acid collected by filtration. The yield was 0.080 g., m.p. 180–185°. Recrystallization from water afforded 0.045 g. of material with m.p. 188–189°. The melting point of the product was not depressed by admixture with an authentic sample. In some instances, the succinic acid was converted to the corresponding di-*p*-bromophenacyl ester which after recrystallization from dioxane–ethanol had m.p. 213–214° (lit.[37] m.p. 211°).

Degradation of succinic acid was achieved by the procedure previously described.[20] The ethylenediamine was converted to the dihydrobromide, colorless plates from alcohol, for radioactive assay. Since the product did not melt but decomposed, the purity was verified by analysis.

Anal. Calcd. for $C_2H_{10}N_2Br_2$: C, 10.81; H, 4.50; N, 12.61; Br, 72.07. Found: C, 10.91; H, 4.67; N, 12.90; Br, 72.00.

CAMBRIDGE 39, MASS.

---

[37] W. L. Judefind and E. E. Reid, THIS JOURNAL, **42**, 1043 (1920).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

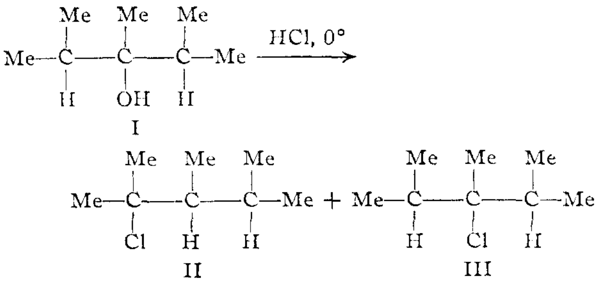
Structure of the Chlorides from 2,2,3-Trimethyl-3-pentanol and 2,3,3-Trimethyl-2-pentanol; Steric Effects as a Factor in the Rearrangements of Highly Branched Carbonium Ions[1]

BY HERBERT C. BROWN AND RACHEL BRITTON KORNBLUM[2]

RECEIVED NOVEMBER 6, 1953

Treatment of 2,2,3-trimethyl-3-pentanol with hydrogen chloride at 0° leads to the formation of 3-chloro-2,2,3-trimethylpentane. Similarly, 2,3,3-trimethyl-2-pentanol yields the corresponding tertiary chloride. In both cases the products were established from rate of hydrolysis data and melting points to be essentially pure compounds, free of detectable amounts of any rearranged chlorides. The assignment of structures to the two chlorides was confirmed by photochemical chlorination of the 2,2,3- and 2,3,3-trimethylpentanes and comparison of the rates of hydrolysis of the tertiary chlorides formed in these chlorinations with the corresponding data for the chlorides obtained from the alcohols. The conversion of these tertiary alcohols into their chlorides without rearrangement contrasts strongly with the ready rearrangement observed in the reaction of 2,2-dimethyl-3-ethyl-3-pentanol with hydrogen chloride. It is suggested that the presence of the two ethyl groups in the latter compound results in a geometrical arrangement which blocks approach to either face of the planar carbonium ion. Such steric hindrance to substitution reactions of highly branched carbonium ions may be an important structural requirement for ready rearrangements in highly branched structures. If this interpretation is valid, it suggests that rearrangements in the reactions of highly branched tertiary alcohols and related derivatives may take place in the carbonium ions after their formation rather than by a synchronous ionization–rearrangement process. The available evidence leads to the conclusion that simple carbonium ions, without special features, are best represented in their classical forms. There is, at present, no evidence available to indicate that the direct formation of bridged ionic intermediates is of importance in the reactions of simple aliphatic derivatives containing bulky substituents.

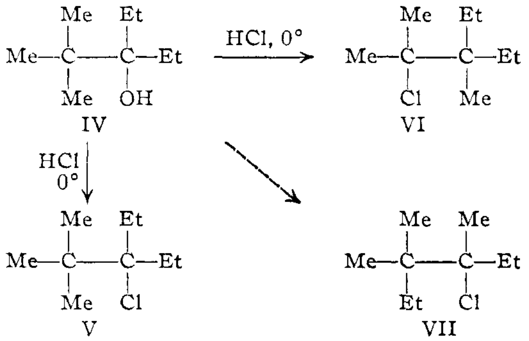
Treatment of 2,3,4-trimethyl-3-pentanol (I) with hydrogen chloride at 0° leads to the formation of a product which contains two different tertiary chlorides, as shown by an analysis of the solvolysis data.[3] These two chlorides were identified as 2-chloro-2,3,4-trimethylpentane (II) and 3-chloro-2,3,4-trimethylpentane (III) by chlorinating the parent hydrocarbon and analyzing the solvolysis data for the tertiary chlorides in the reaction mixture.[4] The reaction evidently involves a hydride ion shift in the carbonium ion presumably formed in the reaction.[5]



$$\underset{\text{I}}{\mathrm{Me{-}\underset{H}{\overset{Me}{C}}{-}\underset{OH}{\overset{Me}{C}}{-}\underset{H}{\overset{Me}{C}}{-}Me}} \xrightarrow{\mathrm{HCl,\ 0^\circ}}$$

$$\underset{\text{II}}{\mathrm{Me{-}\underset{Cl}{\overset{Me}{C}}{-}\underset{H}{\overset{Me}{C}}{-}\underset{H}{\overset{Me}{C}}{-}Me}} + \underset{\text{III}}{\mathrm{Me{-}\underset{H}{\overset{Me}{C}}{-}\underset{Cl}{\overset{Me}{C}}{-}\underset{H}{\overset{Me}{C}}{-}Me}}$$

