pared 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 ($n^{20}D$ 1.4441) was prepared from the alcohol ($n^{20}D$ 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 ($n^{20}D$ 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, $n^{20}D$ 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, $n^{20}D$ 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]

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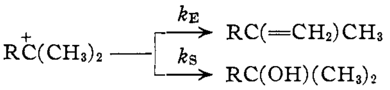
The available experimental data support the conclusion that steric strains represent an important factor in unimolecular eliminations. Consideration of the influence of steric strain provides a simple, consistent explanation for the effect of structure on the extent and direction of unimolecular elimination. 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.



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

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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[1] Post-doctorate assistant at Purdue University 1951-1953, on a contract supported by the Office of Naval Research for the study of "Steric Strains in Chemical Reactions."

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

[3] H. C. Brown, *Science*, **103**, 385 (1946).

[4] H. C. Brown and R. S. Fletcher, THIS JOURNAL, **72**, 1223 (1950).

[5] H. C. Brown and H. L. Berneis, *ibid.*, **75**, 10 (1953).

[6] H. C. Brown and I. Moritani, *ibid.*, **77**, 3607 (1955).

[7] H. C. Brown and M. Nakagawa, *ibid.*, **77**, 3610 (1955).

[8] H. C. Brown and M. Nakagawa, *ibid.*, **77**, 3614 (1955).

[9] H. C. Brown and Y. Okamoto, *ibid.*, **77**, 3619 (1955).

[10] E. D. Hughes, C. K. Ingold, *et al.*, *J. Chem. Soc.*, 2093 (1948).

However, the drift is understood readily in terms of the increasing steric requirements of the group R and its probable effect upon the rate of substitution (k_S).[11]

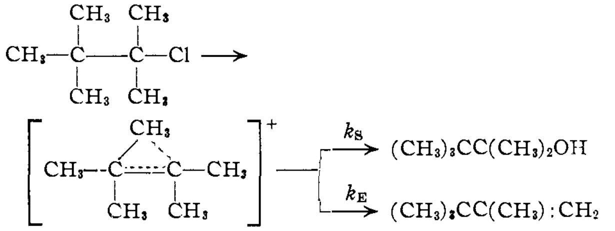
Treatment of diethyl-*t*-butylcarbinol with hydrogen chloride results in the formation of rearranged chlorides,[12] whereas under identical conditions the related tertiary alcohol, ethylmethyl-*t*-butylcarbinol, yields the unrearranged chloride.[13] Here also the results point to a great difference in the rates of substitution of the respective carbonium ions. It was suggested that the slow rate of substitution of the severely hindered ion, diethyl-*t*-butylcarbonium ion, permits the fast rearrangement reaction to become important, whereas in the less hindered ion, ethylmethyl-*t*-butylcarbonium ion, substitution is faster than the rearrangement reaction and product is therefore formed without structural change.[13]

Hughes, Ingold and Shiner suggest that the increased yield of olefin observed in the solvolysis of dimethyl-*t*-butylcarbinyl chloride may arise from elimination with Wagner–Meerwein rearrangement.[2]

$$HCH_2CMe(Me)\overset{+}{C}Me_2 \longrightarrow H^+ + CH_2{:}CMeCMe_2(Me)$$

However, it has now been shown that the solvolysis of the two related halides, methylethyl-*t*-butylcarbinyl chloride and dimethyl-*t*-amylcarbinyl chloride, proceed without rearrangement[14] although in these cases also high yields of olefin are realized.[9] Consequently, the proposal by Hughes, Ingold and Shiner that the high yield of olefin observed in the solvolysis of highly branched tertiary halides arises from elimination with Wagner–Meerwein rearrangement no longer appears tenable.

