The residual crude acetate was distilled through a short distillation head. The small amount of low boiling fraction was placed in a small flask, cooled to 0°, and evacuated to remove any residual ether.

The data on the yield, physical properties and composition of the acetates are summarized in Table III.

The identity of the acetates isolated from the acetolysis of the brosylates with those synthesized from the carbinols is evident from the infrared spectra (Figs. 1 and 2). Comparison of the spectra of the acetates isolated from the solvolysis of 4,4-dimethyl-2-pentyl brosylate (Fig. 2,A) and 4-methyl-2-pentyl brosylate (Fig. 2,B) with the spectra of synthetic samples of the acetates (Figs. 1,A and 1,B, respectively) indicated that the products were essentially pure, containing no more than very minor amounts of the rearranged acetate (Table VII).

The availability of both 2- and 3-pentyl acetate permitted a more detailed analysis for the rearranged product. Blank experiments revealed that it was possible to determine small amounts of the 3-pentyl acetate in the 2-derivative to within ±0.5%. Typical analyses of this kind are reported in Table VII. Application of this procedure to the acetate obtained in the solvolysis of 2-pentyl acetate indicated the presence of a maximum of 1-2% of 3-pentyl acetate in the product (Table VII).

TABLE VII

INFRARED ANALYSIS OF ACETATES PRODUCED IN THE ACETOLYSIS OF SECONDARY BROSYLATE

Acetate unknown	Solution Acetate, g.	Solution CS_2, g.	Wave length, μ	Analysis, %
4,4-Dimethyl-2-pentyl[a]	0.1051	1.4050	8.95	105
			10.63	101
4-Methyl-2-pentyl[a]	.1111	1.3152	8.90	101
			9.50	101
			10.67	98
2-Pentyl[a]	.5005	1.2423	12.27	101(2-)
			11.3	1.4(3-)
2-Pentyl[b]	.4942(2-)	1.2465	12.27	98.7(2-)
	.0088(3-)		11.3	1.2(3-)
2-Pentyl[c]	.2425(2-)	0.6469	12.27	98.2(2-)
	.0056(3-)		11.3	1.8(3-)

[a] Product from acetolysis of brosylate. [b] Synthetic mixture: 98.3% 2- and 1.7% 3-pentyl acetate. [c] Synthetic mixture: 97.7% 2- and 2.3% 3-pentyl acetate.

Acknowledgment.—The generous assistance of Dr. Kenneth W. Greenlee and the American Institute Project No. 45 at The Ohio State University in supplying samples of the pure olefins is gratefully acknowledged. We also wish to express our appreciation of the assistance rendered by Mr. Y. Okamoto with several of the infrared analyses.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Steric Effects in Elimination Reactions. IV. The Question of Rearrangements as a Factor in the Extent and Direction of Unimolecular Elimination

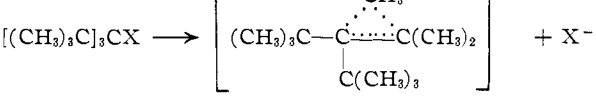
BY HERBERT C. BROWN AND Y. OKAMOTO[1]

RECEIVED OCTOBER 21, 1954

The solvolysis of 2-chloro-2,3,3-trimethylpentane in 80% aqueous ethanol forms pure 2,3,3-trimethyl-1-pentene in 58% yield. The mixture of alcohol and ethyl ether in the solvolysis is converted by hydrogen chloride into a tertiary chloride with identical properties with the original material. In 80% acetone the solvolysis proceeds to give the pure olefin (50% yield) and pure 2,3,3-trimethyl-2-pentanol (20% yield). The solvolysis of 3-chloro-2,2,3-trimethylpentane in 80% aqueous acetone results in the formation of pure 2,3,3-trimethyl-3-pentanol (18% yield) and olefin (58% yield). The olefin fraction contains none of the rearranged structure, 2,3,3-trimethyl-1-pentene. Treatment of the olefin fraction with hydrogen chloride converts it into 3-chloro-2,2,3-trimethylpentane. Careful examination of the products by infrared analysis reveals the absence of any measurable rearrangement within the limits of the analytical method, 1-2%. It appears, therefore, that the ionization, substitution and elimination reactions of these highly branched derivatives proceed without significant rearrangement. It is concluded that there is presently no evidence that bridging and rearrangements play any significant role in affecting either the rate of ionization or the extent and direction of elimination in these and related highly branched alkyl halides.

