Olefin Behavior in 73% Sulfuric Acid

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Branched olefins have been found to undergo slow, stepwise proton exchange in 73% sulfuric acid. The relative reactivity of pairs of olefins forming the same cation shows the thermodynamically more stable isomer to be about as reactive or more reactive than the less stable isomer. Proton elimination from the ion leads to products approaching those obtained in solvolysis. The relative tendencies of the ions to form acid-soluble compounds diminishes as their size increases.

The general behavior of olefins in acid media is broadly understood in terms of the formation and fate of carbonium ion intermediates. In strong aqueous acids such as concentrated sulfuric acid, olefins generally react *via* a myriad of paths which convert them essentially quantitatively into nonolefinic products. The results of various exchange studies[1-10] strongly indicate that in this media olefins are in equilibria with carbonium ions and that proton exchange is very rapid. Studies of alkylation,[11,12] hydride transfer,[13-16] and the composition of acid sludge[17-19] have also shown that cations in this media will readily extract hydride ions from a variety of donors, add to olefins and undergo β-fission reactions of the type studied by Whitmore.[20,21]

In slightly weaker sulfuric acid of 80–90% strength, the reactivity of olefins is substantially modified. Aliphatic cations now show a reduced tendency to polymerize and hydride-transfer reactions are severely limited. Instead, hydration, limited isomerization, and the formation of bisulfates and some ethers occur. Tertiary cations tend to form alcohols and little, if any, stable bisulfate while secondary cations form alcohols and relatively stable bisulfates. At ambient conditions tertiary cations will add to branched and linear olefins but secondary cations are much less reactive or their sources are much less ionized and dissociated so that the coupling of linear olefins is essentially nonexistent in 80% H_2SO_4.

This report deals with a tracer study of the fate of these olefins in 73% H_2SO_4 containing tracer quantities of T_2O. Information relating to hydrogen exchange, to the nature and extent of isomerization, and to the relative extents of isomerization or proton exchange and the formation of acid-soluble products is reported. Attempts were also made to obtain kinetic comparisons of the relative reactivities of a homologous series of olefins. These comparisons are not so informative as had been hoped for, the systems were heterogeneous, and a major factor affecting the kinetics appears to be the solubility of the olefins. The relative rate data and the apparent temperature dependence of some representative systems clearly show that this factor dominates in any comparison of olefins of different size. An attempt to measure the olefin solubilities is now planned but information is not yet available.

Experimental Section

Reactions were run by vigorously contacting equal volumes of 73% sulfuric acid and a hexane solution of one or two olefins for about 1 min. The hexane phase was analyzed by gas chromatography after which the separated components were passed through an internal flow radiation detector. The acid had a specific activity of about 1 mCi/ml.

By a procedure to be described below it was found that 2,3- and 2,4-dimethylpentene incorporate tritium *via* a slow and stepwise process. Thus, when 2,3-dimethyl-1-pentene isomerized to 2,3-dimethyl-2-pentene, the specific activity of the latter provided a measure of the radioactivity to be found in an olefin which had fully equilibrated one proton with the acid. This value can be used as an internal standard to estimate how much starting olefin has been re-formed by proton loss from an ionic intermediate.

The olefins also formed acid-soluble products. The total amount of these materials were determined by the difference in olefin concentration of the hexane layer. No attempt was made to recover the acid-soluble products.

The relative reactivity of olefins were usually measured in competitive runs with 2,2,3-trimethylbutene as the reference compound. The total conversion of each component into acid-soluble products and to recoverable hydrocarbons was assumed to measure the reactivity of each component. In making this estimate we have generally assumed that an olefin protonated by tritium releases a proton, H^+, and not T^+ when being re-formed in the back reaction.

