N-Methyl-*p*-hydroxybenzylamine Hydrochloride.[9]—A solution of XI (1.35 g., 0.0082 mole) in ethanol (10 ml.) and concentrated hydrochloric acid (3 ml.) was refluxed 17 hr. The reaction mixture was distilled to dryness with the water pump, and the white residue was crystallized from ethanol–ether to give 1.29 g. (91%) of the amine hydrochloride, m.p. 188–189°. A sample for analysis was crystallized first from ethanol–ether and then from methanol–ether; melting point unchanged.

Anal. Calcd. for $C_8H_{12}ClNO$: Cl, 20.42. Found: Cl, 20.73.

N-Methyl-*o*-hydroxybenzylamine Hydrochloride.[8]—A sample of XII (0.884 g., 0.0054 mole) was ground in an agate mortar and refluxed 17 hr. in a solution of ethanol (7.5 ml.) and concentrated hydrochloric acid (3 ml.). The solvent was removed with the aspirator, and the residue was crystallized from methanol–ether to give 0.719 g. (77%) of off-white crystals. Recrystallization from isopropyl alcohol–ether and then ethanol–ether gave the analytical sample, m.p. 141–145°.

Anal. Calcd. for $C_8H_{12}ClNO$: Cl, 20.42. Found: Cl, 20.81.

N-Formyl-N-methylaminomethylisothiouronium Chloride (XIV).—I (5.85 g., 0.05 mole) was added to thiourea hydrochloride (6 g., 0.053 mole) in dimethylformamide (100 ml.). On standing crystals precipitated and within a few hours the reaction was complete. The crude product, 8.0 g. (87%), m.p. 117–121° dec., was crystallized three additional times from methanol–ether for analysis, m.p. 127–128° dec.

Anal. Calcd. for $C_4H_{10}ClN_3OS$: C, 26.16; H, 5.49; N, 22.88; S, 17.46. Found: C, 26.34; H, 5.99; N, 22.57; S, 17.42.

The above product (3.1 g., 0.0169 mole) was refluxed 3 hr. with β-naphthol (2.48 g., 0.0172 mole), ethanol (25 ml.), and concentrated hydrochloric acid (1 ml.). The solution was cooled, and ether was added, precipitating 2.02 g. (53.4%) of methyl-(2-hydroxynaphthylmethyl)amine hydrochloride, m.p. 188–194° dec., m.p. 196–198° dec. after crystallization from ethanol–ether.

Anal. Calcd. for $C_{12}H_{14}ClNO$: Cl, 15.85. Found: Cl, 16.23.

Reaction of N-Acetoxymethylphthalimide (XVI).—XVI (11.5 g., 0.0525 mole), prepared as described by Nefkens, *et al.*,[15] was dissolved by heating in ethanol (100 ml.), and concentrated hydrochloric acid (5 drops) was added. After standing overnight, crystals (7 g.) precipitated. These proved to be unreacted XVI, m.p. 116–118°. The crystals were redissolved in the mother liquor with the aid of more ethanol. Concentrated hydrochloric acid (10 drops) was added, and the solution was refluxed 5.5 hr. The solvents were removed with the water pump, and the crystalline residue was crystallized from acetone. Two crops, 8.5 g. (91.5%), were obtained, m.p. 148–151°. The infrared spectrum was identical with that of N-hydroxymethylphthalimide.

Fragmentation, Rearrangement, and Elimination in Heptamethylpropane Derivatives[1,2]

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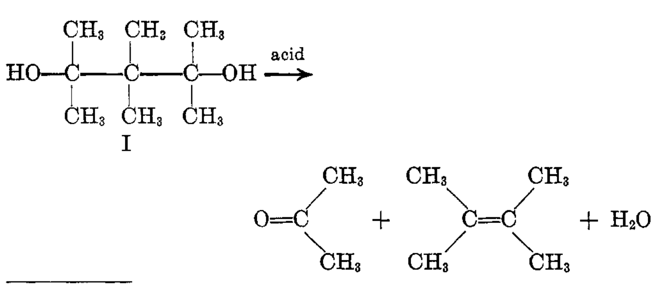
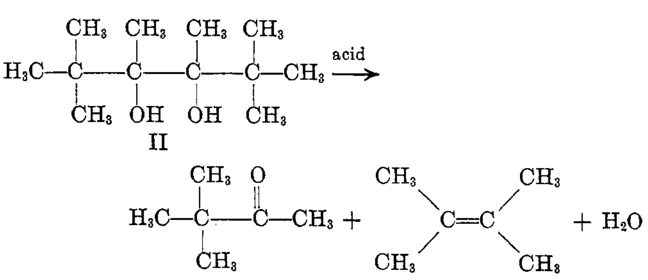
2,3,3,4,4-Pentamethyl-2-chloropentane (XII) was found to solvolyze in 93% aqueous acetone at 25° with the specific first-order rate constant of 2.92×10^{-3} sec.$^{-1}$ to form 2,3,3,4,4-pentamethyl-1-pentene (XI). No fragmentation was observed. 2,2,3,4,4-Pentamethyl-3-chloropentane (V) solvolyzed in 80% aqueous ethanol at 25° with the specific first-order rate constant of 1.725×10^{-4} sec.$^{-1}$. In 70% aqueous dioxane the solvolytic products of the latter compound are 83% 1,1-di-*t*-butylethylene (VIII), 10% methyldi-*t*-butylcarbinol (VI), and 7% 1-methyl-1-triptylethylene (XI). Isotope-exchange studies in dioxane–sulfuric acid-d_2 mixtures show that, for every 200 2,3,3,4,4-pentamethyl-2-pentyl cations (X) formed by protonation of 2,3,3,4,4-pentamethyl-1-pentene (XI), three undergo tertiary butyl migration and one fragments; methyl migration is not observed.