In earlier publications it has been proposed that the enhanced rate of ionization[2] and the increased tendency toward elimination[3] of highly branched tertiary halides resulted from the operation of steric strain. Evidence has been presented in the present group of papers in support of this interpretation.[4,5]

However, a number of alternative proposals have appeared recently, based upon the possible formation of relatively stable bridged carbonium ions.[6] Thus, it has been suggested that the enhanced rate of solvolysis of tri-*t*-butylcarbinyl derivatives may be due to the formation of a relatively stable bridged intermediate in the ionization stage.



$$[(CH_3)_3C]_3CX \longrightarrow \left[(CH_3)_3C\text{—}\underset{\displaystyle C(CH_3)_3}{C}\overset{CH_3}{\cdots\cdots} C(CH_3)_2 \right]^+ + X^-$$

Similarly Hughes, Ingold and Shiner[8] would prefer not to attribute the large quantities of olefins formed in the solvolysis of highly branched tertiary halides to the operation of steric strain. Instead, they propose that "synartetic" effects (*i.e.*, bridging) are responsible for the high proportion of olefin obtained in the solvolysis of the tertiary chloride, *t*-$BuCClMe_2$.

$$H{\cdot}CH_2{\cdot}CMe(Me){\cdot}\overset{+}{C}Me_2 \longrightarrow H^+ + CH_2{:}CMe{\cdot}CMe_2(Me)$$

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[1] Research assistant at Purdue University, 1952-1955, on a contract supported by the Office of Naval Research for the study of "Steric Strains in Chemical Reactions,"

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

(3) H. C. Brown and R. S. Fletcher, *ibid.*, **72**, 1223 (1950).

(4) H. C. Brown and I. Moritani, *ibid.*, **77**, 3607 (1955).

(5) H. C. Brown and M. Nakagawa, *ibid.*, **77**, 3610, 3614 (1955).

(6) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, pp. 211-213.

(7) P. D. Bartlett, *J. Chem. Education*, **30**, 22 (1953); *Bull. soc. chim.*, **18**, 100 (1951).

(8) E. D. Hughes, C. K. Ingold and V. J. Shiner, *J. Chem. Soc.*, 3827 (1953).

TABLE I

PHYSICAL PROPERTIES OF 2,3,3-TRIMETHYL-2-PENTANOL AND 2,2,3-TRIMETHYL-3-PENTANOL AND DERIVATIVES

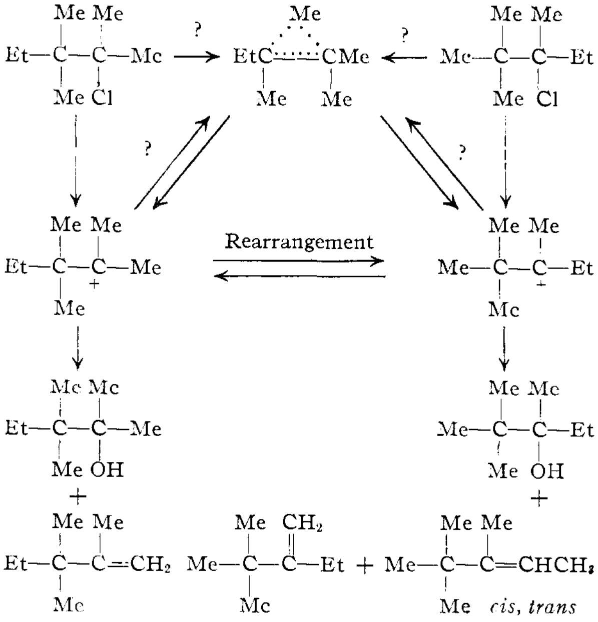
Compound	B.p., °C.	Mm.	M.p., °C.	$n^{20}D$	k_1, hr.$^{-1}$	Lit. ref.
2,3,3-Trimethyl-2-pentanol	77.8–78.0	40	− 1.29	1.4420		b
2-Chloro-2,3,3-trimethylpentane			9.5–10.5	1.4460	0.187[a]	b
			10.6	1.4457		c
2,3,3-Trimethyl-1-pentene	108.4	760		1.4174		c
2,2,3-Trimethyl-3-pentanol	44.5–45.0	11	− 6.05	1.4357		b
3-Chloro-2,2,3-trimethylpentane			−15 to −14	1.4441	0.227[a]	b
			−17.9	1.4441		c
3,4,4-Trimethyl-2-pentene (*cis–trans* mixture)	112.3	760		1.4235		

[a] In 80% ethanol, d^{25}_4 0.87175. [b] Ref. 13. [c] F. L. Howard, T. W. Mears, A. Fookson, P. Pomerantz and D. B. Brooks, *J. Research Natl. Bur. Standards*, **38**, 365 (1947).