A quantitative estimate of the actual k_T/k_H ratio is difficult to make. The β C–H bonds to be cleaved in the ion should be weaker than normal sp^3 C–H bonds, and the isotope effect should be lower than expected for such bonds initially containing their full zero-point energies. Melander provides both a theoretical estimate of k_T/k_H as 0.02 to 0.05 for the breaking of normal C–H and C–T bonds and an experimental estimate of k_T/K_H as $1/7.4 = 0.135$ for electrophilic hydrogen exchange in benzene.[22a] These estimates, together with the findings of MacLean and Mackor of an activation energy of about 8 kcal/mol for intra- or intermolecular proton exchange of proton complexes of substituted benzenes in HF,[22b] suggest that there is considerable stability in the bond to be cleaved. If this behavior is approached with alkyl cations the assumption of no C–T cleavage in the back reac-

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(1) O. Beeck, J. W. Otvos, D. P. Stevenson, and C. D. Wagner, *J. Chem. Phys.*, **17**, 418 (1949).

(2) R. L. Burwell, Jr., and G. S. Gorden, III, *J. Amer. Chem. Soc.*, **70**, 3128 (1948).

(3) R. L. Burwell, Jr., L. G. Maury, and R. B. Scott, *ibid.*, **76**, 5828 (1954).

(4) R. L. Burwell, Jr., R. B. Scott, L. G. Maury, and A. S. Hussey, *ibid.*, **76**, 5822 (1954).

(5) G. S. Gorden, III, and R. L. Burwell, *ibid.*, **71**, 2355 (1949).

(6) I. V. Gostunskaya and B. A. Kazanskii, *J. Gen. Chem. USSR*, **25**, 1995 (1955).

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

(8) J. W. Otvos, D. P. Stevenson, D. C. Wagner, and O. Beeck, *J. Amer. Chem. Soc.*, **73**, 5741 (1951).

(9) V. N. Setkina, D. N. Kursanov, O. D. Sterligev, and A. L. Liberman, *Dokl. Akad. Nauk SSSR*, **85**, 1045 (1952).

(10) D. P. Stevenson, C. D. Wagner, O. Beeck, and J. W. Otvos., *J. Amer. Chem. Soc.*, **74**, 3269 (1952).

(11) R. M. Kennedy, *Catalysis*, **6**, 1 (1958).

(12) J. E. Hofmann and A. Schriesheim, *J. Amer. Chem. Soc.*, 957 (1962).

(13) G. M. Kramer, *J. Org. Chem.*, **30**, 2671 (1965).

(14) G. M. Kramer, *ibid.*, **32**, 920 (1967).

(15) G. M. Kramer, *ibid.*, **32**, 1916 (1967).

(16) J. E. Hofmann, *ibid.*, **29**, 3039 (1964).

(17) N. C. Deno, D. B. Boyd, J. D. Hodge, C. U. Pittman, and J. A. Turner, *J. Amer. Chem. Soc.*, **86**, 1745 (1964).

(18) N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 140 (1964).

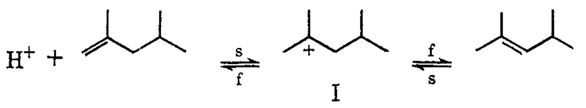
(19) V. N. Ipatieff and H. Pines, *J. Org. Chem.*, **1**, 464 (1936).

(20) F. C. Whitmore and E. E. Stahly, *J. Amer. Chem. Soc.*, **67**, 2158 (1945); F. C. Whitmore and E. E. Stahly, *ibid.*, **55**, 4135 (1933).

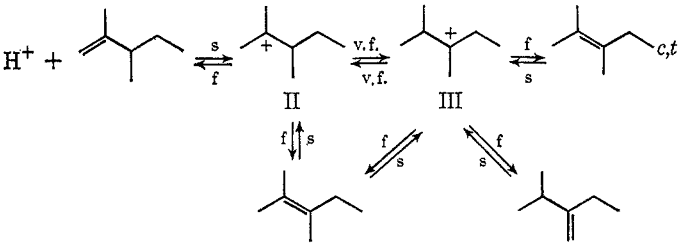
(21) F. C. Whitmore and W. A. Mosher, *ibid.*, **68**, 281 (1946).