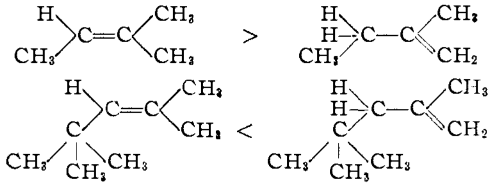
They further state: "Even if group migration does not actually occur, the presence of a system with that potentiality may have kinetic effects...." It is difficult to see how the olefin yield can be drastically affected by a system in which there is a potential but no actual group migration. The only apparent mechanism for this to occur would involve the formation of an unsymmetrical "bridged" structure which could then undergo elimination and substitution without rearrangement. One would then have to postulate that such an unsymmetrical "bridged" structure is more stable for some reason than the symmetrical structure and possesses an unusually large preference for elimination reactions.



However, considerable evidence is now available that "bridged" structures are not important in the reactions of aliphatic carbonium ions.[15–17] Moreover, arguments have been presented that they are not important in the reactions of highly branched tertiary carbonium ions related to the structures under discussion here.[9,13] If the symmetrical bridged structures do not possess sufficient stability to play an important role in carbonium ion reactions, there appears little reason to consider that unsymmetrical structures will be of more significance in these reactions.

It therefore appears that all of the available experimental results are consistent with the steric interpretation previously advanced for the enhanced yields of olefin observed in the solvolysis of highly branched tertiary halides. No evidence is presently available that either Wagner–Meerwein rearrangements or a tendency toward such rearrangements contribute in any way to the high olefin yields in these reactions.

Hughes, Ingold and Shiner also object to the proposed interpretation of the role of steric strain in controlling the direction of elimination.[5] For example, the solvolyses of dimethylneopentylcarbinyl halides proceed with the formation of 81% 1-olefin[6,7] a case of Hofmann-type elimination in an unimolecular elimination. This was attributed to steric strain in the 2-olefin arising from the conflicting steric requirements of the *cis*-*t*-butyl and methyl groups. It was suggested that such strain is sufficiently large as to overcome the greater hyperconjugative stabilization of the 2-olefin.[5]



This interpretation is supported by the present results[7] on the ratio of 1- to 2-olefin in the solvolyses of the series $RCH_2CBr(CH_3)_2$

$CH_3CH_2CBr(CH_3)_2$	1-/2- = 0.27
$C_2H_5CH_2CBr(CH_3)_2$	1-/2- = .41
$(CH_3)_2CHCH_2CBr(CH_3)_2$	1-/2- = .70
$(CH_3)_3CCH_2CBr(CH_3)_2$	1-/2- = 4.26

The gradual increase in the ratio from Me to *i*-Pr, with the sharp increase for *t*-Bu is in line with the predicted degree of steric strain in the 2-olefin. Because of the spherical symmetry of the *t*-butyl group, it is not possible to reduce the steric interaction in the 2-olefin by rotation of the group. On the other hand, rotation of the ethyl and isopropyl groups permits a reduction of the steric interactions to a point where they should be but little greater than for the methyl group.

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[11] The values given represent the actual recovery of olefins. In experiments in 80% ethanol in which the olefins were determined by bromometric analysis, the values were 34% for *t*-amyl chloride and 65% for dimethylneopentylcarbinyl chloride. See also Table III, ref. 6.

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

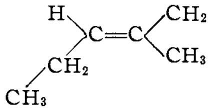
[13] H. C. Brown and R. B. Kornblum, *ibid.*, **76**, 4510 (1954).

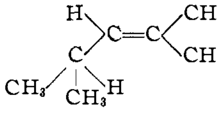
[14] In an even more pertinent experiment J. D. Roberts and J. A. Yancey have demonstrated that the olefin in the solvolysis of dimethyl-*t*-butylcarbinyl chloride (labeled with radiocarbon) exhibits but 1–2% rearrangement (Symposium on Reaction Mechanisms, American Chemical Society Meeting, Sept. 7, 1951; J. A. Yancy, Ph.D. Thesis, Massachusetts Institute of Technology, 1952).

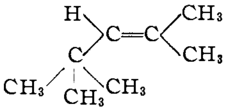
[15] S. Winstein and B. K. Morse, THIS JOURNAL, **74**, 1133 (1952).