In 1907 Slavjanov[5] reported that treatment of hexamethyl-1,3-propanediol (I) with acids yielded acetone, tetramethylethylene, and water; Couturier[6a] and later Delacre[6b] observed that 1,2-dimethyl-1,2-di-*t*-butylethylene glycol (II) under the influence of acid formed pinacolone, tetramethylethylene, and water. Nasarov[7] examined the reactions with acid of a large number of mono- and di-*t*-alkylcarbinols and of the corresponding unrearranged dehydration products. Earlier, Whitmore and co-workers[8] had started investigations on similar systems. While Nasarov had interpreted his results in terms of a radical mechanism, Whitmore in-



I



II

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[1] Based upon a thesis submitted by G. F. Meier in July 1964 to the Graduate School of Indiana University in partial fulfillment of the requirements for the Ph.D. degree.

[2] Fragmentations are reactions in which molecules break apart heterolytically or homolytically to form two or more fragments, as indicated in the generalized scheme shown.[3] Where b, c, and d are carbon atoms, this

$$\text{a—b—c—d—x} \longrightarrow \text{a—b}^{\oplus} + \text{c=d} + \text{x}^{\ominus}$$

type of reaction has also been referred to as β cleavage and the fragment a–b$^{\oplus}$ as "β fragment," in analogy to the well-known related β eliminations where a–b$^{\oplus}$ is a hydrogen ion.

[3] C. A. Grob in Theoretical Organic Chemistry, Papers Presented to the Kekule Symposium Organized by the Chemical Society, London, Sept. 1958, Butterworth and Co. (Publications) Ltd., London, 1959, p. 114. See also C. A. Grob, H. R. Kiefer, H. Lutz, and H. Wilkens, *Tetrahedron Letters*, **No. 39**, 2901 (1964), and earlier papers.

[4] Graduate School Fellow, 1962.

[5] A. N. Slavjanov, *J. Russ. Phys. Chem. Soc.*, **39**, 140 (1907); *Chem. Abstr.*, **1**, 2077 (1907).

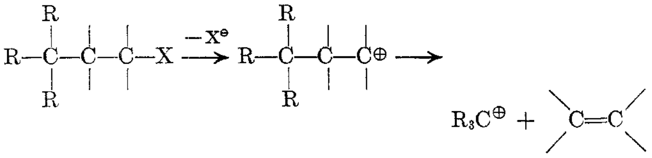
[6] (a) F. Couturier, *Ann. chim.* (Paris), [6] **26**, 433 (1892); (b) M. Delacre, *Bull. soc. chim. France*, [4] **1**, 539 (1907).

[7] (a) I. N. Nasarov, *Compt. rend. acad. sci. URSS*, **2**, 82 (1934); **3**, 609 (1934); (b) *ibid.*, **10**, 75 (1936); *Ber.*, **69**, 18 (1936); (c) *ibid.*, **70**, 606, 617 (1937).

[8] (a) F. C. Whitmore, *J. Am. Chem. Soc.*, **54**, 3274 (1932); (b) F. C. Whitmore and E. E. Stahly, *ibid.*, **55**, 4153 (1933); (c) *ibid.*, **67**, 2158 (1945); (d) for a complete list of this author's work on the subject, see F. C. Whitmore, L. H. Sommer, D. L. Bailey, G. M. Goldberg, C. E. Buck, T. S. Bye, and F. J. Evans, *ibid.*, **76**, 1613 (1954), and the preceding papers.

troduced the concept of the carbonium ion as the critical reaction intermediate. In three fundamental papers[8a–c] he and his co-workers developed and tested experimentally[8d] the general reaction scheme of heterolytic cleavage, of rearrangement in the intermediate carbonium ions, and of formation of fragments from intermediates with certain special structural features.

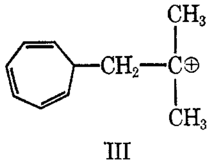
The driving force for the Wagner–Meerwein rearrangements[9,10] was attributed to the tendency to form a more stable carbonium ion. The structural feature required for fragmentation was concluded to be a chain of an even number of atoms which developed at one end a positive charge by loss of a nucleophile and carried at the other end some group which would separate as a positive ion, as in the following example, in which a tertiary carbonium ion is eliminated.



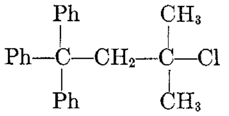
$$R{-}\overset{R}{\underset{R}{C}}{-}C{-}C{-}X \xrightarrow{-X^{\ominus}} R{-}\overset{R}{\underset{R}{C}}{-}C{-}C^{\oplus} \longrightarrow R_3C^{\oplus} + {>}C{=}C{<}$$

Whitmore further pointed out that such cleavage reactions are the exact reverse of cationic polymerizations which involve the addition of a carbonium ion to an olefin followed by proton elimination or further addition.