Likewise, Shiner[9] has suggested that "rearrangement forces" are at the basis of the enhanced elimination exhibited by highly branched derivatives.

Recently Winstein, Roberts and their co-workers have demonstrated that bridged structures are of little importance in the reactions of primary and secondary carbonium ions.[10–12] However, tertiary carbonium ions, particularly those containing one or more large bulky groups, are crowded and presumably strained. Bridging might provide a means of relieving this strain.[7] Consequently, even though it has been demonstrated that bridging is not important in the reactions of primary and secondary carbonium ions, it is not possible on this basis alone to conclude that such structures are not important in tertiary carbonium ions, particularly those containing large bulky groups.

It was demonstrated previously that treatment of 2,2,3-trimethyl-3-pentanol and 2,3,3-trimethyl-2-pentanol with hydrogen chloride converted them into the corresponding tertiary chlorides without rearrangement.[13] This is a reaction which presumably proceeds through carbonium ions. Unfortunately, the reaction has been studied but little. It, therefore, appeared desirable to examine the question of rearrangement as a factor in the reactions of highly branched carbonium ions by utilizing a reaction whose carbonium ion character has been established clearly. The solvolysis of tertiary chlorides is such a reaction.[14] Accordingly, a study of the solvolysis of 2-chloro-2,3,3- and 3-chloro-2,2,3-trimethylpentanes was undertaken. Identification of the solvolysis products of reaction should provide definite evidence whether the ionization and elimination reactions proceed with or without rearrangement.[15]



Results

For ready reference the physical properties of the alcohols, chlorides and olefins derived from the two structures under consideration are listed in Table I.

Solvolysis of 2-Chloro-2,3,3-trimethylpentane in 80% Ethanol.—2,3,3-Trimethyl-2-pentanol ($n^{20}D$ 1.4420) was treated with dry hydrogen chloride at 0°. The product exhibited the following constants: m.p. 10–10.4°, $n^{20}D$ 1.4460, k_1 0.182.[16] A sample of this chloride was dehydrochlorinated with 2,6-lutidine to form 2,3,3-trimethyl-1-pentene, b.p. 107–109° (745 mm.), $n^{20}D$ 1.4175. The infrared spectrum of the olefin is recorded in Fig. 1, D.

The tertiary chloride was solvolyzed at 25° in 80% ethanol. The olefin was separated from the alcohol plus ether by distillation through a Todd micro column. A 58% yield of olefin was obtained, b.p. 107.5–109° (749 mm.), $n^{20}D$ 1.4175. The infrared spectrum of the olefin (Fig. 1, C) is practically identical with that of the sample of 2,3,3-trimethyl-1-pentene obtained by dehydrochlorination of the tertiary chloride, Fig. 1, D.

The alcohol–ethyl ether residue from the above fractionation distilled in a small Claisen flask at 150–155° (745 mm.) with $n^{20}D$ 1.4342. The yield was approximately 20%. No convenient method of separation of the *t*-alkyl ethyl ether from the tertiary alcohol suggested itself. The mixture therefore was treated with hydrogen chloride to form the tertiary chloride which exhibited a solvolysis rate of 0.182 hr.$^{-1}$. Thus the original tertiary chloride had undergone solvolysis to form alcohol

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(9) V. J. Shiner, Jr., THIS JOURNAL, **76**, 1603 (1954).

(10) S. Winstein and B. K. Morse, *ibid.*, **74**, 1133 (1952).

(11) J. D. Roberts, W. Bennett, R. E. McMahon and E. W. Holroyd, *ibid.*, **74**, 4283 (1952).

(12) J. D. Roberts and J. A. Yancey, *ibid.*, **74**, 5943 (1952).