(22) (a) L. Melander, "Isotope Effects on Reaction Rates," Ronald Press Co., New York, N. Y., 1960, pp 22, 119; (b) C. MacLean and E. L. Mackor, *Discussions Faraday Soc.*, **34**, 165 (1962).

Scheme I



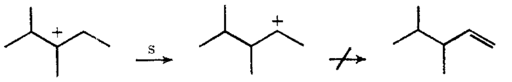
Scheme II



tions is reasonable and will introduce only a small error into the results.

Results and Discussion

Preliminary studies showed that 2,4-dimethyl-1-pentene readily equilibrates with 2,4-dimethyl-2-pentene and 2,3-dimethyl-1-pentene isomerizes to 2,3-dimethyl-2-pentene, 2-ethyl-3-methyl-1-butene, and *cis*- and *trans*-3,4-dimethyl-2-pentene in 73% sulfuric acid. Using tritiated acid the four isomers in the 2,3 system were found to form in a constant ratio to each other without yielding 3,4-dimethyl-1-pentene. The equilibrations could occur *via* carbonium ion paths illustrated in Scheme I and II. Failure to observe 3,4-dimethyl-1-pentene suggests that a hydride shift to yield a secondary ion, eq 1, is slow and implies



(1)

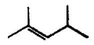
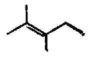
that the double bond in the 2,4-dimethylpentene system is also localized to the side of the molecule in which it was originally contained. It may also be noted that in the time span employed methyl migrations were negligible.

Intramolecular 1,2-hydride shifts which interconvert tertiary ions appear to be very fast because of the production at a constant ratio at low conversion levels of the four 2,3-dimethylpentenes in Scheme I. The relative amounts could only be constant if ions II and III are in rapid equilibrium. These may be equilibrated either by a very fast hydride shift or very fast proton exchange with the acid, and the latter is ruled out by the following considerations.

The tracer experiments show that tritium is incorporated into the olefins during the isomerization. The question of the extent of the exchange, *i.e.*, how many hydrogens have equilibrated with the tritiated acid and how much radioactivity is to be found per exchanged proton, may be resolved by simultaneously isomerizing 2,3-dimethyl-1-pentene and 2,4-dimethyl-1-pentene in tritiated acid and determining the specific activity (in counts per mole) of the product olefins.

Table I

Relative Specific Activities of Products of Isomerization of 2,4-Dimethyl-1-pentene and 2,3-Dimethyl-1-pentene

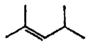
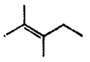
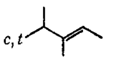
Product	A	B	C
	0.23	0.23	0.25
	0.24	0.25	0.26

If the exchange is slow, the specific activity of 2,4-dimethyl-2-pentene and of the product 2,3-dimethylpentenes will be the same. If the exchange is rapid and secondary ion formation is excluded, ion I will equilibrate eight protons with the acid and 2,4-dimethyl-2-pentene will contain seven exchanged protons. Products from 2,3-dimethyl-1-pentene will be derived from the equilibrating ions II and III and therefore will contain eleven exchanged protons. The ratio of the specific activity of the latter products to those of the former will therefore be 11:7. Table I contains the results of appropriate experiments which show the specific activity of the product ions to be the same and hence suggest that the exchange is slow.

One might also consider the possibility of rapid exchange and secondary ion formation which would lead to total equilibration of all protons in the products and hence identical specific activities. This could be reconciled with the data if the absence of 3,4-dimethyl-1-pentene from our products was due to its having a small equilibrium value. If total exchange was occurring, however, the initial products would have a maximum specific activity because they have equilibrated with the most radioactive acid and the activity at higher conversion levels would decrease. Contrary to this the specific activity of the products increase with reaction time as is expected for a stepwise exchange process (Table II). The data therefore are only consistent with the occurrence of a slow, stepwise exchange process.