Similarly, treatment of 2,2-dimethyl-3-ethyl-3-pentanol (IV) with hydrogen chloride leads to the formation of a product which, from solvolysis data, contains at least two different tertiary chlorides[4] (V, VI). Unfortunately, we encountered difficulties in attempting to establish the structures of these products.[6] It appeared that these difficulties might be the result of the formation of a third chloride (VII) arising from a double alkyl group shift in the carbonium ion intermediate.



$$\underset{\text{IV}}{\mathrm{Me{-}\underset{Me}{\overset{Me}{C}}{-}\underset{OH}{\overset{Et}{C}}{-}Et}} \xrightarrow{\mathrm{HCl,\ 0^\circ}} \underset{\text{VI}}{\mathrm{Me{-}\underset{Cl}{\overset{Me}{C}}{-}\underset{Me}{\overset{Et}{C}}{-}Et}}$$

$$\xrightarrow{\mathrm{HCl,\ 0^\circ}} \underset{\text{V}}{\mathrm{Me{-}\underset{Me}{\overset{Me}{C}}{-}\underset{Cl}{\overset{Et}{C}}{-}Et}} \qquad \underset{\text{VII}}{\mathrm{Me{-}\underset{Et}{\overset{Me}{C}}{-}\underset{Cl}{\overset{Me}{C}}{-}Et}}$$

In order to eliminate this possible complication we decided to undertake a study of the reaction of 2,2,3-trimethyl-3-pentanol (VIII) with hydrogen chloride. In the course of this study we encountered unusual results which made it desirable to extend the study to the isomeric alcohol, 2,3,3-trimethyl-2-pentanol (IX). These compounds possess the obvious advantage that each should form only a single rearranged tertiary chloride (XI, X) in addition to the unrearranged isomer (X, XI).

---

[1] Chemical Effects of Steric Strains. XI.

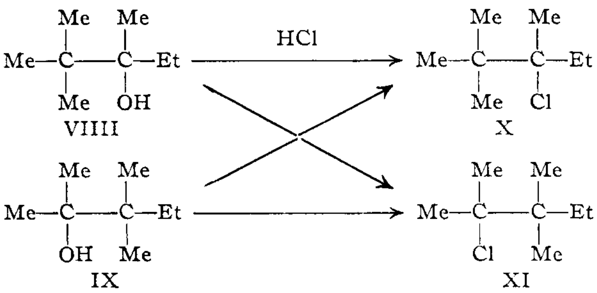
[2] Based upon a thesis submitted by Rachel Britton Kornblum in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] H. C. Brown and R. S. Fletcher, THIS JOURNAL, **71**, 1845 (1949).

[4] H. C. Brown and R. S. Fletcher, *ibid.*, **73**, 1317 (1951).

[5] F. C. Whitmore, *ibid.*, **54**, 3274 (1932), and numerous subsequent papers in THIS JOURNAL.

[6] R. S Fletcher, Ph.D. Thesis, Purdue University.



Results

2,2,3-Trimethyl-3-pentanol was prepared by treating pinacolone with ethylmagnesium bromide in 50% yield. No significant improvement in yield (51–52%) resulted by carrying the reaction out in the presence of magnesium bromide.[7] The product was carefully purified and the purity established as 99.6 ± 0.1 mole per cent. by a time–temperature cooling curve (b.p. 44.5–45.0° at 11 mm., n^{20}D 1.4357, m.p. from cooling curve −6.05°).

Treatment of this alcohol with hydrogen chloride at 0° resulted in a product, m.p. −15 to −14°, n^{20}D 1.4441. The kinetics of solvolysis for the crude reaction product in 80% ethanol at 25° were determined. A plot of log $(a - x)$ *versus* time (Fig. 1) gave an excellent straight line, characteristic of the first-order solvolysis of a pure halide. The first order constant was 0.227 hr.$^{-1}$.

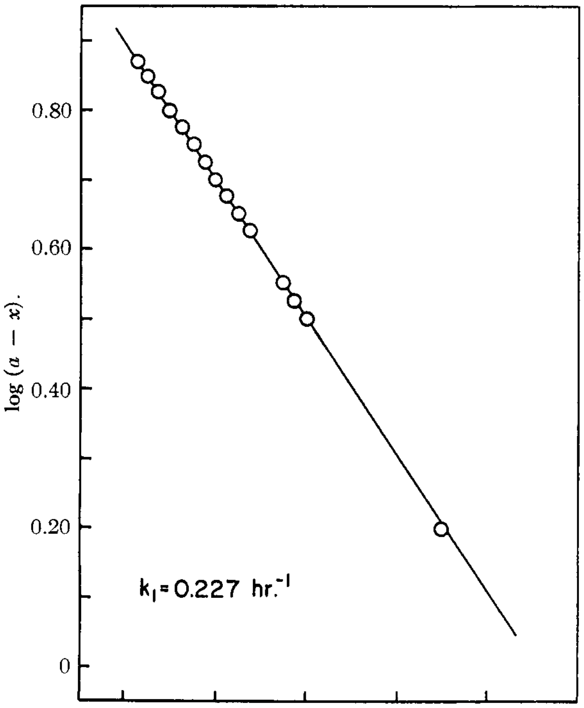


Fig. 1.—Solvolysis data (80% ethanol, 25°) for the reaction product of hydrogen chloride and 2,2,3-trimethyl-3-pentanol.