(13) H. C. Brown and R. B. Kornblum, *ibid.*, **76**, 4510 (1954).

(14) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapt. VII.

(15) A similar study has been made by J. D. Roberts and J. A. Yancey utilizing 2-chloro-2,3,3-trimethylbutane labeled with radiocarbon. See footnote 11, ref. 13. The present investigation was facilitated by a complete exchange of information with Professor Roberts.

(16) 80% aqueous ethanol, d^{25}_4 0.8502.

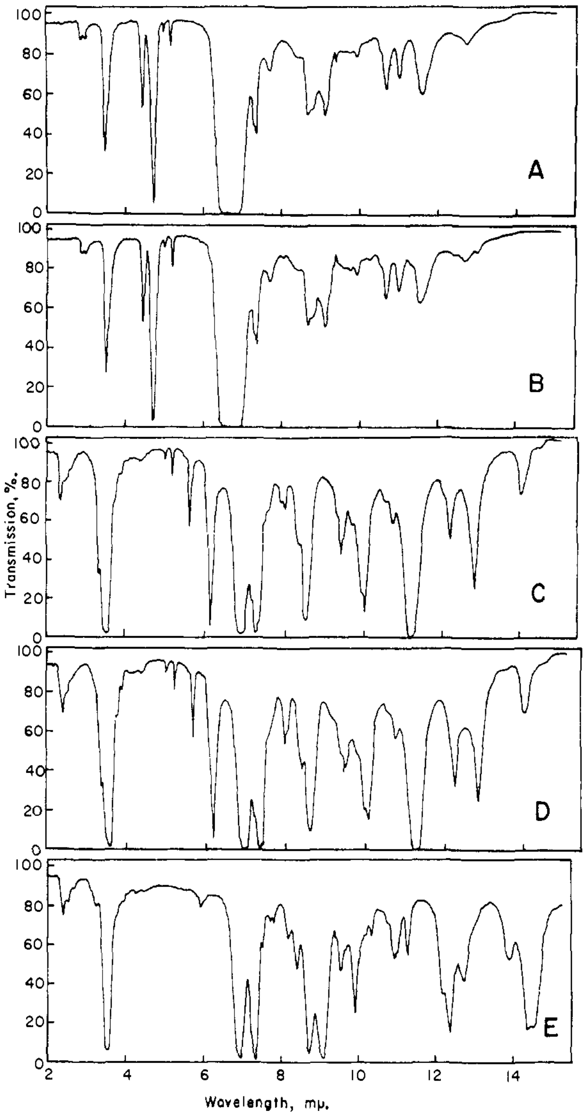

Fig. 1.—Infrared spectra: A, 2,3,3-trimethyl-2-pentanol; B, alcohol isolated from the solvolysis of 2-chloro-2,3,3-trimethylpentane; C, olefin isolated from the solvolysis of 2-chloro-2,3,3-trimethylpentane; D, 2,3,3-trimethyl-1-pentene; E, 2-chloro-2,3,3-trimethylpentane.

and ether, and these products reformed tertiary chloride with the identical solvolysis rate as that of the original halide.[17]

No rearrangement therefore is apparent either in the olefin fraction or the alcohol–ether fraction.

Solvolysis of 2-Chloro-2,3,3-trimethylpentane in 80% Acetone.—In order to permit isolation and identification of the alcohol fraction, the solvolysis of 2-chloro-2,3,3-trimethylpentane was repeated in 80% aqueous acetone at 35–40°. There was obtained a 50% yield of olefin, b.p. 107–107.5° (729 mm.), $n^{20}D$ 1.4174.