Table II

Effect of Time upon Relative Specific Activity of Isomer Products[a]

Product	0.5 min	5.5 min
	0.23	0.37
	0.25	0.34
	0.25	0.39

[a] Reactants: 2,4-dimethyl-1-pentene and 2,3-dimethyl-1-pentene.

Isomerization of the dimethylpentenes thus qualitatively follows Schemes I and II. The rate-determining step is pictured as protonation of the olefin, but our observations would also be compatible with the existence of a π-complexed intermediate composed of the olefin and a proton, which undergoes a slow isomerization to a carbonium ion. Such an intermediate has been proposed by Taft as participating in olefin hydration.[23] It is interesting to recall that the hydration of isobutylene in dilute acid proceeds without much back reaction,[24] so that at low conversions in weak D_2SO_4, detectable quantities of exchanged isobutylene are

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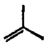
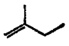
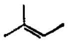
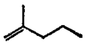
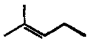
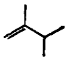
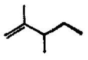
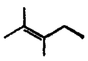
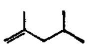
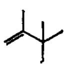
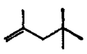
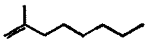
(23) R. W. Taft, *J. Amer. Chem. Soc.*, **74**, 5372 (1952).

(24) E. L. Purlee and R. W. Taft, *ibid.*, **78**, 5807 (1956).

not recovered. In the tracer experiments with 73% $HTSO_4$ it was also found that isobutylene hydration proceeds with very little back reaction, and over 90% reaction occurred before radioactive isobutylene could be easily detected. On the other hand, the dimethylpentenes re-form olefins without forming significant quantities of acid-soluble species which we shall assume to be alcohols in the following discussion. In general we find that the tendency to form olefins rather than alcohol increases with the size of the carbon skeleton.

The energy profile for reaction of the olefins thus appears to shift from that shown in Figure 1 to that in Figure 2 as the size of the olefin increases. The relative stabilities of the protonated alcohols are not known, and hence whether the lack of formation of the large alcohols is due to a kinetic or thermodynamic limitation. However, it seems likely that the stability of the large protonated alcohols and the transition state leading to them is decreased relative to that of *t*-butyl alcohol because of less solvation so that the profile of curve 2b applies. This would impose a kinetic limitation on the hydration rate and perhaps an equilibrium restriction as well. The kinetically controlled product distributions for olefins reacting *via* either scheme will naturally shift toward an equilibrium distribution at greater reaction times. Those olefins following Figure 1 will show increasing percentages of olefins while those following Figure 2 will acquire increasing quantities of alcohol. The distributions will thus be very sensitive to reaction conditions and indeed there is considerable fluctuation in the values reported in Table III.

TABLE III
PRODUCT DISTRIBUTIONS[a]

Reactant	Acid soluble, %	Olefins, %
	95 ± 5	5 ± 5
	81	19
	90	10
	61	39
	68	32
	10 ± 10	90 ± 10
	0	100
	0	100
	0	100
	53	47
	0	100
	0	100

[a] Comparisons are made after 30-sec reaction times.

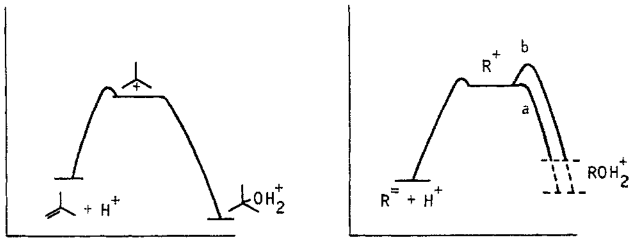
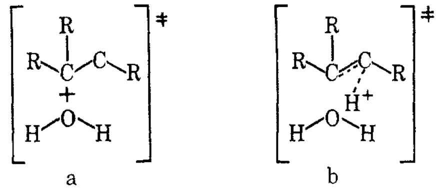


Figure 1.