This result was both unexpected and puzzling. Several possible explanations suggested themselves. First, the product might be a mixture of two chlorides which hydrolyze at essentially the same rate. Second, the product might be pure X with no rearrangement occurring in the reaction. Third, the product could be the completely rearranged chloride XI.

It appeared that this question could be answered by a study of the product formed by the action of hydrogen chloride on the isomeric alcohol IX. Ethyl 2,2-dimethylbutanoate was synthesized in 60% yield from *t*-amylmagnesium chloride and ethyl chlorocarbonate. The ester was converted into the desired alcohol in 45% yield by treatment with the methyl Grignard reagent. The product, 2,3,3-trimethyl-2-pentanol, was purified by distillation and the purity established as 96.6 ± 1.7 mole per cent. by a time–temperature cooling curve (b.p. 77.8–78.0° at 40 mm., n^{20}D 1.4420, m.p. from cooling curve −1.29°).

On conversion of this alcohol to the chloride with gaseous hydrogen chloride at 0°, a chloride was obtained, m.p. +9.5 to 10.5°, n^{20}D 1.4460. Here also the kinetics of solvolysis of the crude reaction product in 80% ethanol at 25° gave data which result in a perfectly linear first-order plot (Fig. 2) with the rate constant having the value 0.187 hr.$^{-1}$.

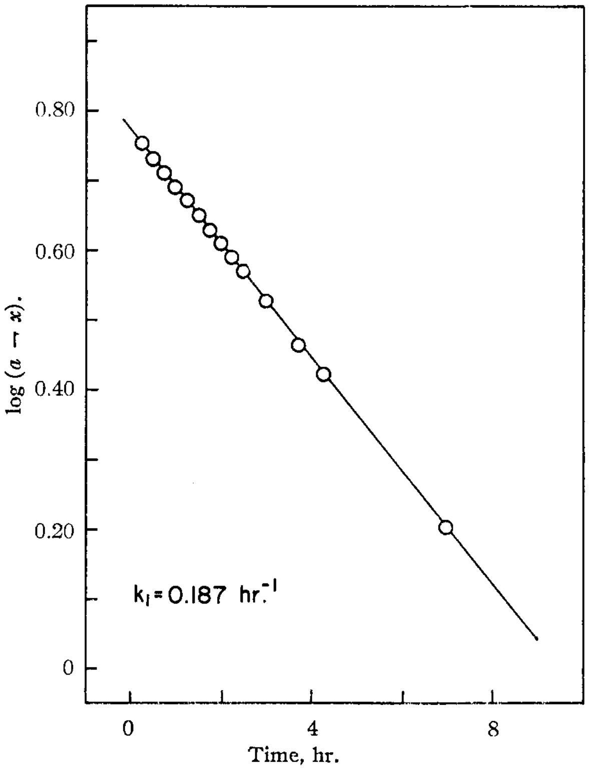


Fig. 2.—Solvolysis data (80% ethanol, 25°) for the reaction product of hydrogen chloride and 2,3,3-trimethyl-2-pentanol.

In order to test the homogeneity of the product XI, the tertiary chloride was distilled at reduced pressure and several fractions were collected. The three major fractions were each solvolyzed in 80% ethanol at 25°. The observed rate constants were essentially the same for each fraction and identical with the value obtained for the crude reaction product before distillation: fraction 2, k_1 = 0.182 hr.$^{-1}$; 3, 0.182; 4, 0.181. Then the tertiary

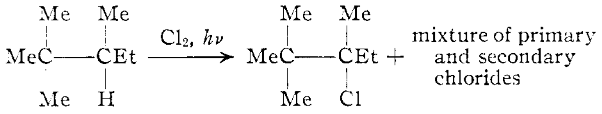
---

(7) C. G. Swain and H. B. Boyles, THIS JOURNAL, 73, 870 (1951).

chloride XI was fractionally crystallized and solvolysis rates determined for both the solid and liquid fractions: solid, $k_1 = 0.177$ hr.$^{-1}$; liquid, 0.179.

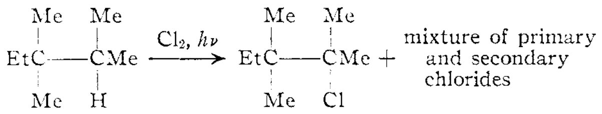
These results appear to establish conclusively that treatment of the two tertiary alcohols VIII, IX with hydrogen chloride results in the formation of the pure, unrearranged tertiary chlorides X, XI. We then took a pure sample of 2,2-dimethyl-3-ethyl-3-pentanol (IV) and treated it with hydrogen chloride under identical conditions. The results completely verified the earlier observations.[3,5] It therefore appears that the alcohol with two ethyl groups on the carbinol carbon IV readily rearranges under conditions which cause no rearrangement in the tertiary alcohol containing one methyl and one ethyl in the same position.