Grob generalized the scheme of Whitmore to include systems which contain heteroatoms.[3] Whitmore and co-workers had observed fragmentation by heating alcohols or olefins in acid, a procedure which would not yield products characteristic of kinetic control. Thus, the partitioning of the carbonium ions among substitution, elimination, rearrangement, and fragmentation could not be quantitatively evaluated. Under kinetically controlled conditions Hughes, Ingold, and Shiner[11] observed no fragmentation in the solvolysis of dimethylneopentylcarbinyl chloride, even though the high rate of this reaction was proposed to be related to hyperconjugation of the β-C–γ-C bond and to the latent tendency to fragment. Similarly, Fischer, Grob, and Schwarz[12] found no fragmentation products in the ethanolysis of *cis*- and *trans*-3,3,5-trimethylcyclohexyl tosylates. However, Conrow[13] observed that reactions which are thought to proceed through carbonium ion III led, probably under conditions of kinetic control, to products of fragmentation as well as elimination and substitution. No rate data on these reactions were reported. This partial, even though incomplete, fragmentation is apparently due to the special stability of the tropylium ion which is eliminated. On the other hand, 2-methyl-4,4,4-triphenyl-2-chlorobutane (IV), which solvolyzes in 80% aqueous ethanol only 36 times as fast as *t*-butyl chloride, does not yield any observable fragmentation products despite the stability of the trityl ion which would be formed.[14] It has been reported[15] that tetramethylethylene and isobutylene were the main fragmentation products of the reaction of methyldi-*t*-butylcarbinol (VI) with acid. It was assumed that methyl migration had preceded fragmentation.



III



$$Ph{-}\overset{Ph}{\underset{Ph}{C}}{-}CH_2{-}\overset{CH_3}{\underset{CH_3}{C}}{-}Cl$$

IV

Bartlett and Swain[16] examined a number of highly sterically hindered tertiary alcohols and their esters and found that mixtures of highly branched chlorides obtained by treatment of the alcohols with hydrogen chloride were minor products accompanying major amounts of olefins. The rate of solvolysis of the reaction mixture obtained by treatment of methyldi-*t*-butylcarbinol (VI) with hydrogen chloride could be interpreted in terms of two first-order rate constants, $k_1' = 5.5 \times 10^{-5}$ sec.$^{-1}$ and $k_1 = 6.5 \times 10^{-2}$ sec.$^{-1}$ in 80% aqueous acetone at 25°. With the methods then available it was not possible to assign structures unambiguously to the chlorides obtained. However, because of the absence of spin–spin splitting, these materials should give simple proton magnetic resonance spectra which should suffice for identification. It therefore appeared that a further investigation of the behavior of these highly branched carbon systems which might undergo fragmentation under controlled conditions would be worthwhile.

Procedure and Results

A. Solvolysis of Chlorides.—Methyldi-*t*-butylcarbinol (VI) was prepared using the procedure of Howard and co-workers.[15] Dimethyltriptylcarbinol (IX), which has not been described previously, was obtained from the reaction of methyllithium with methyl triptyl ketone,[17] a procedure which Petrov, Ch'ing-lang, and Semenkin had used to prepare analogous compounds.[18] Methyl triptyl ketone was formed by the acid-catalyzed rearrangement of di-*t*-butyl ketone.[19,20] The reaction of methyldi-*t*-butylcarbinol (VI) with hydrogen chloride gas at 0° was shown by n.m.r. analysis to yield a mixture of compounds. Methyldi-*t*-butylcarbinyl chloride (V) was the major product; a smaller amount of product proved to be the rearranged dimethyltriptylcarbinyl chloride (XII) which, because of its greater reactivity, could be removed by fractional solvolysis in absolute ethanol. The residual methyldi-*t*-butylcarbinyl chloride (V) was purified by vacuum sublimation to a melting point of 86.5–87.0° and gave an equivalent weight of 180–184 (calcd. 174.5).

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[9] G. Wagner, *J. Russ. Phys. Chem. Soc.*, **31**, 680 (1899); *Ber.*, **32**, 2302 (1899).

[10] H. Meerwein, *Ann.*, **405**, 129 (1914); **417**, 255 (1918).

[11] E. D. Hughes, C. K. Ingold, and V. J. Shiner, Jr., *J. Chem. Soc.*, 3827 (1953).

[12] H. Fischer, C. A. Grob, and W. Schwarz, *Tetrahedron Letters*, **No. 1**, 25 (1962).

[13] K. Conrow, *J. Am. Chem. Soc.*, **81**, 5461 (1959).

[14] V. J. Shiner, Jr., and S. D. Parfitt, unpublished results.

[15] F. L. Howard, T. W. Mears, A. Fookson, P. Pomerantz, and D. B. Brooks, *J. Res. Natl. Bur. Std.*, **38**, 365 (1947).

[16] P. D. Bartlett and M. S. Swain, *J. Am. Chem. Soc.*, **77**, 2801 (1955).