Figure 2.

The energy profile for olefin hydration changes from that in Figure 1 to those in Figure 2 as olefin size increases.

The shift from alcoholic to olefinic products suggests that there is little difference in the ability of the intermediate carbonium ions to act as Lewis or Brønsted acids toward water. Thus, the transition states leading toward alcohol and olefin, as a and b, respectively, can be pictured as



transition states leading to alcohol a and olefin b

Activation energies for isobutylene hydration and dehydration in dilute acidic systems have been estimated by Franklin[25] and determined by Eberz and Lucas[26,27] and Dostrovsky and Klein.[28] Conversion of $t\text{-}C_4H_9OH_2^+$ into the *t*-butyl cation in dilute acid requires about 30 kcal/mol and an additional 2.2 are needed to reach the transition state leading to isobutylene. It is suggested that no activation energy is required to re-form the $t\text{-}C_4H_9OH_2^+$ ion. Thus, factors which might lead to a small change in the relative stability of transition states leading to olefin and alcohol might be expected to have a large effect on the product distribution.

If it is assumed that similar energetic factors apply to the dehydration of *t*-amyl alcohol and the formation of 2-methyl-1-butene, it can be rationalized that the increased proportion of olefin from the *t*-amyl ion is due to the possibility of forming a second olefin, 2-methyl-2-butene, which also happens to be thermodynamically more stable. As alkyl groups which would be expected to stabilize an olefinic product are substituted in the *t*-butyl cation, increasing proportions of olefins are found. The order of group efficiency is methyl < ethyl < isopropyl.

Two methyl groups are better than one, but three methyl groups restrict the product to a single external olefin and more alcohol is formed. The formation of these olefins follows a Saytzeff type of elimination in that the more highly substituted isomer is preferentially obtained.

Introduction of a *t*-butyl group also leads to the production of olefinic products with experimentally insignificant amounts of alcohol. However, it is difficult to attribute this to *t*-butyl's ability to stabilize 2,4,4-trimethyl-2-pentene since its isomer 2,4,4-trimethyl-1-pentene is preferentially formed. The trimethylpentene distribution is close to that obtained by Brown

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(25) J. Franklin, *Trans. Faraday Soc.*, **48**, 443 (1952).
(26) H. J. Lucas and W. F. Eberz, *J. Amer. Chem. Soc.*, **56**, 460 (1934).
(27) W. F. Eberz and H. J. Lucas, *ibid.*, **56**, 1234 (1934).
(28) I. Dostrovsky and F. S. Klein, *J. Chem. Soc.*, 791 (1955).