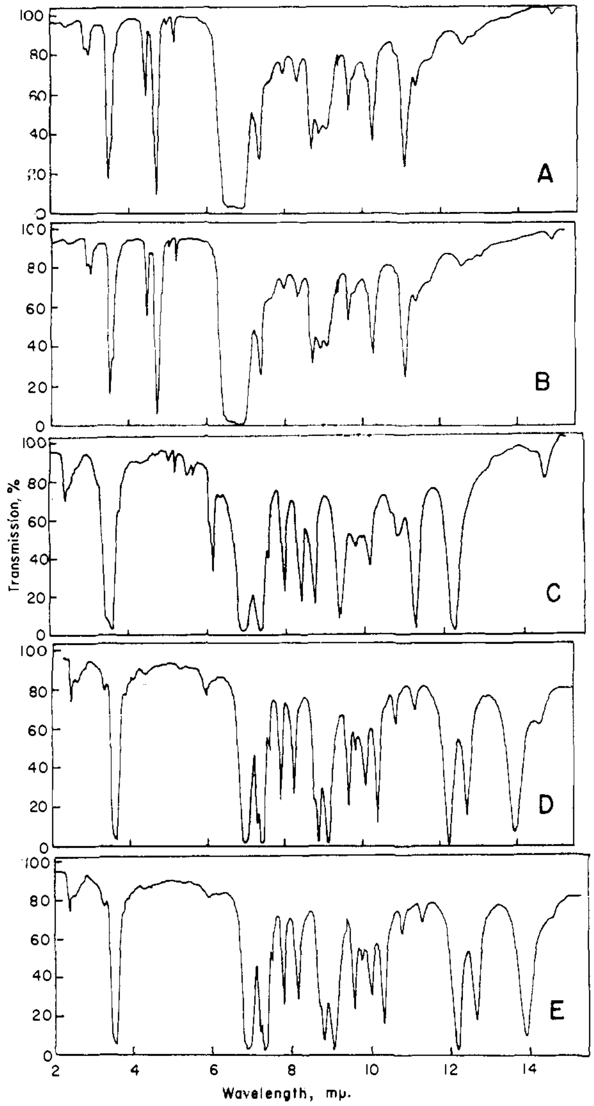

Fig. 2.—Infrared spectra: A, 2,2,3-trimethyl-3-pentanol; B, alcohol isolated from the solvolysis of 3-chloro-2,2,3-trimethylpentane; C, olefin isolated from the solvolysis of 3-chloro-2,2,3-trimethylpentane; D, chloride from olefin isolated in solvolysis of 3-chloro-2,2,3-trimethylpentane; E, 3-chloro-2,2,3-trimethylpentane.

The alcohol fraction distilled at 77° (42 mm.) with $n^{20}D$ 1.4415. The yield was 20%. The infrared spectrum of a solution in carbon disulfide (Fig. 1, B) is almost identical with that of a solution of the original 2,3,3-trimethyl-2-pentanol in this solvent (Fig. 1, A). Analysis by the base line method, using the characteristic peak at 10.67 μ, of the concentration of 2,3,3-trimethyl-2-pentanol in the alcohol recovered from the solvolysis resulted in a value of 101%. It is concluded that no detectable amount of the isomeric alcohol, 2,2,3-trimethyl-3-pentanol, can be formed in the reaction.

Solvolysis of 3-Chloro-2,2,3-trimethylpentane in 80% Acetone.—2,2,3-Trimethyl-3-pentanol ($n^{20}D$ 1.4357) was treated with hydrogen chloride at 0°. The product possessed the following constants: m.p. -17.5 to $-16°$, $n^{20}D$ 1.4441, k_1 0.223.[16]

The 3-chloro-2,2,3-trimethylpentane was solvo-

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(17) The *t*-alkyl ethyl ether presumably would be converted to the tertiary chloride and ethyl alcohol under these conditions. It was shown that ethyl alcohol does not interfere in this reaction by treating a mixture of 2.0 g. of 2,2,3-trimethyl-3-pentanol and 0.2 g. of ethyl alcohol with hydrogen chloride. The resulting product solvolyzed at a rate of 0.222 hr.$^{-1}$ as compared to a rate constant of 0.223 hr.$^{-1}$ for the chloride obtained from the pure alcohol.

lyzed in 80% acetone at 35–40°. The olefin fraction was recovered in 58% yield by distillation through the Todd micro column: b.p. 109–111° (750 mm.), n^{20}D 1.4224. The infrared spectrum of the olefin does not have the characteristic absorption of the isomeric compound, 2,3,3-trimethyl-1-pentene at 5.65 and 12.85 μ.

Because of the possibilities for the presence of three different compounds in the olefin fraction, no attempt was made to compare the spectrum with those for the pure synthetic samples. Instead the entire fraction was converted into tertiary chloride by treatment with hydrogen chloride. The product, n^{20}D 1.4442, exhibited an infrared spectrum (Fig. 2, D) identical with that of the original chloride (Fig. 2, E).