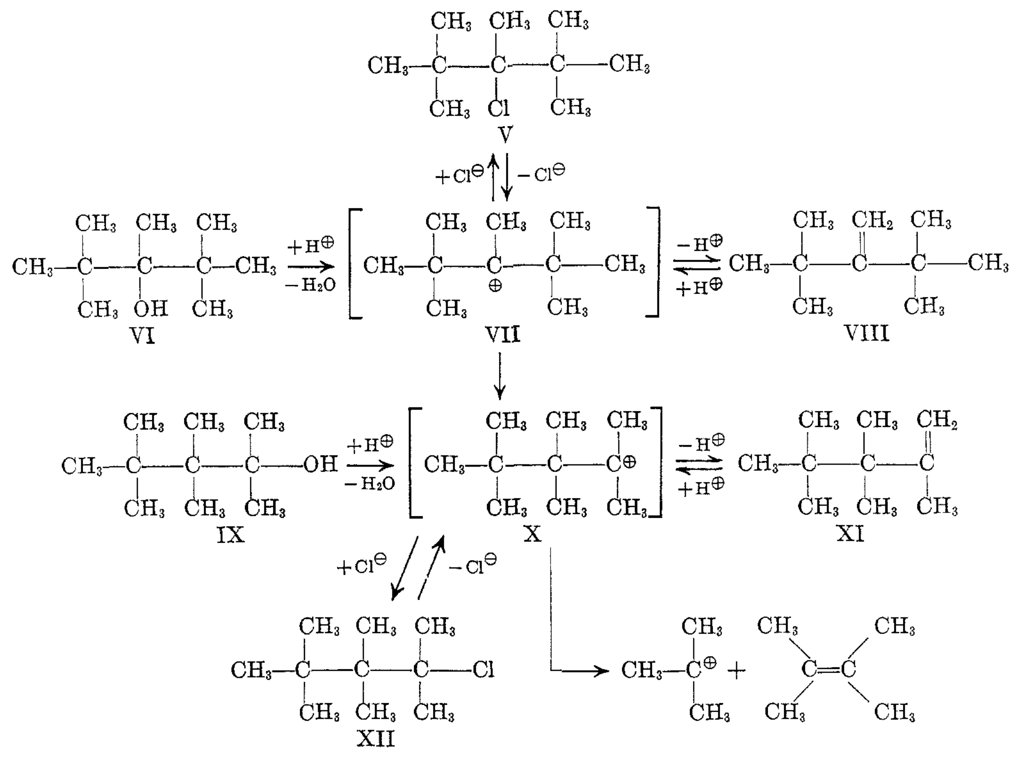
[17] Triptyl = 2,3,3-trimethyl-2-butyl.

[18] A. D. Petrov, Kao Ch'ing-lang, and V. M. Semenkin, *J. Gen. Chem. USSR*, **30**, 387 (1960).

[19] P. D. Bartlett and A. Schneider, *J. Am. Chem. Soc.*, **67**, 141 (1945).

[20] (a) S. Barton and C. R. Porter, *Nature*, **169**, 373 (1952); *J. Chem. Soc.*, 2483 (1956); (b) H. D. Zook, W. E. Smith, and J. L. Greene, *J. Am. Chem. Soc.*, **79**, 4436 (1957).

CHART I



Dimethyltriptylcarbinol (IX) was also treated with hydrogen chloride gas and sublimed in vacuum at room temperature. Because of its tendency to eliminate hydrogen chloride spontaneously, this product, which n.m.r. showed to be dimethyltriptylcarbinyl chloride, was used immediately without further purification. Its solvolysis rate constant measured conductometrically[21] in 93% aqueous acetone was 2.92×10^{-3} sec.$^{-1}$, while that of methyldi-*t*-butylcarbinyl chloride was 1.725×10^{-4} sec.$^{-1}$ in 80% aqueous ethanol. The solvolysis of the latter compound (V) was also measured in 80% aqueous acetone at 25°, giving a rate constant of 3.34×10^{-5} sec.$^{-1}$. This result is in fair agreement with the value obtained by Bartlett and Swain[16] for the slower reacting of the two components in the mixture they examined. From the two quoted rates the value of m for methyldi-*t*-butylcarbinyl chloride is 1.06 compared to 1.00 for the standard *t*-butyl chloride.

Whereas methyldi-*t*-butylcarbinyl chloride (V) is observed to be 18.4 times as reactive as *t*-butyl chloride[21] in 80% aqueous ethanol, dimethyltriptylcarbinyl chloride (XII) is estimated from the Grunwald–Winstein equation to solvolyze 89,000 times as fast as *t*-butyl chloride in 93% aqueous acetone, giving reasonable agreement with the value of 6.5×10^{-2} sec.$^{-1}$ reported for 80% aqueous acetone by Bartlett and Swain[16] for the faster reacting of their two compounds. This comparison is based on a Y value of -2.454 for 93% aqueous acetone, obtained by extrapolation of the equation given by Fainberg and Winstein[22] which provides solvent parameters in agreement with those determined experimentally in the range of 30 to 90 vol. % aqueous acetone.

Product Studies.—Dimethyltriptylcarbinyl chloride (XII) solvolyzed in water–dioxane (1:2) to give exclusively 1-methyl-1-triptylethylene (XI). No fragmentation was observed. Methyldi-*t*-butylcarbinyl chloride solvolyzed in water–dioxane to give 83% 1,1-di-*t*-butylethylene (VIII), 10% methyldi-*t*-butylcarbinol (VI), and 7% 1-methyl-1-triptylethylene (XI).