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

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







Hughes, Ingold and Shiner have suggested that the "*t*-butyl-to-carbon bond may be able to hyperconjugate like the hydrogen-to-carbon bond, and that, even in reactions in which no actual chain-splitting occurs, such hyperconjugation may affect reactivity. This assumption could account both for the accelerated heterolysis of our alkyl chloride and for the promoted development of unsaturation in its methyl branches:

$$t\text{-Bu}\overset{\curvearrowright}{-C}H_2\text{-}CMe_2\overset{\curvearrowright}{-C}l,\ t\text{-Bu}\overset{\curvearrowright}{-C}H_2\text{-}CMe\overset{\curvearrowright}{=C}H_2$$

. . . this interpretation . . . does seem to fit the few facts we know, as the theory of steric strain does not."

On the basis of the explanation proposed by Hughes, Ingold and Shiner, a relatively regular increase in the ratio of 1- to 2-olefin would be expected in the series $RCH_2CBr(CH_3)_2$ for R = Me, Et, *i*-Pr, *t*-Bu. However, as was pointed out, such a regular increase is observed only for the first three members of the series (0.27, 0.41, 0.70 for R = Me, Et, *i*-Pr), while for R = *t*-Bu there occurs a very sharp increase in the ratio (4.26 for R = *t*-Bu).

Additional evidence is available. If electron release from the *t*-butyl-to-carbon bond is an important factor in directing the elimination to form the 1-olefin, the effect should be greater in a secondary derivative than in the tertiary. Ionization of a secondary derivative is more difficult than for a tertiary and should therefore make a much larger demand upon bonds capable of contributing an electron pair through hyperconjugation.

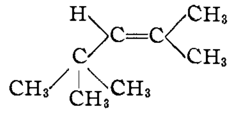
The solvolyses of the corresponding secondary series, $RCH_2CH(OBs)CH_3$, do not show such an enhanced contribution of the alkyl group.[8] Indeed, the results show much smaller values for the ratio of 1- to 2-olefin with increasing bulk of the group R.

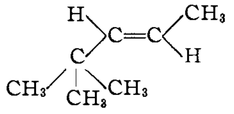
$CH_3CH_2CH(OTs)CH_3$	1-/2- = 0.11
$C_2H_5CH_2CH(OBs)CH_3$	1-/2- = .19
$(CH_3)_2CHCH_2CH(OBs)CH_3$	1-/2- = .25
$(CH_3)_3CCH_2CH(OBs)CH_3$	1-/2- = .32

In the case of R = *t*-Bu, the 2-olefin is still the predominant product, so that elimination is still in accord with the Saytzeff rule. It is especially significant that the 2-olefin in this case is almost entirely the *trans* derivative. This represents a very sharp change for R = *t*-Bu as compared to R = Me, Et and *i*-Pr.

$CH_3CH_2CH(OTs)CH_3$	*trans/cis* = 1.08
$C_2H_5CH_2CH(OBs)CH_3$	*trans/cis* = 1.39
$(CH_3)_2CHCH_2CH(OBs)CH_3$	*trans/cis* = 1.94
$(CH_3)_3CCH_2CH(OBs)CH_3$	*trans/cis* = 83

This behavior is in excellent agreement with the steric strain interpretation. In 2,4,4-trimethyl-2-pentene the *t*-butyl group cannot avoid being *cis* to a methyl group. In the 2-olefin from $(CH_3)_3CCH_2CH(OBs)CH_3$, the *t*-butyl group can avoid steric interactions with the methyl group by assuming the *trans* conformation.





In other words, in 2,4,4-trimethyl-2-pentene the olefin can benefit from the hyperconjugative stabilization afforded by the 2-olefin only at the cost of large steric strains resulting from the steric interactions of the *cis-t*-butyl and methyl groups. On the other hand, in *trans*-4,4-dimethyl-2-pentene, the molecule can benefit from the hyperconjugative stabilization of the 2-olefin without suffering from the steric disadvantages of the *cis-t*-butyl-methyl arrangement.