The alcohol was obtained in 18% yield by distillation through a short column: b.p. 72.5° (46 mm.), n^{20}D 1.4357. The spectrum of the alcohol in carbon disulfide (Fig. 2, B) is almost identical with that of the original sample of 2,2,3-trimethyl-3-pentanol in the same solvent (Fig. 2, A). Analysis by the base line method, using the characteristic absorption at 10.25 μ indicated the presence of a minimum of 98% 2,2,3-trimethyl-3-pentanol in the alcohol isolated from the solvolysis product.

Discussion

It was established previously that the treatment of 2,3,3-trimethyl-2-pentanol and 2,2,3-trimethyl-3-pentanol with hydrogen chloride leads to the formation of the corresponding tertiary chlorides without rearrangement.[13] The present study further establishes that the solvolyses of these tertiary chlorides likewise proceed without measurable rearrangement.

These tertiary chlorides exhibit both enhanced rates of solvolysis and enhanced tendencies to undergo elimination. The failure to undergo any measurable rearrangement in the course of solvolysis casts doubt upon explanations of these enhanced rates which are based upon hypothetical "synartetic effects"[8] or "rearrangement forces."[9] It appears that steric strain in these highly branched derivatives provides the basis for a more satisfactory interpretation of the observed phenomena.

In the case of the very highly branched tertiary derivatives, such as tri-*t*-butylcarbinyl halides, the possibility cannot now be eliminated that bridging may become important under the severe crowding resulting from the presence of these bulky substituents.[7] However, it has been shown that enhanced rates of ionization, and increased tendencies for elimination and rearrangement[13] are encountered in highly branched tertiary halides where the evidence is against the participation of bridged structures. Therefore, even in the case of compounds such as tri-*t*-butylcarbinol and its derivatives, in the absence of any compelling experimental data requiring the existence of bridging for their understanding, it appears desirable to proceed with caution in attributing the enhanced ionization and rearrangement tendencies to the participation of stable bridged structures.

Experimental Part

Materials.—The preparation and check of purity of 2,3,3-trimethyl-2-pentanol and 2,2,3-trimethyl-3-pentanol were described previously.[13] The 80% ethanol (d^{25}_4 0.8502) and 80% acetone were prepared by mixing 20 parts by volume of water with 80 parts by volume of the anhydrous organic solvent.

The following procedure is typical of that used for the preparation and isolation of the tertiary chlorides.

2,3,3-Trimethyl-2-pentanol (n^{20}D 1.4420), 17 g., was placed in a 50-ml. flask and cooled to 0°. Hydrogen chloride was slowly passed into the alcohol for 3 hr., when no further increase in weight was observed. The lower aqueous phase was removed with a fine capillary, and the upper layer dried with a small quantity of calcium chloride and then subjected to a vacuum of 10–20 mm. for one hour in order to remove dissolved hydrogen chloride. The refractive index of the product thus obtained (n^{20}D 1.4460) is in excellent agreement with the value previously reported for the pure chloride (Table I).

2,3,3-Trimethyl-1-pentene was prepared as follows. Five grams of 2-chloro-2,3,3-trimethylpentane was added to 30 ml. of 2,6-lutidine (b.p. 143° (747 mm.), n^{20}D 1.4978) and the mixture, attached to the Todd column, was heated under gentle reflux for 2 hr. At the end of this time the olefin was taken as overhead at 107–109° (745 mm.). The distillate was washed with water to remove traces of 2,6-lutidine, and dried over magnesium sulfate. A total of 3.5 g., 88% yield of olefin was obtained. The refractive index, n^{20}D 1.4175, was in excellent agreement with the literature value (Table I) for the carefully purified product.

Kinetic Measurements.—The procedure was similar to those previously described.[2,13] Slightly greater precision in the "infinity" titers was attained by running aliquots into flasks which were maintained at 40–50° for 24 hr., followed by titration under identical conditions as those used for the individual aliquots during the run.