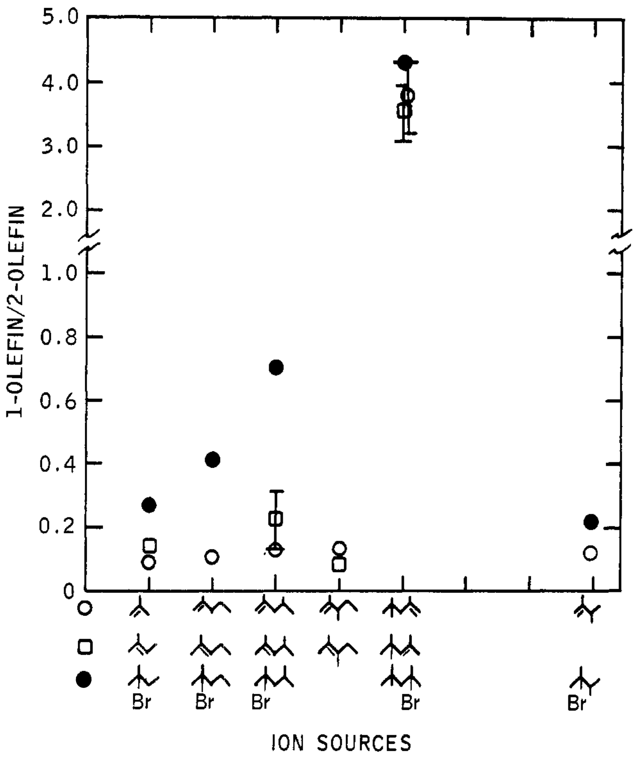


Figure 3.—Product olefin ratios during solvolysis[37] and exchange.

and Hughes and Ingold during their classic studies of unimolecular elimination reactions.[29–37] Brown has repeatedly made the point that increasing the bulk about a carbonium ion center ought to retard substitution reactions which would yield a strained product, in this case 2,4,4-trimethyl-2-pentanol, and tend to augment proton expulsion.[31] This is a reasonable explanation for the over-all distribution of solvolysis products and for the internal distribution of trimethylpentene-1 and -2.

In 73% sulfuric acid the ratio of 1 olefin to 2 olefin approximates Brown's findings in the solvolyses of alkyl bromides in 85% *n*-Butyl Cellosolve[37] (Figure 3). However, the importance of steric interactions in controlling the ratio of elimination products appears to be minimal until a *t*-butyl group is positioned *β* to the charged carbon. Within the limits of experimental error the 1 olefin/2 olefin ratio is 0.11 ± 0.03 with methyl, ethyl, isopropyl, 2-methyl, and methyl + ethyl substitution in isobutylene. The *t*-butyl group shifts the ratio to 3.7 ± 0.7.

One interpretation of this is that an alkyl substituent stabilizes the transition state leading to olefin by a few kilocalories more than a hydrogen atom, but that the electron-donating ability of the methyl, ethyl, and isopropyl groups are very similar. This leads to a difference in the loss ratio of primary and secondary hydrogens of 0.11:6 to 1:2 or 0.037. With two alkyl substituents in the 2,3-dimethylbutyl cation the primary to tertiary elimination ratio is 0.11:6 to 1 or 0.018. The tertiary/secondary/primary reactivities are then 56:27:1. The reactivity of the tertiary proton in the latter ion is significantly less than would be expected by extrapolation of the effect of a single alkyl substituent. This may be due to steric interference with approach of the base in the transition state.

A similar explanation may also hold for the 2,3-dimethyl-2-pentyl cation where $k_{\text{primary}}/k_{\text{tertiary}}$ is 0.018, but the situation is more complicated because of the simultaneous formation of other olefinic products.

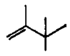
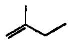
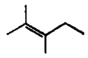
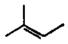
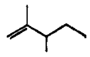
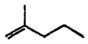
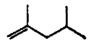
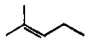
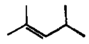
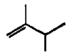
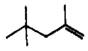
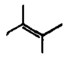
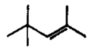
The change in the olefin ratios shows a fairly abrupt switch from a Saytzeff to a Hofmann type of elimination with the introduction of the *t*-butyl group. The change in 73% sulfuric acid is sharper than originally found by Brown but the data still appear to be consistent with the suggestion that both steric and electromeric[34] effects govern the course of the elimination. It seems likely that the solvent also plays a partial role in the reaction. Thus the apparent gradual onset of steric requirements found in the solvolyses of alkyl bromides in 85% *n*-Butyl Cellosolve may at least partially reflect a stronger association of the developing carbonium ion and the solvent than is realized in sulfuric acid.

Reactivity as a Function of Size and of Isomers.—The apparent relative over-all rates of reaction of a series of olefins are reported in Table IV. The data do not represent valid comparisons of the true relative reactivities of the various compounds because heterogeneous reaction conditions were employed, and the authors do not know the distribution coefficient for olefin solubility in the acid and hydrocarbon phases. Nevertheless one may obtain useful information by comparing the behavior of olefins of a similar size since they should have about the same distribution coefficient.