The structures of the two chlorides were further established by photochemically chlorinating the two hydrocarbons, 2,2,3-trimethylpentane (XII) and 2,3,3-trimethylpentane (XIII).



$$\mathrm{Me}\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{C}}}\text{——}\overset{\mathrm{Me}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{Et} \xrightarrow{\mathrm{Cl_2},\ h\nu} \mathrm{Me}\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{C}}}\text{——}\overset{\mathrm{Me}}{\underset{\mathrm{Cl}}{\mathrm{C}}}\mathrm{Et} + \text{mixture of primary and secondary chlorides}$$

XII X

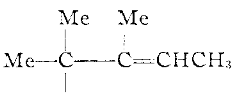


$$\mathrm{Et}\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{C}}}\text{——}\overset{\mathrm{Me}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{Me} \xrightarrow{\mathrm{Cl_2},\ h\nu} \mathrm{Et}\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{C}}}\text{——}\overset{\mathrm{Me}}{\underset{\mathrm{Cl}}{\mathrm{C}}}\mathrm{Me} + \text{mixture of primary and secondary chlorides}$$

XIII XI

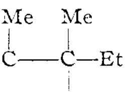
Solvolysis of the crude chlorination product from XII gave rate data which indicated the presence of a tertiary chloride with $k_1 = 0.228$ hr.$^{-1}$ in excellent agreement with the first-order rate constant for the tertiary chloride from the alcohol X. Similarly the product from XIII showed the presence of a single tertiary chloride with $k_1 = 0.184$ hr.$^{-1}$, corresponding to the constant obtained for the chloride from the alcohol XI.

These results further support the structure assignments as well as the conclusion that no rearrangements are involved in these reactions. In this connection it is also significant that hydrogen chloride has been reported to add to the olefins XIV and XV to produce the corresponding tertiary chlorides X ($n^{20}\mathrm{D}$ 1.4441, m.p. $-17.9°$) and XI ($n^{20}\mathrm{D}$ 1.4457, m.p. 10.6°).[8]



$$\mathrm{Me}\text{—}\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{C}}}\text{——}\overset{\mathrm{Me}}{\mathrm{C}}\mathrm{{=}CHCH_3}$$

XIV

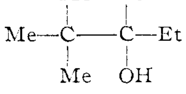


$$\mathrm{H_2C{=}}\overset{\mathrm{Me}}{\mathrm{C}}\text{——}\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{C}}}\text{—Et}$$

XV

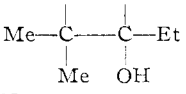
Discussion

The great similarity in the structures of the two alcohols IV and VIII is apparent. Consequently, the sharp difference in their behavior toward hydrogen chloride is very striking.



$$\mathrm{Me}\text{—}\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{C}}}\text{——}\overset{\mathrm{Et}}{\underset{\mathrm{OH}}{\mathrm{C}}}\text{—Et}$$

IV, rearrangement



$$\mathrm{Me}\text{—}\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{C}}}\text{——}\overset{\mathrm{Me}}{\underset{\mathrm{OH}}{\mathrm{C}}}\text{—Et}$$

VIII, no rearrangement

Presumably this marked difference in the behavior of the two alcohols must be related intimately to the mechanism of carbonium ion formation and rearrangement. A clear understanding of the basis for the difference in the reactions of the two alcohols might therefore contribute to clarification of the presently highly fluid state of carbonium ion theory.

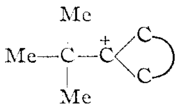
It is here proposed that both alcohols undergo ionization to unrearranged carbonium ions with significantly different steric requirements. The less hindered ion from VIII should be capable of undergoing relatively rapid substitution without appreciable rearrangement. On the other hand, the more hindered ion from IV should react much more slowly and thereby have ample opportunity to undergo extensive rearrangement before substitution occurs.

The postulation of a large difference in the substitution rates of the two carbonium ions is rendered reasonable by detailed examination of the molecular models. In the carbonium ion from IV the central carbon atom carries a bulky *t*-butyl group and two ethyl groups. The ethyl groups cannot lie in the plane defined by the carbonium carbon atom and its three bonds. With either of the two possible conformations having a planar arrangement (Figs. 3 and 4), severe crowding would result in a high degree of steric strain.[9] Such strain would be relieved by rotation of one ethyl group in one direction out of the plane of the carbonium carbon atom and rotation of the second ethyl group in the opposite direction (Fig. 5). Although this conformation results in a reduction in strain, it places the ethyl groups in such a position that they must block approach to the carbonium ion from both above and below the plane of the ion.

With approach to the carbonium carbon atom blocked in this way, reaction with chloride ion or with other molecular or ionic species to form the product should be severely hindered. This should result in a greatly increased half-life for the carbonium ion and give ample opportunity for facile rearrangement to structures which are both less strained and more favorable for the addition of chloride ion or other nucleophilic species.