The results are, therefore, not in accord with the suggestion made by Hughes, Ingold and Shiner, but are consistent with the steric strain interpretation.

The series $R^1R^2R^3CCl$ = Me_3CCl, Me_2EtCCl, $MeEt_2CCl$, Et_3CCl, also is considered by these authors to provide evidence for predominant control by electromeric effects and against any control by steric effects. Unfortunately, in this area no new experimental data are available. However, it appears appropriate to discuss the available data in the light of our present understanding of the role of electromeric and steric effects in unimolecular elimination reactions.

The yield of olefin in this series in 80% ethanol at 25° rises initially, but is sensibly constant for the last two members.[4]

Me_3CCl	Me_2EtCCl	$MeEt_2CCl$	Et_3CCl
16%	34%	41%	40%

Considerable data are now available to support the conclusion that the rate of substitution, k_S, must decrease with the increasing bulk of the alkyl substituents on a carbonium ion.[7,8,13] Therefore it would be expected that the value of k_S would decrease with the increasing number of ethyl groups. Since the yield of olefin is given by k_E/k_S, it follows that the yield of olefin should increase unless k_E likewise decreases.

$$\frac{k_E^{t\text{-Bu}}}{k_S^{t\text{-Bu}}} = \frac{16}{84} \quad \frac{k_E^{t\text{-Am}}}{k_S^{t\text{-Am}}} = \frac{34}{66} \quad \frac{k_E^{t\text{-Hex}}}{k_S^{t\text{-Hex}}} = \frac{41}{59} \quad \frac{k_E^{t\text{-Hep}}}{k_S^{t\text{-Hep}}} = \frac{40}{60}$$

The yields of olefin in the case of the last three members exhibit only small variations. On the reasonable basis that k_S must decrease somewhat with the increasing steric hindrance to the substitution reaction, it follows that k_E must decrease with the increasing number of alkyl groups. If it is assumed that ethyl groups may not be as effective as methyl groups in stabilizing a double bond through hyperconjugation, then a slight decrease in k_E can be accounted for. However, purely on a statistical basis, an increase in k_E of roughly from 1 to 2 to 3 would have been anticipated for 1, 2 and 3 ethyl groups. Such a statistical factor would be expected to be considerably larger than any factor dependent upon the minor differences in the hyperconjugative ability of methyl and ethyl groups.

The argument suggests, but does not prove, that there may also be steric hindrance to the elimination of the proton. Such a factor would presumably be less important than steric hindrance to substitution, but could be sufficiently large to provide a reasonable explanation for the apparent decrease in k_E in this series.

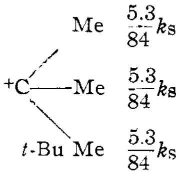
With very large bulky groups present, steric strain should become an important factor and contribute to the ease of expulsion of a proton. However, it has been pointed out that the planar configuration of carbonium ions apparently permits the accommodation of relatively large bulky groups without the generation of large strains.[7,8] The presence of three ethyl groups in triethylcarbonium ion should therefore offer steric hindrance to substitution and, probably, to elimination, but should not result in sufficient strain to provide steric assistance for the expulsion of the proton.

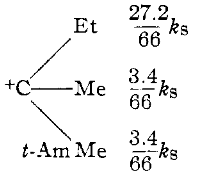
Hughes, Ingold and Shiner consider that the behavior of this series is entirely explicable in terms of the electromeric effect without the need to consider the possible contributions of steric effects on the substitution and elimination reactions. They claim that when R^1 is changed from Me to Et in the series $R^1R^2R^3CCl$, the establishment of the double bond in R' is accelerated by a factor of 6 and its entrance into R^2 and R^3 is retarded by a factor of 2/3. Using these factors they are able to reproduce closely the yield and distribution of olefin in this series.