The reactivity of six pairs of olefins which form the same carbonium ion upon protonation are tabulated in

Table IV

Apparent Relative Reactivities of Olefins in 73% HTSO$_4$

Olefin	$\Delta F°_{298}$[a]	$k_{\text{olefin}}/k_{2,3,3\text{-TMB}}$[b]	Olefin	$k_{\text{olefin}}/k_{2,3,3\text{-TMB}}$[b]
	13.88	5.28		1
	15.51	2.08		0.80[c]
	14.26	4.14		0.76
	17.47	1.16		0.62
	16.34	1.01		0.59
	17.43	0.93		0.42
	16.52	1.65[c]		0.18

[a] F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimental, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953, pp 475, 476. [b] Assuming that C–T bond breaking is negligible; 2,3,3-TMB, 2,3,3-trimethylbutene. [c] On a per site basis.

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(29) H. C. Brown and I. Moritani, *J. Amer. Chem. Soc.*, **77**, 3607 (1955).

(30) H. C. Brown and H. L. Berneis, *ibid.*, **75**, 10 (1953).

(31) H. C. Brown and I. Moritani, *ibid.*, **77**, 3623 (1955).

(32) H. C. Brown and Y. Okamoto, *ibid.*, **77**, 3619 (1955).

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

(34) M. L. Dhar, E. D. Hughes, C. K. Ingold, A. M. M. Mandour, G. A. Maw, and L. I. Woolf, *J. Chem. Soc.*, 2093 (1948).

(35) E. D. Hughes, C. K. Ingold, and V. J. Shiner, Jr., *ibid.*, 3827 (1953).

(36) M. L. Dhar, E. D. Hughes, and C. K. Ingold, *ibid.*, 2065 (1948).

(37) H. C. Brown and M. Nakagawa, *J. Amer. Chem. Soc.*, **77**, 3610 (1955).

Table IV along with values of the free energy of formation for some of the olefins. It is generally found that the thermodynamically more stable isomer reacts at about the same rate or more rapidly than its partner. The rate and stability differences are such that the more stable isomer is reacting with a lower activation energy in all cases. This implies that the free-energy relationships which exist for the isomerization of the olefins under kinetically controlled conditions have the shape of Figure 4. The transition states thus appear to reflect the ground-state stability of the olefin. This model implies that in the transition state for the proton elimination process extensive C–H bond breaking and formation of the double bond has taken place. These considerations appear to hold whether Saytzeff or Hofmann elimination is occurring. Unfortunately, the authors do not know of accurate thermodynamic data for the trimethylpentenes but the ratio of the 1 to 2 olefin found in the solvolysis and exchange studies, if it is assumed to approximate equilibrium, bears this out.

The relative reactivity of the five heptenes generally reflects the ability of alkyl groups to increase the nucleophilicity of a double bond. Thus, in the series 2,4-dimethyl-1-pentene, 2,3-dimethyl-1-pentene, and 2,3,-3-trimethylbutene, there is a progressive replacement of allylic hydrogens in isobutylene by one, two, and three alkyl groups which results in a continual increase in reactivity.

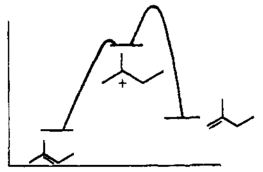
Figure 4.—Free-energy relationships during olefin isomerization.

In summary olefins have been found to undergo a slow stepwise exchange process in 73% sulfuric acid. The intermediate carbonium ions show a progressively decreasing tendency to form acid-soluble compounds as their size is increased. Proton elimination from the ion yields Saytzeff and Hofmann products approaching those distributions found in classical solvolysis studies, but with a somewhat sharper distinction of the onset of steric factors. The relative reactivity of pairs of isomers generally shows the more stable isomer to be about as reactive as or more reactive than its partner and implies that the transition state leading to the ions has much olefinic character.

