromine and ethanolamine in the usual way, then with 92% sulfuric acid at 0° for five minutes. It was distilled from the latter until the residue had a vapor pressure of 30 mm. at 0°. The product (*ca.* 1 g.) then contained 1.3% ether and 4.0% benzene. It was fractionally distilled in a Podbielniak apparatus, using *n*-heptane as a "chaser." Middle cuts amounting to roughly three-fifths of the total contained no detectable ether and 0.2% benzene.

EMERYVILLE, CALIF.

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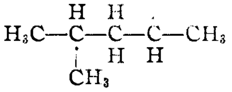
[21] A relatively non-volatile liquid residue left in the fractional distillation analyzed carbon, 84.2%; hydrogen, 15.43%, corresponding well with $C_{12}H_{26}$, for which one should obtain carbon, 84.6%; hydrogen, 15.36%. This material, probably 2,4,5,7-tetramethyloctane, may be formed by combination of the radicals



$$H_3C—\underset{\underset{CH_3}{\vdots}}{\overset{H}{C}}—\underset{H}{\overset{H}{C}}—\underset{H}{\overset{\cdot}{C}}—CH_3$$

or by the reaction

$$C_6H_{13}^- + C_6H_{13}Br \longrightarrow C_{12}H_{26} + Br^-$$

[CONTRIBUTION FROM THE SHELL DEVELOPMENT COMPANY]

The Preparation of Organo-phosphines by the Addition of Phosphine to Unsaturated Compounds

BY A. R. STILES, F. F. RUST AND W. E. VAUGHAN

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A series of organo-phosphines has been readily prepared by the free-radical sensitized addition of phosphine to a variety of unsaturated compounds. The products were mixtures of primary, secondary and tertiary phosphines, the relative amounts of each being dependent upon the original ratio of phosphine to unsaturate. Separation was effected by fractional distillation and identification was by the elemental analyses of the phosphines and their products of oxidation with nitric acid.

Since the demonstration by Kharasch and Mayo that hydrogen bromide will add "abnormally" to olefins by a free radical chain mechanism, a considerable number of compounds have been shown to follow an analogous path of addition.[1] It has now been found that phosphine can be added by photo- or peroxide-sensitization to unsaturated compounds. The reaction appears to parallel the addition of hydrogen sulfide to unsaturates[2] and affords an apparently generally applicable method for the synthesis of organo-phosphines. The sequence of steps, which can be initiated by radiation of certain frequencies, by organic peroxides and by other free radical sources, may be summarized as

$$R_2PH + (h\nu \text{ or } R') \longrightarrow R_2P + (H \text{ or } R'H)$$

$$\overset{|}{R_2P} + RCH{=}CH_2 \longrightarrow R_2PCH_2\overset{|}{C}HR$$

$$R_2PCH_2\overset{|}{C}HR + R_2PH \longrightarrow R_2PCH_2CH_2R + \overset{|}{R_2P}$$

$$R = \text{H, alkyl or substituted alkyl}$$

Photochemical initiation of these reactions is possible because phosphine absorbs radiation below about 2300 Å. and the primary step, which is reversible, is the formation of PH_2 and a hydrogen atom with a quantum efficiency of approximately 0.5.[3] Light of longer wave length is effective if a photosensitizer such as acetone is included in the reaction mixture. Di-*t*-butyl peroxide will also promote the addition of phosphine to olefins when the reaction is carried out at an elevated temperature.

Experimental

Phosphine was prepared in a vacuum line by heating anhydrous phosphorous acid at 200 to 210°, at which temperature the gas is smoothly evolved

$$4\,H_3PO_3 \xrightarrow{\text{heat}} 3\,H_3PO_4 + PH_3$$

The gas was passed through a trap immersed in Dry Ice to remove water vapor and collected by freezing with liquid nitrogen. The phosphine was then degassed several times

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[1] See F. R. Mayo and C. Walling, *Chem. Revs.*, **27**, 351 (1940).

[2] W. E. Vaughan and F. F. Rust, *J. Org. Chem.*, **7**, 472 (1942).

[3] W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941, pp. 383–384.