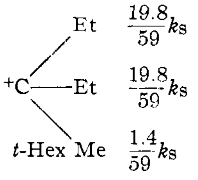
C		C		C		C	
Me	5	Et	28	Et	19	Et	13
Me	5	Me	3	Et	19	Et	13
Me	5	Me	3	Me	2	Me	13
Total	15		34		40		39

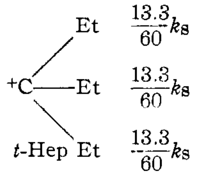
This procedure works well for this series of compounds, but is not satisfactory for the two other series studied, $RCH_2CBr(CH_3)_2$ and $RCH_2CH(OBs)CH_3$, and is particularly bad for the two compounds previously discussed, $(CH_3)_3CCBr(CH_3)_2$ and $(CH_3)_3CCH_2CBr(CH_3)_2$.

It is puzzling why any such factors should be expected to apply in view of the fact that the olefin yields depend upon both k_E and k_S and we are unable at present to determine the value of each independently of the other. Since we can determine only the value of k_E/k_S, this factor should be applied in estimating the relative rate of double-bond development in each branch of the olefin. On this basis, instead of the values estimated by Hughes, Ingold and Shiner, the following results are obtained.



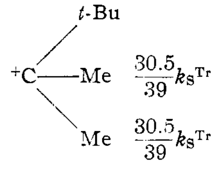






Now the relative rate of development of a double bond in the ethyl groups of t-amyl as compared to a methyl group in t-butyl is given by the ratio: $0.41k_S^{t\text{-Am}}/0.063k_S^{t\text{-Bu}}$ or $6.53k_S^{t\text{-Am}}/k_S^{t\text{-Bu}}$. Similarly the relative rate of development of a double bond in one of the methyl groups of t-amyl as compared to a methyl group in t-butyl is given by $0.816k_S^{t\text{-Am}}/k_S^{t\text{-Bu}}$. In discussing the relative rates of development of double bonds in the different alkyl groups of a single carbonium ion, the factors $k_S^{t\text{-Bu}}$ and $k_S^{t\text{-Am}}$ drop out and can be ignored. However, these factors cannot be ignored in comparing the relative rate of double bond formation in different carbonium ions. The treatment of the results proposed by Hughes, Ingold and Shiner fails to consider the contributions of these factors to the experimental results.

If the same treatment is applied to dimethyl-t-butylcarbinyl chloride, we come out with a very different factor.

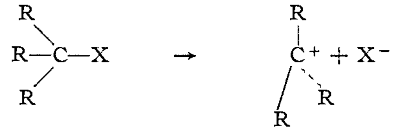


Comparing the rate of development of a double bond in one of the methyl groups in this compound with that in a methyl group in t-butyl, we come out with the ratio $12.4k_S^{Tr}/k_S^{t\text{-Bu}}$. On the basis of the assumption, discussed previously, that all values of k_S are identical, we should reach the conclusion that the rate of elimination of a proton from t-butyldimethylcarbonium ion is some 12 times that of the t-butyl and 15 times that of the t-amylcarbonium ion. It appears much more reasonable that the rate of substitution of dimethyl-t-butylcarbonium ion is smaller than that of the simpler carbonium ions and that these differences in the magnitudes of the respective values for k_S play an important part in the enhanced olefin formation.

We therefore are forced to the conclusion that the factors used by Hughes, Ingold and Shiner must be considered as empirical values which reproduce the olefin yield and isomer distribution reasonably well for the series of four compounds under consideration. The factors are not satisfactory for the other compounds for which elimination data are available and cannot be considered to correspond to the actual relative rates of double bond formation in the different branches. It would therefore appear dangerous to attribute the success of these factors in this limited series to a dominant control of the extent of olefin formation by the electromeric factor.