Registry No.—Sulfuric acid, 7664-93-9; $HTSO_4$, 16878-40-3.

The Chemistry of Nitrogen Radicals. VIII. The Free-Radical Addition of Monoalkyl-N-chloramines to Substituted Olefins

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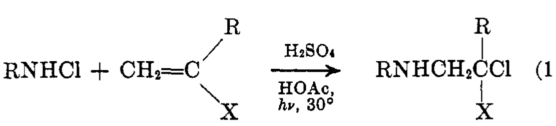
The addition of monoalkyl-N-chloramines RNHCl in a sulfuric acid–acetic acid medium to olefins substituted in the vinylic or allylic position is described. Yields of the resulting substituted β-chloramines were 40–70%.

We have recently described the free-radical addition of N-chlorodialkylamines in strongly acidic media to olefinic hydrocarbons[1] and to a variety of vinyl and allyl compounds.[2] In Table I are summarized the results obtained when N-chloro*mono*alkylamines R–NHCl were used in this type of reaction (eq 1). Most


$$RNHCl + CH_2{=}C\begin{array}{l}\diagup R\\ \diagdown X\end{array} \xrightarrow[\text{HOAc},\ h\nu,\ 30^\circ]{H_2SO_4} RNHCH_2\overset{\overset{R}{|}}{\underset{\underset{X}{|}}{C}}Cl \qquad (1)$$

X = Cl, F, CH_2Cl, CH_2CN: 50–70%
X = Br, $CH{=}CH_2$, $Si(CH_3)_3$, OR: no adduct

of the olefins substituted with a vinylic or allylic halogen atom gave the expected products, although in yields averaging about 20% lower[3] than were realized in the case of the dialkylchloramines. Since the adducts are secondary amines, the potential now exists to carry out further reactions at the nitrogen, such as acylation and alkylation. These results further extend the generality of the chloramine–olefin addition reaction as a synthetically important route to derivatives of β-chloramines.

In sharp contrast to the results in Table I, several olefins which gave good to excellent yields of adducts with dialkylchloramines now gave no adducts with monoalkylchloramines. Thus, chloramine decomposition within 30–50 min was observed in reactions of butadiene, trimethylvinylsilane, vinyl bromide, allyl ethyl ether, or allyl 2,4-dichlorophenyl ether, but no isolable adducts were formed. Allyl ethyl ether and *t*-butylchloramine were also irradiated in 70% (vol.) H_2SO_4 in water, since this solvent had previously[2] been suitable for preparing the adduct of N-chloropiperidine and allyl ethyl ether in 64% yield; again, however, no adduct of the monoalkylchloramine was isolated. Only a small amount (~15%) of a crude product, probably the adduct, was obtained from allylbenzene, but the adduct could not be purified. Finally, none of the anticipated 2:1 adduct was obtained when **10**, the 1:1 adduct of isopropylchloramine and 2-chloropropene, was converted into its N-chloro derivative and treated under standard conditions with 2-chloropropene; instead, 50% of the original compound **10** was recovered.

Evidence for the fate of allyl 2,4-dichlorophenyl ether was sought by working up this reaction mixture

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(1) R. S. Neale, *J. Org. Chem.*, **32**, 3263 (1967).

(2) R. S. Neale and N. L. Marcus, *ibid.*, **32**, 3273 (1967).

(3) Perhaps coincidentally, the yield was also significantly lower when N-bromovaleramide instead of the N-alkyl analog N-*t*-butyl-N-bromovaleramide was rearranged in a radical chain reaction to the 4-bromo isomer: R. S. Neale, N. L. Marcus, and R. G. Schepers, *J. Amer. Chem. Soc.*, **88**, 3051 (1966).