B. Reaction of Alcohols and Olefins with Acid.—Since the carbonium ions formed irreversibly through loss of halide ion did not give observable amounts of fragmentation, their behavior on formation reversibly from the corresponding alcohols and olefins was examined. In order to obtain quantitative results, the following procedure was followed. Varying amounts of concentrated sulfuric acid were added to equal volumes of anhydrous dioxane, and the acid concentration of the solution was determined by titration. An aliquot of the compound to be investigated was dissolved in a solution having an acid concentration determined by preliminary experiments to allow a convenient measurement of the disappearance of a representative peak in the n.m.r. spectrum; tetramethylsilane was added as an internal standard. That region of the spectrum showing the representative peak of the reacting compound was then swept and integrated at known time intervals. Only initial rates were used for the calculation of rate constants. The reproducibility by this method and in the solvent system chosen is not very good. Therefore, only major effects lend themselves to interpretation. Dioxane was chosen as solvent medium because it readily dissolves concentrated sulfuric acid up to a concentration of about 2.5 M; however, it has the disadvantage of dissolving reactants and products only to a limited extent.

Preliminary experiments showed that, although the reaction rates were proportional to acid concentration in dilute solution, above 0.5 M the rates increased much more rapidly. A better, but still unsatisfactory,

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(21) B. L. Murr, Jr., and V. J. Shiner, Jr., *J. Am Chem. Soc.*, **84**, 4672 (1962).

(22) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

CHART II

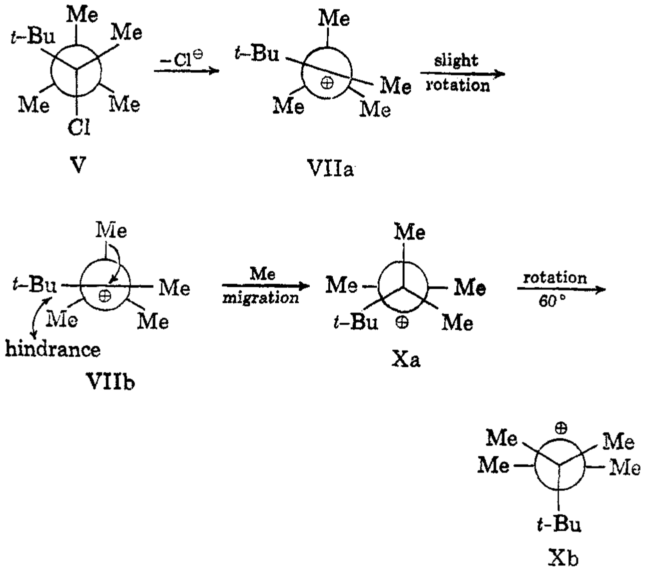
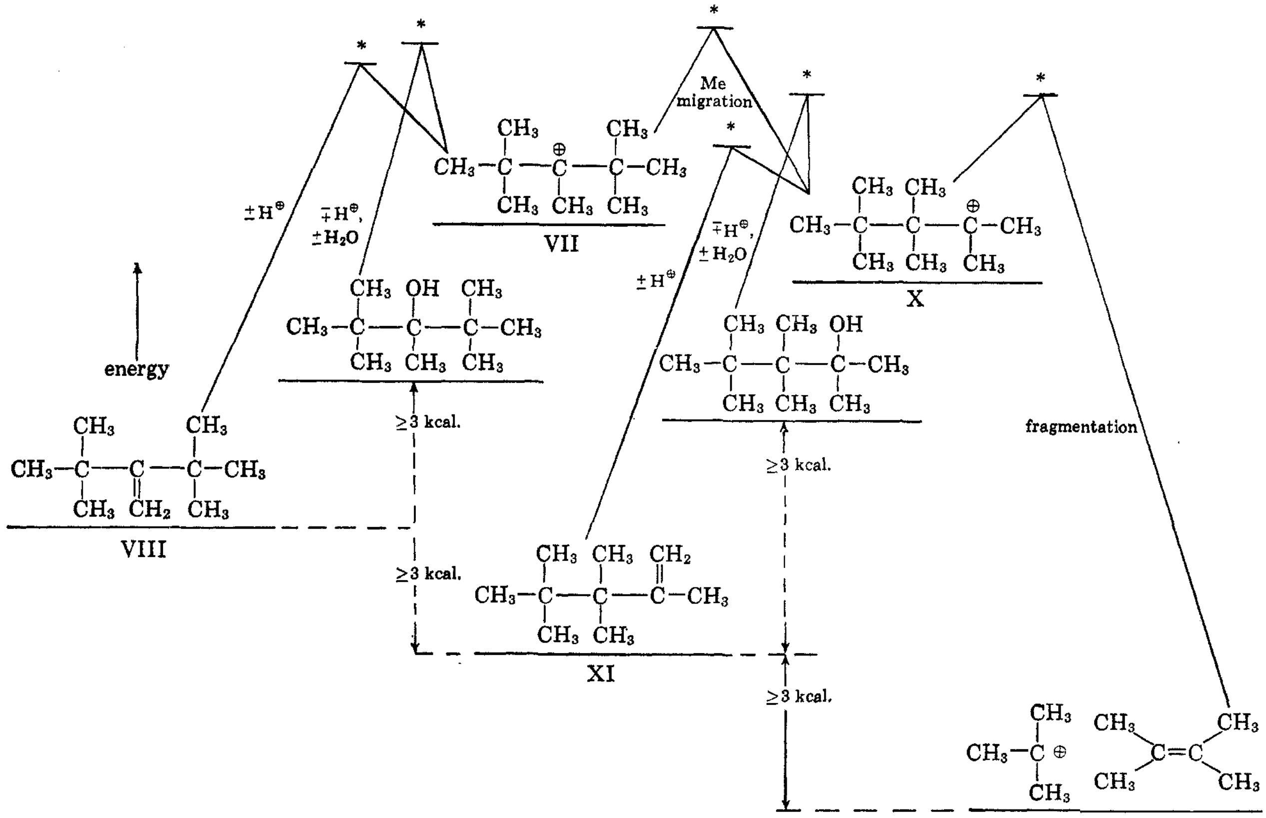