In conclusion, it appears that the steric factor must play an important role in the extent of olefin formation in dimethyl-t-butylcarbinyl chloride and in the extent and direction of olefin formation in the dimethylneopentylcarbinyl halides. Moreover, the results on the extent and direction of olefin formation in the two series $RCH_2CBr(CH_3)_2$ and $RCH_2CH(OBs)CH_3$, are simply explicable in terms of the steric effects of the group R and cannot be explained in terms of electromeric effects alone. The series $Me_{3-x}Et_xCCl$ is less simple, but arguments have been advanced to support the conclusion that here also both steric and electromeric effects must play a part in the elimination reaction. In view of the mass of evidence now available, it appears safe to conclude that the extent and direction of unimolecular elimination will be controlled by *both* electromeric and steric effects and both of these factors must be considered in any comprehensive treatment of the elimination reactions of highly branched carbonium ions.

Steric Strain in Carbonium Ion Reactions.—Some time ago it was proposed that steric strain is an important factor in the reactions of highly branched carbon compounds.[3] It was suggested that steric strain in highly branched tertiary alcohols and halides is largely relieved in the planar carbonium ion. Such relief of strain should facilitate the formation of the carbonium ion (steric assistance).



With rate data now available for 2-chloro-2,3,3-trimethylpentane,[13] it is now possible to observe the effect of an increase in the bulkiness of the group R in the series RMe$_2$CCl with R varying systematically from methyl to t-amyl (Table I).

TABLE I

RATE DATA FOR THE TERTIARY CHLORIDES, RMe$_2$CCl, IN 80% ETHANOL

Compound	Rate constant, k_1 hr.$^{-1}$	Relative rate
MeCMe$_2$Cl	0.033	1.00
EtCMe$_2$Cl	.055	1.67
i-PrCMe$_2$Cl	.029	0.88
t-BuCMe$_2$Cl	.040	1.21
t-AmCMe$_2$Cl	.187	5.67

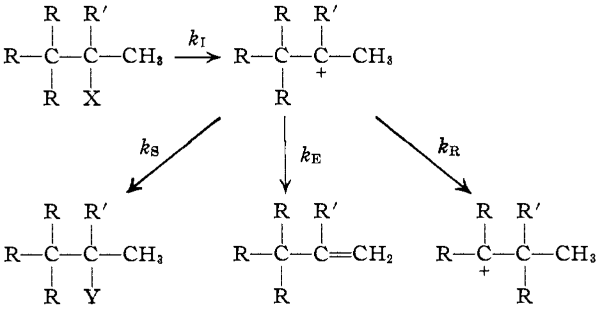
The increase observed in t-BuCMe$_2$Cl over i-PrCMe$_2$CCl is small, but runs counter to the trend expected from hyperconjugative stabilization of the carbonium ion, from the effect of decreased solvation of the sterically hindered ion, and from steric interference with electrophilic attack of the solvent on the chlorine atom in the ionization process.[12] It therefore was believed justifiable to ascribe the increase to steric assistance in the ionization step afforded by the relief of strain.

Steric effects are characterized by a rapid increase in magnitude with increasing bulk. It therefore was expected that the effect would be magnified with tertiary halides containing bulkier substituents. Such increases were observed.[12] However, the tendency for many of these compounds to undergo rearrangement has led to proposals that the ionization was being facilitated by synchronous rearrangement in the ionization stage.[2,18,19] In the present case it has been demonstrated that the compound t-AmCMe$_2$Cl does not undergo rearrangement in the solvolysis.[9] One cannot call upon synchronous rearrangement to account for the increased rate of ionization exhibited by this tertiary halide.

Similarly, the ratio of solvolysis rates for the two compounds t-BuCMeEtCl and MeCMeEtCl is 4.0. Here also it has been demonstrated that solvolysis occurs without rearrangement.[9]

These results support the steric assistance interpretation (B-strain) which was originally proposed.[3,12]

It appears desirable at this time to summarize our views on the effect of steric strain on reactions other than ionization. A carbonium ion once formed (k_I) can undergo substitution (k_S), elimination (k_E) or rearrangement (k_R).