Solvolysis of 2-Chloro-2,3,3-trimethylpentane in 80% Ethanol.—A total of 15.8 g. (0.107 mole) of 2-chloro-2,3,3-trimethylpentane was added to 200 ml. of the 80% ethanol containing 20 g. of potassium bicarbonate. The reaction mixture was stirred for 24 hr. at 25°. To the reaction mixture was added 300 ml. of water saturated with potassium bromide. The olefin–alcohol–ether layer was separated, washed with water and dried with magnesium sulfate. 2,6-Lutidine, 5 ml., was added to the product (to counteract the effects of possible traces of unsolvolyzed chloride) and the mixture distilled in the micro column. Olefin was collected at 107.5–109° (749 mm.). The distillate was washed with water and dried with magnesium sulfate. The yield was 6.47 g., 58%, with n^{20}D 1.4175, identical with the value obtained in the preparation experiment utilizing 2,6-lutidine.

The distillation residue, containing 2,6-lutidine and the alcohol–ether product, was treated with 0.09 *N* hydrochloric acid to the neutral point. The upper layer was separated, washed with dilute potassium bicarbonate solution, with water and then dried. The product, 2.74 g., n^{20}D 1.4342, distilled through a simple Claisen flask at 150–155°. This material was treated with hydrogen chloride following the precise procedure described above for the preparation of 2-chloro-2,3,3-trimethylpentane. The product solvolyzed at a rate of 0.182 hr.$^{-1}$, identical with the rate constant exhibited by the original chloride used in the solvolysis experiment.

Solvolysis of 2-Chloro-2,3,3-trimethylpentane in 80% Acetone.—The tertiary chloride, 11.66 g. (0.078 mole), was added to 150 ml. of 80% acetone containing 10 g. of potassium bicarbonate. The solution was stirred at 35–40° for 60 hr. (rough rate measurements previously had shown that this time would be required for a reaction 98–99% complete). The olefin and alcohol produced in the solvolysis were separated by adding 200 ml. of water saturated with ammonium sulfate. The olefin–alcohol layer was washed with water and dried over magnesium sulfate. 2,6-Lutidine, 5 ml., was added and the mixture was distilled in the micro column. The olefin was obtained at 107–107.5° (729 mm.). The distillate was washed and dried (magnesium sulfate). A total of 4.5 g., 50% yield, of olefin (n^{20}D 1.4174) was obtained.

The distillation residue was treated with cold 0.1 *N* hydrochloric acid to the neutral point. The alcohol fraction which separated was washed with dilute potassium bicarbonate, water, and dried. The alcohol, distilled through a short column, was obtained in 2.1 g., 20% yield, with b.p. 77° (42 mm.), n^{20}D 1.4415. From the infrared spectra (Fig. 1, B: 0.0198 g. in 0.4837 g. of carbon disulfide), compared to that of the authentic sample (Fig. 1, A: 0.0210 g. in 0.4839 g. of carbon disulfide), it is estimated that the concentration of 2,3,3-trimethyl-2-pentanol in the solvolysis product is 101%.

Solvolysis of 3-Chloro-2,2,3-trimethylpentane in 80% Acetone.—The tertiary chloride ($n^{20}_{\rm D}$ 1.4441) was prepared from the alcohol ($n^{20}_{\rm D}$ 1.4420) by the identical procedure described above for the isomeric derivative. The 3-chloro-2,2,3-trimethylpentane, 28.25 g. (0.19 mole), was placed in 270 ml. of the 80% acetone containing 20 g. of potassium bicarbonate. The solution was stirred at 35–40° for 50 hr. The olefin–alcohol fraction was separated by adding 600 ml. of water saturated with ammonium sulfate. After the usual washing treatments, 5 ml. of 2,6-lutidine was added and the product distilled. The olefin distilled at 109–111° at 750 mm. A total of 12.3 g., 58% yield, of the olefin ($n^{20}_{\rm D}$ 1.4224 was obtained). Hydrogen chloride was added to 3.0 g. of the olefin at 0° until no further increase in weight was observed. The product was dried over calcium chloride and then transferred under 0.5 mm. pressure into a weighed tube by condensation. A 3.6-g. yield of the chloride, $n^{20}_{\rm D}$ 1.4442, was obtained. The infrared spectrum (Fig. 2, D) indicated that it was identical with the original sample of 3-chloro-2,2,3-trimethylpentane (Fig. 2, E) used in the solvolysis experiment.