CHART III

RELATIVE ENERGIES OF REACTANTS, TRANSITION STATES, AND PRODUCTS[a]



[a] * = transition states.

correlation could be based on the acidity function h_0 using *p*-nitroaniline as indicator.[23] Solutions with an acid concentration greater than 0.5 *M*, required to cover the range of reactivities involved, could be used through the determination of their relative reactivities with a given substrate. Thus, rough acid-independent second-order rate constants referring to dilute solutions of sulfuric acid in dioxane could be calculated.

Methyldi-*t*-butylcarbinol (VI) dehydrated completely to form 1,1-di-*t*-butylethylene (VIII) with the rate constant of 5×10^{-4} l./mole sec. 1,1-Di-*t*-butylethylene rearranged completely to 1-methyl-1-triptylethylene (XI) with the rate constant 1×10^{-5} l./mole sec. Dimethyltriptylcarbinol (IX) dehydrated completely to form 1-methyl-1-triptylethylene (XI) with $k = 5 \times 10^{-3}$ l./mole sec. 1-Methyl-1-triptylethylene fragmented completely to tetramethylethylene and *t*-butyl alcohol and/or isobutylene with $k = 2 \times 10^{-7}$ l./mole sec. Chart I summarizes these results.

When the reactions were allowed to continue for a sufficient period of time, no starting material was detectable. Since analysis by n.m.r. spectroscopy permits detection of as much as 5% of the starting material, it was concluded that the free energy of the products was lower than that of the reactants by 3 kcal./mole or more.[24] The following series of stabilities thus applies: fragmentation products > 1-methyl-1-triptylethylene > 1,1-di-*t*-butylethylene > methyldi-*t*-butylcarbinol; and 1-methyl-1-triptylethylene > dimethyltriptylcarbinol. Sufficient combustion and hydrogenation data on these compounds are not available to allow a quantitative comparison of stabilities.

Experiments in D_2SO_4 with 1-Methyl-1-triptylethylene (XI).—1-Methyl-1-triptylethylene shows in the n.m.r. spectrum (apart from the two multiplets arising from the vinyl protons, denoted as d), three peaks, the singlets a (*t*-butyl group) and b (dimethylethylidene group), and c (a triplet for the methyl group attached to the double bond and not completely resolved)

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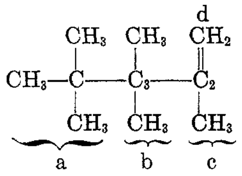
[23] (a) L. P. Hammett and A. J. Deyrup, *J. Am. Chem. Soc.*, **54**, 2721 (1932); (b) E. A. Braude, *J. Chem. Soc.*, 1971 (1948).

[24] Under the conditions used the alcohols were completely dehydrated, although in principle their stability relative to the dehydration products would depend on the activity of water present.

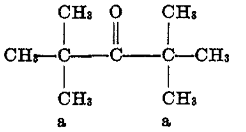
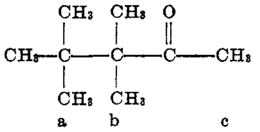
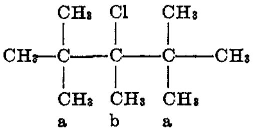
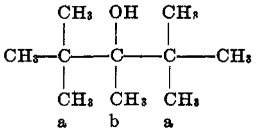
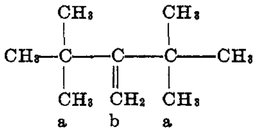
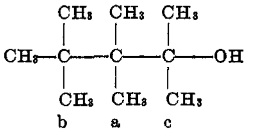
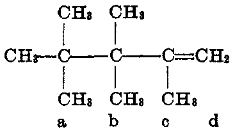
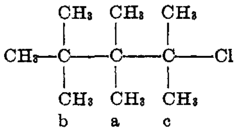