The presence of substituents with considerable bulk, which assists the ionization stage (k_I large), will result in a carbonium ion which will itself have relatively large steric requirements. Addition of a solvent molecule or some other molecular or ionic species to the carbonium ion to regenerate the original strained structure will be hindered (k_S small). Accordingly there should be increased opportunity for the carbonium ion to follow some other reaction path, elimination and rearrangement.

Steric strain should be much smaller in the carbonium ion than in the original tetrahedral structure. Therefore, groups of sufficient bulk to increase the rate of ionization and decrease the rate of substitution may be expected not to affect greatly the rate of elimination. The increase in olefin yield observed in such molecules[4,7,8] appears to be due primarily to the effect of the substituents in decreasing the substitution rate.[7,8]

With much larger substituents, steric strain should be considerable even in the carbonium ion. Such structures may be expected to exhibit an enhanced tendency to expel a proton (k_E large).

It follows that bulky substituents should increase the quantity of olefin formed in solvolysis both by their effect in decreasing k_S and increasing k_E. With substituents of moderate bulk (as in Et$_3$C$^+$), the effect on k_S should be more important. With more bulky substituents (as in t-Bu$_2$MeC$^+$), both k_S and k_E should change in a manner to result in increased yield of olefin.

Unfortunately, it has not been possible to determine the value of k_E independently of k_S. However, it has been established that highly branched tertiary halides give markedly increased olefin formation,[4,7] an increase which corresponds to an increased ratio of k_E/k_S. As would be expected, the effect of the increasing bulk of substituents on the yield of olefin is much less in the secondary series[8] than in the tertiary. Therefore the change in the k_E/k_S ratio is in the direction and magnitude predicted, even though we are unable to state the

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[18] V. J. Shiner, Jr., THIS JOURNAL, **76**, 1603 (1954).

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

individual contributions of k_E and k_S to the altered ratios.

With increasing bulk of the alkyl substituents there occur shifts in the ratio of the 2- to 1-olefin as well as shifts of the ratio of the *cis*- to *trans*-2-olefins.[7,8]

Finally, with decreasing rate of substitution, a highly hindered carbonium ion will have an increased opportunity to undergo rearrangement as well as elimination. That is, k_R/k_S should exhibit increasing values with increasing steric requirements of the substituents.

The increasing value of k_R/k_S could result either from a decrease in k_S or from an increase in k_R (or both). The difference in the behavior of the two ions, $Me_3CCEt_2^+$ and $Me_3CCEtMe^+$, has been attributed primarily to a large change in k_S for the two structures. A considerable difference in the magnitude of k_R for the two ions would not be expected. However, replacement of the three methyl groups on the quaternary carbon atoms by other groups of large steric requirements would be expected to cause increased strain at the branched center and result in an increased value of k_R (steric assistance). Unfortunately, at the present time we are unable to determine the value of k_R alone and must be content with the ratio of k_R/k_S. Nevertheless, it is apparent from the available results that the value of k_R/k_S does indeed increase with increasing branching.

In conclusion the theory of B-strain appears capable of accounting for the data now available on the behavior of highly branched carbonium ions in ionization, substitution, elimination and rearrangement reactions.

LAFAYETTE, INDIANA

[CONTRIBUTION OF THE SCHOOL OF SCIENCE, BRANDEIS UNIVERSITY]

Phenyl-azo-diphenylmethane and the Decomposition of Azo Compounds[1]