In the carbonium ions derived from 2,2,3-trimethyl-3-pentanol (VIII) and 2,3,3-trimethyl-2-pentanol (XI) this difficulty does not arise. With only one ethyl group attached to the central carbon atom (in addition to a *t*-butyl and a methyl group), the carbonium ion retains one face relatively free for the approach of the anion.

On this basis it follows that enclosure of the two ethyl groups of IV in a ring system, as in 1-*t*-butylcyclopentanol or 1-*t*-butylcyclohexanol, should result in a marked reduction in hindrance of the approach to the face of the carbonium ion XVI and,



XVI

---

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

[9] The conformations and conclusions are similar to those previously discussed for the addition compound of trimethylboron and diethylamine: H. C. Brown and M. D. Taylor, THIS JOURNAL, **69**, 1332 (1947). It should be pointed out that this addition compound, $\mathrm{Me_3B{:}NHEt_2}$, and the parent hydrocarbon, $\mathrm{Me_3CCHEt_2}$, are homomorphic structures.

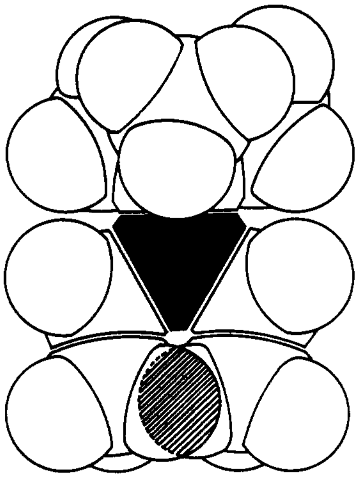


Fig. 3.—Molecular model for the *t*-butyldiethylcarbonium ion showing strain in one of the planar conformations.

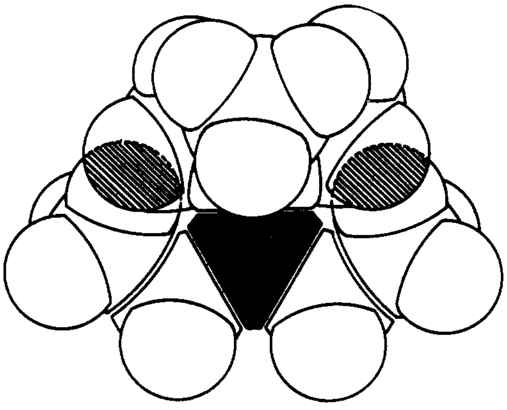
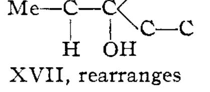


Fig. 4.—Molecular model for the *t*-butyldiethylcarbonium ion showing strain in the other planar conformation.

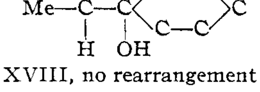
consequently, a decreased tendency toward rearrangement. We plan to examine this prediction.

Some evidence that this is the case is presently available. We have previously shown that treatment of 2-methyl-3-ethyl-3-pentanol (XVII) with hydrogen chloride results in a rearranged product,[3] whereas Bartlett[10] has reported that no rearrangement is oberved in the reaction of hydrogen bromide with the related cyclohexane derivative XVIII. Although it would be highly desirable to have an examination of the behavior of these systems under identical conditions, these results are in accord with our suggestion that the formation of the ring should avoid the peculiar blocking of the carbonium carbon by the two ethyl groups and reduce the tendency for rearrangement of the ion.



$\mathrm{Me{-}\overset{Me}{\underset{H}{C}}{-}\underset{OH}{C}(C{-}C)_2}$

XVII, rearranges



$\mathrm{Me{-}\overset{Me}{\underset{H}{C}}{-}\underset{OH}{C}\langle(C{-}C)_2\rangle C}$

XVIII, no rearrangement

The same arguments used above in interpreting the rearrangement of IV can be used to account for the rearrangements of 2,3,4-trimethyl-3-pentanol (I).[3,4] Moreover, the theory is consistent with the observation that the related alcohol, 2,3,3-trimethyl-2-butanol, and the corresponding chloride are able to undergo carbonium ion reactions without rearrangement.[11]

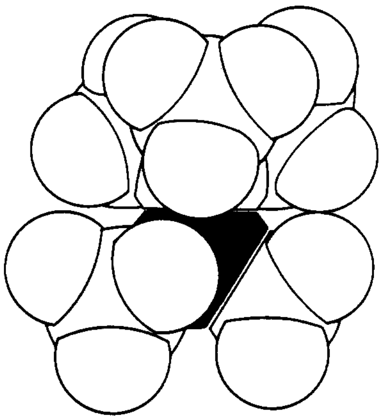
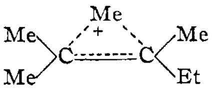


Fig. 5.—Molecular model for the *t*-butyldiethylcarbonium ion showing relatively strain-free conformation with steric blocking of the approach to the carbonium carbon atom.

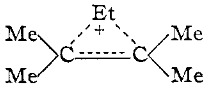
In recent years there has been detailed consideration of the possible importance of bridged structures in the formation and reactions of carbonium ions.[12,13] Consequently it is of interest to point out certain conclusions which may be drawn from the present study with regard to the role of bridged structures in the reactions of carbonium ions without special structural features.[14]

The results of this study definitely exclude the formation of a common bridged ion from VIII and IX.