XI

in the ratio a:b:c = 3:2:1. If the olefin XI undergoes H–D exchange in excess D_2SO_4–dioxane without any rearrangement, then after a certain time the positions c and d become fully deuterated, but the peaks for positions a and b would retain their height. The rate constant for this exchange, observed as decrease of position c only, was found to be 8×10^{-6} l./mole sec. Assuming no isotope effect on proton loss, the rate constant for carbonium ion formation would be six times this or 5×10^{-5} l./mole sec. Methyl migration from C-3 to C-2 to form the methyldi-*t*-butyl carbonium ion would be followed by reverse migration, scrambling of the methyl groups, and the appearance of deuterium in XI on all carbon atoms. If methyl migration does not take place, but *t*-butyl migration does, then the peak for position a will remain constant, but positions b, c, and d will become fully deuterated. If both methyl and *t*-butyl migration take place, all positions will decrease in hydrogen and increase in deuterium content. However, methyl migration from C-3 to C-2 was not observed, for the *t*-butyl peak did not decrease through H–D exchange. Also 1,1-di-*t*-butylethylene (VIII), which would be formed by proton loss from the rearranged carbonium ion, was not detected. Since the peak for position b did, but that for position a did not, decrease with time, it can be concluded that *t*-butyl migration takes place. From the rate of change of the absorption spectrum, the rate constant for *t*-butyl migration was determined to be 7×10^{-7} l./mole sec. Thus, the ratio of carbonium ion formation to *t*-butyl migration is approximately 70, and *t*-butyl migration occurs about three times as fast as fragmentation.

TABLE I

OBSERVED CHEMICAL SHIFTS IN δ (P.P.M.) FROM TETRAMETHYLSILANE IN CARBON TETRACHLORIDE

Compound		a	b	c	d
		1.21			
		0.90	1.07	2.04	
	V	1.21	1.56		
	VI	1.05	1.13		
	VIII	1.28	4.95		
	IX	0.88	1.02	1.25	
	XI	0.89	1.03	1.68	4.73–4.89
	XII	1.03	1.06	1.70	

Discussion

Methyl migration is the slowest of all the reactions of carbonium ion VII. Elimination would be sterically favored because one hydrogen of the methyl group is perpendicular to the plane of the carbonium ion. On the other hand, methyl migration is probably made more difficult because the bulky *t*-butyl group tends to prevent the methyl group from assuming such a perpendicular position (VIIa) (see Chart II). However, once rearrangement has taken place (VIIb → Xa), a rotation around the C-2–C-3 bond by 60° allows the new carbonium ion to assume a conformation (Xb) in which the *t*-butyl group exerts the least possible steric hindrance. From the Newman projection it seems that the reverse of this process, which is in fact not observed, would also be hindered sterically. It is not possible to demonstrate directly from our experiments that carbonium ion X is more stable than VII, but the following argument is strongly suggestive.

Olefin XI is more stable and protonates more rapidly than VIII. Thus the transition state for the former reaction is of lower free energy than that for the latter. To the extent that these transition states reflect the stabilities of the corresponding ions, X is more stable than VII, consistent with the expectation from conformational analysis and steric interactions. Chart III summarizes what can be concluded concerning the relative stabilities of the olefins, carbonium ions, fragmentation products, and transition states in this system.

From the ratio of 70 carbonium ions being formed compared to one ion undergoing *t*-butyl migration, a symmetrical nonclassical structure for ion X can be excluded.

Experimental Section

Methyldi-*t*-butylcarbinol was prepared according to Howard and co-workers[15]: m.p. 42°.

Dimethyltriptylcarbinol was prepared from methyl triptyl ketone[20] and methyllithium in the same way as methyldi-*t*-butylcarbinol, however, in much lower yield (10–20%)[17]: m.p. 63–64°.

2,2,3,4,4-Pentamethyl-3-chloropentane, methyldi-*t*-butylcarbinyl chloride, was prepared according to the method of Bartlett and Swain.[16] The reaction of methyldi-*t*-butylcarbinol with gaseous hydrogen chloride at 0° in anhydrous ether gave after work-up essentially pure methyldi-*t*-butylcarbinyl chloride, with a small amount of rearranged product. Since the impurity was rearranged alkyl halide (which reacts much faster than methyldi-*t*-butylcarbinyl chloride) and olefin, the total solid was stirred for 1 hr. in absolute ethanol to allow fractional solvolysis. The solvent was evaporated and the residue was vacuum sublimed at room temperature twice. Methyldi-*t*-butylcarbinyl chloride was obtained as pure white crystals, m.p. 86.5–87°, lit.[16] m.p. 68–70° dec. Thin layer chromatography in ethyl acetate–chloroform, chloroform, benzene, or *n*-hexane, developed with iodine, showed only one peak. The substance shows the same retention time before and after fractional solvolysis. If the purified substance is subjected to the conditions of its preparation from the alcohol, it can be recovered unchanged.

Equivalent Weight Determination.—An aliquot of methyldi-*t*-butylcarbinyl chloride was dissolved in excess base and back titrated with acid, giving equivalent weights in two determinations of 180 and 184.3 (calcd. 176.5).

2,3,3,4,4-Pentamethyl-2-chloropentane, dimethyltriptylcarbinyl chloride, was prepared from dimethyltriptylcarbinol in the same way as 2,2,3,4,4-pentamethyl-3-chloropentane. Purification was achieved by vacuum sublimation at room temperature. Contact with air caused decomposition; thus, for kinetic measurements direct transfer from the sublimation device to the conductance cell was necessary. Physical constants, except the n.m.r. spectrum, were not obtained.