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Phenyl-azo-diphenylmethane, $C_6H_5—N{=}N—CH(C_6H_5)_2$ (I), was prepared by reduction of benzophenone phenylhydrazone, followed by oxidation of the hydrazo compound. It decomposed at 124.5 and at 144.5° in decalin with first-order kinetics, $k = 1.66 \times 10^{14}\ e - 34{,}000/RT$. Comparison with $C_6H_5—N{=}N—C(C_6H_5)_3$, and with $(C_6H_5)_2CH—N{=}N—CH(C_6H_5)_2$, indicates that substitution of each α-phenyl for α-hydrogen lowers E_A 6–7 kcal., probably largely by affecting the resonance stabilization of the radicals, and that symmetrical azo compounds may decompose by simultaneous rupture of both carbon–nitrogen bonds. The decomposition of I in decalin led to benzene (*ca.* 70% yield) and to 1,1,2,2-tetraphenylethane (*ca.* 30% yield). The decomposition of I in diphenylmethane led to benzene (*ca.* 20% yield), and to 1,1,2,2-tetraphenylethane (*ca.* 104% yield, based on azo compound).

As part of our study of the effects of structure on the decomposition of azo compounds and on the reactions of the free radicals which are formed, we have prepared and examined the kinetics and products of decomposition of phenyl-azodiphenylmethane, $(C_6H_5)_2CH—N{=}N—C_6H_5$ (I). This compound was of interest for comparison with the previously studied phenyl-azo-triphenylmethane,[2] $(C_6H_5)_3\,C—N{=}N—C_6H_5$ (II) and azo-bis-diphenylmethane,[3] $(C_6H_5)_2\,CH—N{=}N—CH(C_6H_5)_2$ (III).

The compound I was prepared from the isomeric benzophenone phenylhydrazone

$$(C_6H_5)_2C{=}N—NHC_6H_5 \xrightarrow{\text{LiAlH}_4,\ 70°}$$

$$(C_6H_5)_2CHNHNHC_6H_5 \xrightarrow{H_2O_2} (C_6H_5)_2CH—N{=}N—C_6H_5$$

Attempts to effect the reduction by low pressure catalytic hydrogenation or by treatment with lithium aluminum hydride in ether failed, while the latter reagent at 70° led to the hydrazine in 35% yield, accompanied by a small quantity of 1,1,2,2-tetraphenylethane. Lithium aluminum hydride in our experiments has failed to convert benzalazine and benzophenone azine[3] to the corresponding disubstituted hydrazines, and converted the latter, in part, to 1,1,2,2-tetraphenylethane, but did convert the hydrazone[3] and phenylhydrazone of benzophenone to the respective hydrazines. The oxidation of N-benzhydryl-N′-phenylhydrazine to I by hydrogen peroxide proceeded slowly. Compound I had been isolated in low yield from the autoxidation of benzalphenylhydrazone.[4]

The absorption spectra of phenyl-azo-diphenylmethane, and the isomeric benzophenone phenylhydrazone were determined in ethanol. The azo compound shows a small absorption maximum, log ϵ 3.67, at 345 mμ, which is characteristic of aliphatic azo compounds,[5] conjugation with the phenyl group leading to fairly strong end absorption and yellow color log ϵ 2.10 at 450 mμ. However, the phenylhydrazone, unlike aliphatic hydrazone isomers of azo compound,[5] also showed a strong maximum at 345 mμ, log ϵ 4.26, but not accompanied by end absorption and color. The melting points and thermal stabilities of the phenyl-azo compound and the phenylhydrazone were markedly different, the azo compound showing a half-life in solution, as measured by nitrogen evolution of 7 hours at 124.5°, while the hydrazone showed no change in melting point and to this extent no evidence of decomposition when heated in the solid state under these conditions.

The rates of decomposition of phenyl-azo-diphenylmethane in approximately 0.01 molar solution in decalin were determined at 124.5 and at 144.5° by measurement of evolution of nitrogen as a function

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[1] Presented at the meeting of the American Chemical Society, New York, September 13, 1954.

[2] S. G. Cohen and C. H. Wang, THIS JOURNAL, **75**, 5504 (1953).

[3] S. G. Cohen and C. H. Wang, *ibid.*, **77**, 2457 (1955).

[4] M. Busch and H. Kunder, *Ber.*, **49**, 2345 (1916).

[5] G. Fodor and P. Szarvas, *ibid.*, **76B**, 334 (1943).