$\mathrm{Me_2C\overset{\overset{Me}{+}}{\cdots\cdots}C(Me)Et}$

The failure of IX to rearrange could arise as a result of the formation of the symmetrical bridged ion



$\mathrm{Me_2C\overset{\overset{Et}{+}}{\cdots\cdots}CMe_2}$

This possibility could be definitely ruled out only

---

[10] P. D. Bartlett, paper presented at the Organic Symposium at Denver, Colo., June, 1951. E. B. Lefferts, Ph.D. Thesis, Harvard University, 1951.

[11] J. D. Roberts has reported that in the solvolysis of 2-chloro-2,3,3-trimethylbutane (labeled with radiocarbon) the olefin formed showed only 1–2% rearrangement. However, treatment of the alcohol in methylene chloride solution with a large excess of aqueous hydrochloric acid to form the tertiary chloride led to rearrangement which increased with increasing temperature and time to complete equilibrium (symposium on Reaction Mechanisms, American Chemical Society Meeting, Sept. 7, 1951; J. A. Yancey, Ph.D. Thesis, Massachusetts Institute of Technology, 1952). In work in progress with Mr. Y. Okamoto we have observed that the two chlorides X and XI undergo solvolysis in aqueous acetone to re-form the alcohols VIII and IX, without rearrangement.

[12] M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, pp. 211–213.

[13] S. Winstein, *Bull. soc. chim.*, **18**, 55 (1951).

[14] The discussion will be restricted to simple acyclic and alicyclic carbonium ions without the special features of phenyl groups, the cyclopropylmethyl and bicyclic structures. For a discussion of these systems see: S. Winstein, *et al.*, THIS JOURNAL, **74**, 1127, 1140, 1147, 1154, 2165, 2171 (1952); **75**, 147 (1953); D. J. Cram, *et al.*, *ibid.*, **71**, 3863, 3871, 3875, 3883 (1949); **74**, 2129, 2137, 2149, 2152, 2159, 5839 (1952); **75**, 3189 (1953); J. D. Roberts, *et al.*, *ibid.*, **73**, 3542 (1951); **75**, 2069, 3165, 3168 (1953).

by isotopic experiments which have not been performed.[15]

Nevertheless, the failure to observe rearrangements in VIII argues strongly against the formation of a similar bridged ion in the other system. The two carbonium ions are so similar that it appears undesirable to postulate a bridged structure in one carbonium ion and its absence in the other. This is particularly true since the two tertiary chlorides from VIII and IX solvolyze at quite similar rates, with that from IX somewhat the slower of the two. If the chloride from IX underwent ionization to form a relatively stable bridged carbonium ion,[15] a marked enhancement of the solvolysis rate, relative to that of the chloride from VIII, would have been anticipated.

The present study therefore lends additional support to the growing mass of evidence that such bridged structures do not figure in the reactions of simple carbonium ions.[10,16-18]

In view of the complete lack of supporting experimental evidence, it is surprising to note the continued appearance of proposals which assign a significant role to bridged structures and bridging forces in carbonium ion reactions. For example, Roberts and Halman[19] have interpreted rearrangement in the formation of *n*-propyl alcohol from the reaction of *n*-propylamine with nitrous acid as indicating that in this instance methyl participation is fairly important. Similarly, Goering and Olson[20] propose a "non-classical" cation for the intermediate in the rearrangement of *trans*-9-decalyl perbenzoate,[21] while "synartetic effects" have been proposed to account for the enhanced elimination tendencies exhibited by the *t*-butyldimethylcarbonium ion.[22]

For the very highly branched compounds, such as tri-*t*-butylcarbinol, which exhibit greatly enhanced rates of ionization coupled with molecular rearrangements, Bartlett has proposed the formation of bridged ions as a possible mechanism for the release of steric strain.[23] These structures do indeed possess a special feature, very large steric crowding, which could favor the formation of bridged structures. However, in the present paper it has been possible to account for rearrangement phenomena in highly branched carbonium ions in terms of relatively slow substitution rates for highly hindered ions possessing the classical structures. Consequently, in the absence of experimental data supporting bridged structures in ions of this type, we favor a similar classical interpretation for the ions considered by Bartlett.[23]

In summary, then, no evidence is now available which requires that "bridging" or participation by neighboring carbon or hydrogen contributes an important driving force in facilitating the reactions of carbonium ions without special structural features.[14] The possibility cannot be eliminated that bridging and participation may become more important in ions containing substituents more bulky than those considered in the present investigation.[23] However, until more definite evidence is available to establish the importance of these factors in the reactions of carbonium ions, it appears desirable to utilize the concepts of bridging and participation with great caution in interpreting the effect of structure upon carbonium ion reactions.