Dideuteriosulfuric acid was prepared according to Brauer.[25]

Solvents.—Solvents for solvolysis were made up by weight methods[21] even though they are identified in the conventional terminology: *e.g.*, 80% aqueous ethanol refers to a solution that would be obtained by mixing four volumes of ethanol with one volume of water, both measured at 25°.

Kinetic Measurements and Product Studies.—The rates of solvolysis were followed conductometrically[21] and the results were processed by means of a least-squares program on the IBM 709 digital computer.

Products of Solvolysis.—An aliquot of the alkyl halide was dissolved in dioxane–water (about 2:1) and stirred in a closed flask for 48 hr. at room temperature. After completion of the reaction, the flask was connected to a sublimation device with a cold finger kept at −75°. The stopcock was then opened, and under vacuum the cold finger quickly became covered with a solid material. The sublimation was interrupted after a short time, and some of the condensed phase was dissolved in carbon tetrachloride and transferred into an n.m.r. tube. The n.m.r. spectrum did not show in either case any organic material besides dioxane and a small amount of the unfragmented olefins. Therefore, it can be concluded that no low-boiling fragments are formed during solvolysis.

N.m.r. spectra were taken with a Varian A-60 spectrometer. The observed shifts in δ (parts per million) from tetramethylsilane internal reference in carbon tetrachloride solution are given in Table I.

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(25) G. Brauer, "Handbuch der präprativen anorganischen Chemie," Vol. I, F. Enke, Stuttgart, 1960, p. 134.

The Syntheses and Some Reactions of ω-Isocyanatoalkanecarboxylic Acid Chlorides and Isocyanatobenzoyl Chlorides

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3-, 5-, and 6-isocyanatoalkanecarboxylic acid chlorides and *m*- and *p*-isocyanatobenzoyl chlorides were prepared by treatment of the corresponding amino acids or their hydrochlorides with phosgene and hydrogen chloride in dioxane. In the same reaction, 4-aminobutanoic acid and *o*-aminobenzoic acid gave 1-chloroformyl-5-chloro-2,3-dihydropyrrole and isatoic anhydride, respectively. *o*-Isocyanatobenzoyl chloride was obtained by treating isatoic anhydride with thionyl chloride or phosphorus pentachloride. These isocyanatocarboxylic acid chlorides reacted with excess primary and secondary amines, ethanol, and water at both groups, COCl and NCO. With 1 mole of amine or water, they reacted preferentially at the COCl site. In an equimolar reaction with ethanol, aliphatic isocyanatocarboxylic acid chlorides reacted preferentially at the COCl site, but without great selectivity as with amine. The aromatic compounds reacted preferentially with alcohols at the NCO site.

It has previously been reported[1] that 2-isocyanatoalkanecarboxylic acid chlorides were prepared in good yield when 2-aminoalkanecarboxylic acids were treated with phosgene and hydrogen chloride in dioxane, and that the COCl group of the 2-isocyanatocarboxylic acid chloride is more reactive than the NCO group as an electrophile. This investigation was undertaken to extend the previous work to the preparation and reaction of ω-isocyanatoalkanecarboxylic acid chlorides and isocyanatobenzoyl chlorides.

The formation of 3-isocyanatopropanoyl chloride and its 3-aryl-substituted derivatives have been reported without details or yield by Birkofer and Modic.[2] Steinbrunn produced 6-isocyanatohexanoyl chloride and *m*-isocyanatobenzoyl chloride from the corresponding amino acid chloride hydrochlorides and phosgene.[3] It has also been reported that aromatic isocyanatocarboxylic acid chlorides are obtained by treatment of aminobenzoic acids, aminonaphthoic acids or their derivatives with phosgene at 160–180°.[4] However, *o*-isocyanatobenzoyl chloride could not be obtained in these reactions.[3,4]

Our investigation of the reaction of amino acids with phosgene below 70° showed that introduction of hydrogen chloride afforded certain isocyanatocarboxylic acid chlorides in good yield and purity (see Table I). This pronounced effect of hydrogen chloride on the reaction was previously reported in an improved synthesis of 2-isocyanatoalkanecarboxylic acid chlorides from 2-amino acids.[1]

Isocyanatocarboxylic Acid Chlorides.—With aliphatic compounds, 3-aminopropanoic acid gave 3-isocyanatopropanoyl chloride (Ia) in 36% yield without added hydrogen chloride and 92% yield with added hydrogen chloride. Similarly, 6-aminohexanoic acid without added hydrogen chloride gave only a trace of 6-isocyanatohexanoyl chloride (Ic) but the yield was increased to 91% when hydrogen chloride was added. 4-Aminobutanoic acid, however, with hydrogen chloride gave the cyclic product 1-chloroformyl-5-chloro-2,3-dihydropyrrole (IIa) in 40% yield as reported by Steinbrunn,[3] while 5-aminopentanoic acid gave principally (over 65% yield) the 5-isocyanato-

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(1) Y. Iwakura, K. Uno, and S. Kang, *J. Org. Chem.*, **30**, 1158 (1965).

(2) L. Birkofer and R. Modic, *Ann.*, **628**, 162 (1959).

(3) G. Steinbrunn, German Patent 848,808 (1952).

(4) British Patent 752,105 (1956), assigned to the Farbenfabriken Bayer Aktiengesellschaft.