The alcohol was recovered from the distillation residue by the usual treatment with cold dilute hydrochloric acid. After the usual treatment, 6.0 g. of crude alcohol was obtained. On distillation, b.p. 72.5° (46 mm.), there was obtained 4.7 g., 18% yield, of the pure alcohol, $n^{20}_{\rm D}$ 1.4357. The infrared spectrum (Fig. 2, B) of a solution of the alcohol in carbon disulfide (0.1034 g. in 1 ml. of solvent) is practically identical with that of a solution containing the same concentration of an authentic sample of 2,2,3-trimethyl-3-pentanol in the same solvent (Fig. 2, A). From the spectra the concentration of 2,2,3-trimethyl-3-pentanol in the recovered alcohol is 98%, using the base line method of analysis at 10.25 μ. In a test analysis using this procedure the concentration of this alcohol was estimated correctly as 95% in a 95:5 synthetic mixture of the two alcohols.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Steric Effects in Elimination Reactions. V. The Importance of Steric Strains in the Extent and Direction of Unimolecular Elimination. The Role of Steric Strains in the Reactions of Highly Branched Carbonium Ions

BY HERBERT C. BROWN AND ICHIRO MORITANI[1]

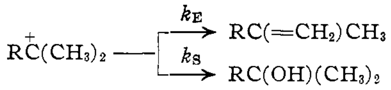
RECEIVED OCTOBER 21, 1954

The available experimental data support the conclusion that steric strains represent an important factor in unimolecular eliminations. Consideration of the influence of steric strain provides a simple, consistent explanation for the effect of structure on the extent and direction of unimolecular elimination. The criticisms of Hughes, Ingold and Shiner are examined. It is concluded that the alternative interpretations they have advanced are no longer tenable in the light of the experimental data reported in the present group of papers. It is pointed out that steric strains provide a satisfactory explanation for the unusual behavior of highly branched carbonium ions in ionization, substitution, rearrangement and elimination reactions.

In a paper recently published under the title, "The Comparative Unimportance of Steric Strain in Unimolecular Elimination," Hughes, Ingold and Shiner[2] have criticized earlier proposals that steric strains[3] play an important role in the extent[4] and direction[5] of unimolecular elimination reactions. The present group of papers[6-9] provides new experimental data for a careful examination of their criticisms and their alternative explanations.

It was pointed out previously[4] that the solvolysis of dimethyl-*t*-butylcarbinyl chloride in 80% ethanol yields 61% olefin instead of the 16% observed for *t*-butyl chloride. The dimethyl-*t*-butylcarbonium ion has six hydrogen atoms in position for elimination as compared to nine for the *t*-butylcarbonium ion. On a purely statistical basis, therefore, the yield of olefin in the former case should have been less than that from the *t*-butylcarbonium ion. If the relative possibilities for electromeric stabilization[10] of the two olefins are considered, the conclusion is also reached that less olefin should be formed in the solvolysis of dimethyl-*t*-butylcarbinyl chloride than in the case of *t*-butyl chloride.

The large yield of olefin was attributed to the operation of steric effects.[4] It was argued that the large alkyl substituent would be expected to reduce the rate of substitution (k_S) for the ion and possibly increase the rate of elimination (k_E). An increased value of k_E/k_S would result and would be observed as an increase in the olefin yield.



$$\overset{+}{\rm R}{\rm C(CH_3)_2} \longrightarrow \begin{cases} \xrightarrow{k_E} {\rm RC({=}CH_2)CH_3} \\ \xrightarrow{k_S} {\rm RC(OH)(CH_3)_2} \end{cases}$$

The proposal that k_S should decrease with the increasing steric requirements of the groups attached to the carbonium ion is now supported by a considerable quantity of experimental evidence. In the second paper of this group[7] it was shown that in the solvolysis in 85% *n*-butyl Cellosolve of the tertiary bromides, $RCH_2CBr(CH_3)_2$, the yield of olefin varied directly with the steric requirements of the group R:

$CH_3CH_2CBr(CH_3)_2$	27% olefin
$C_2H_5CH_2CBr(CH_3)_2$	32.5%
$(CH_3)_2CHCH_2CBr(CH_3)_2$	46%
$(CH_3)_3CCH_2CBr(CH_3)_2$	57%

This group of compounds provides a closely related series in which the electromeric effects should be quite similar. The drift in the yield of olefin does not appear to be explicable in terms of any differences in the electronic interactions of the groups R.

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