Experimental Part

Preparation of 2,2,3-Trimethyl-3-pentanol.—The reaction of ethylmagnesium bromide with pinacolone was used.[24] The product exhibited $n^{20}\text{D}$ 1.4357 as compared to 1.4345 previously reported.[24]

Preparation of 2,3,3-Trimethyl-2-pentanol.—Ethyl pivalate can be synthesized in excellent yield by the reaction of diethyl carbonate with *t*-butylmagnesium chloride.[6] However, under the same conditions *t*-amylmagnesium chloride does not react with the carbonate ester. The desired ester, ethyl 2,2-dimethylbutanoate, was synthesized by the reaction of ethyl chlorocarbonate with *t*-amylmagnesium chloride.[25]

t-Amylmagnesium chloride was prepared in 73% yield from 72 g. (3 g. atoms) of magnesium and 320 g. (3 moles) of *t*-amyl chloride. The reagent was treated with 271 g. (2.5 moles) of ethyl chlorocarbonate. After hydrolysis with ammonium chloride, the product was distilled through a Vigreux column. The product was obviously impure as shown by refractive index values for different fractions ranging from 1.4007 to 1.4152. We were unsuccessful in removing the impurity, apparently unchanged ethyl chlorocarbonate, by refluxing with potassium bicarbonate solution.[25] However, the chlorocarbonate could be easily removed by adding pyridine, washing the quaternary salt out with water, followed by a wash with dilute hydrochloric acid to remove excess pyridine. The product thus treated was free of halogen and readily yielded the pure ester (b.p. 142.8–143.2° at 740 mm., $n^{20}\text{D}$ 1.4024) in 60% yield.

The alcohol, 2,3,3-trimethyl-2-pentanol, was obtained in 45% yield by the reaction of 2 moles of methylmagnesium iodide with 0.5 mole of ethyl 2,2-dimethylbutanoate.[24]

Preparation of the Tertiary Chlorides.—In order to avoid possibility of subsequent changes in the products, the tertiary chlorides were prepared in small amounts at 0° and used without distillation for the measurement of their rates of hydrolysis.

2,2,3-Trimethyl-3-pentanol, 5.1 g., was placed in a 25-ml. flask and cooled to 0° in an ice-bath. Hydrogen chloride was passed slowly into the alcohol for five hours. The lower aqueous layer was removed with a capillary and the upper layer was dried with a small quantity of calcium chloride. The organic layer was transferred to a dry 25-ml. flask and evacuated at 10–15 mm. pressure for one-half hour to remove excess hydrogen chloride. A 1.1517-g. sample of the product, $n^{20}\text{D}$ 1.4441, was hydrolyzed in 50% ethanol for 24 hours. The standard base required to neutralize the acid formed in the hydrolysis corresponded to a purity of 98.9%.

The chloride derived from 2,3,3-trimethyl-2-pentanol was prepared in an identical manner, $n^{20}\text{D}$ 1.4460. Its purity, determined as described above, was 99.8%.

Attempts to establish the purity of these chlorides by a time–temperature cooling curve failed. Apparently the heats of fusion were too low for the equipment we had available. The melting points were therefore determined by visual observation of samples in a test-tube.

Initially the tertiary chlorides were stored at −80° to minimize the possibility of subsequent rearrangement.

---

[15] We are indebted to Professor John D. Roberts for pointing this out.

[16] S. Winstein and B. K. Morse, THIS JOURNAL, **74**, 1135 (1952).

[17] J. D. Roberts and J. A. Yancey, *ibid.*, **74**, 5943 (1952).

[18] J. D. Roberts, W. Bennett, R. E. McMahon and E. W. Holroyd, Jr., *ibid.*, **74**, 4283 (1952).

[19] J. D. Roberts and M. Halman, *ibid.*, **75**, 5759 (1953).

[20] H. L. Goering and A. C. Olson, *ibid.*, **75**, 5853 (1953).

[21] For an alternative viewpoint, see P. D. Bartlett and J. L. Kice, *ibid.*, **75**, 5591 (1953), footnote 10.

[22] E. D. Hughes, C. K. Ingold and V. J. Shiner, Jr., *J. Chem. Soc.*, 3827 (1953). See also V. J. Shiner, Jr., THIS JOURNAL, **76**, 1603 (1954), who suggests "rearrangement forces" as a factor in the fast solvolysis rates exhibited by tertiary chlorides similar to those studied in the present investigation.

[23] P. D. Bartlett, *Bull. soc. chim.*, **18**, 100 (1951); *J. Chem. Educ.*, **30**, 22 (1953).

[24] F. C. Whitmore and K. C. Laughlin, THIS JOURNAL, **54**, 4011 (1932); **55**, 3432 (1933).

[25] F. C. Whitmore and D. E. Badertscher, *ibid.*, **55**, 1559 (1933).

However, we later found that the products were quite stable and this precaution was unnecessary. Thus treatment of 2-chloro-2,3,3-trimethylpentane with hydrogen chloride for 10 additional hours did not affect the physical properties or the solvolysis rate. Moreover, another sample was kept at room temperature for two months without observable change in the solvolysis rate.

Rate Determinations.—Aqueous ethanol prepared by mixing eight volumes of absolute ethanol with two volumes of water was used as the solvent. A large sample of the solvent (d^{25}_4 0.8517) was prepared and used for all of the kinetic measurements.

The rate measurements were carried out as previously described.[3] An improved indicator was used. It consisted of a solution of two parts of a 0.1% methyl red solution and three parts of a 0.1% brom cresol green solution, both in absolute ethanol.

In the rate determinations many individual points were taken, especially in the early part of the run, in an effort to detect any curvature of the first-order plot which would be diagnostic of the presence of a second chloride. However, the data defined excellent straight lines in the usual first-order plots (Figs. 1 and 2). To illustrate the precision of the measurements, five different rate measurements for 3-chloro-2,2,3-trimethylpentane at 25° yielded first-order rate constants[26] of 0.219, 0.227, 0.227, 0.230 and 0.223 hr.$^{-1}$.

The solvolysis of 2-chloro-2,3,3-trimethylpentane was carried out on the crude reaction product (n^{20}_D 1.4460, k_1 0.187 hr.$^{-1}$), on individual fractions after distillation (2, b.p. 37.8° (6 mm.), n^{20}_D 1.4460, k_1 0.182; 3, b.p. 37.8° (6 mm.), n^{20}_D 1.4459, k_1 0.182; 4, b.p. 37.8° (6 mm.), n^{20}_D 1.4461, k_1 0.181), and on the partially crystallized product (solid, k_1 0.177; liquid, k_1 0.179).

Chlorination of 2,2,3- and 2,3,3-Trimethylpentanes.—Samples of the hydrocarbons were obtained from the American Petroleum Institute Project No. 45 at the Ohio State University. Sixty grams of 2,2,3-trimethylpentane (n^{20}_D 1.4030, purity 94.7 mole %) was placed in a 200-ml. 3-neck flask, equipped with an inlet tube for chlorine, a ground glass stirrer and a reflux condenser. Oxygen-free nitrogen was passed through the hydrocarbon to remove oxygen and then chlorine gas was passed in under illumination. An amount of chlorine reacted equivalent to 5 mole %. The excess hydrocarbon was removed under vacuum and returned for further chlorination. After several chlorinations had been carried out, the products were combined for the hydrolysis studies. By operating at the high ratio of hydrocarbon to chlorine (20/1) the amount of polychlorination was maintained low.

In the same manner 50 g. of 2,3,3-trimethylpentane (n^{20}_D 1.4076, purity 97.6 mole %) was chlorinated, again at a mole ratio of approximately 20/1.

Solvolysis of the Chlorination Products.—In both cases no attempt was made to isolate the tertiary chloride formed in the reaction from the simultaneously formed primary and secondary chlorides. Instead, 2 ml. of the crude chlorination product was added to 125 ml. of the 80% ethanol solvent and the solvolysis followed for an extended period. The ml. of base required was plotted against time. After approximately 24 hours, the tertiary halide was almost completely hydrolyzed, but the acidity of the solution continued to increase, presumably due to the hydrolysis of other halides present. The linear portion of the curve, after 24 hours, was extrapolated to zero time and this value taken as a measure of the initial concentration of the tertiary halide. The rate constants could now be determined. The type of data obtained and the methods used in handling the data are shown in Fig. 6.

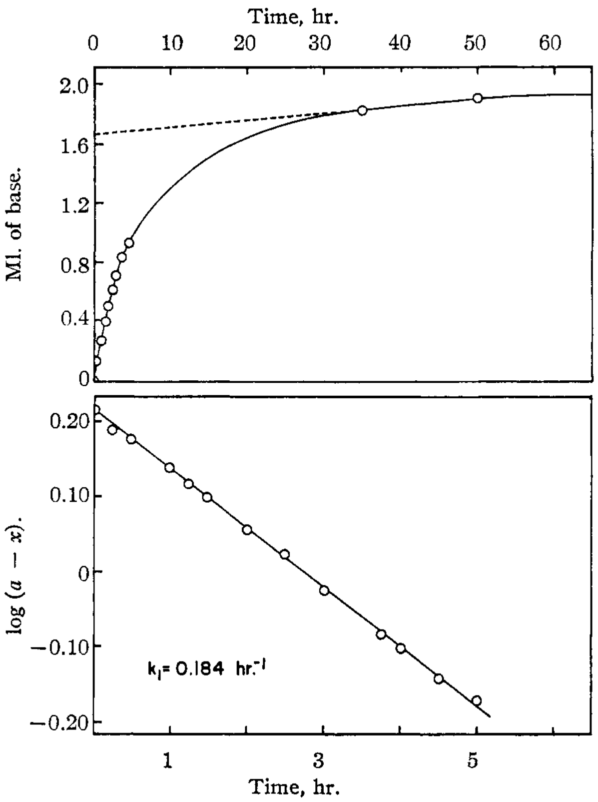


Fig. 6.—Solvolytic data for the crude reaction product from the chlorination of 2,3,3-trimethylpentane.

The product from the chlorination of 2,2,3-trimethylpentane yielded a rate constant of 0.228 hr.$^{-1}$, whereas that from the chlorination of 2,3,3-trimethylpentane gave a value of 0.184 hr.$^{-1}$ (Fig. 6).

Acknowledgment.—The generous assistance of Dr. Kenneth W. Greenlee and the American Petroleum Institute Project No. 45 at The Ohio State University is gratefully acknowledged. We also wish to express our appreciation for the very deep interest and many helpful suggestions of Professor Nathan Kornblum in this investigation.

LAFAYETTE, IND.

---

[26] The values of 0.227 and 0.187 hr.$^{-1}$ for the two chlorides, reported in the Results, represent the best determinations and differ slightly (~1%) from the average value of all the determinations.