JOURNAL
OF
THE CHEMICAL SOCIETY

---

1. *Unstable Intermediates. Part XI.* Allylic Carbonium Ions.*

By J. Rosenbaum and M. C. R. Symons.

The ultraviolet absorption spectra of solutions thought to contain simple allylic carbonium ions, including $CH_2{:}CH{\cdot}CH_2^+$, are recorded. In most instances sulphuric acid was the solvent, and solutes included allyl alcohols and halides, diols, dienes, and epoxides. The nature of the electronic transitions is discussed and an attempt has been made to estimate pK values for allene and buta-1,3-diene.

Allylic carbonium ions are thought to be important intermediates in various acid-catalysed reactions involving allyl halides and 1,3-dienes. Whilst there is considerable kinetic evidence for their transient existence, direct methods of detection do not appear to have been used.

Since other work strongly suggests that dilute solutions of simple aliphatic carbonium ions in sulphuric acid are remarkably stable,[1,2] we have applied the same experimental techniques[3] in an attempt to prepare solutions of allylic carbonium ions in sulphuric acid.

The electronic structure of the ion $CH_2{:}CH{\cdot}CH_2^+$ has been extensively discussed since it is one of the simplest organic π-electron systems. In particular, Lefkovits, Fain, and Matsen[4] have included calculations on certain excited states for this ion, and from their results we estimate that there should be an intense band in the 250 mμ region.

Experimental and Results

Materials.—Sulphuric acid and oleums were purified as described earlier.[5] 2,4-Dimethylpenta-1,3-diene, prepared by the action of methylmagnesium iodide on mesityl oxide, had b. p. 90—93°, n^{20} 1·443. Allene, prepared by treating 2,3-dichloropropene with zinc dust and methanol, was collected in a solid carbon dioxide trap and found to be at least 90% pure by gas chromatography, the major impurity being propyne.

Other solvents and solutes were highest-grade commercial products, purified by standard methods.

The concentrations of buta-1,3-diene and allene were estimated from their ultraviolet absorption spectra in ethanol. This was accurate for butadiene, which has an intense band at 217 mμ ($\varepsilon_{\text{max.}}$ 21,000), but inaccurate for allene, for which we could detect only a rising absorption in the 220 mμ region, despite the report that there is a band of low intensity in this region for gaseous allene.[6]

Preparation of Solutions.—The reactants used, including allyl alcohol and halides, dienes,

---

* Part X, *Mol. Phys.*, 1960, **3**, 205.

[1] Rosenbaum and Symons, *Proc. Chem. Soc.*, 1959, 92.
[2] Rosenbaum and Symons, *Mol. Phys.*, 1960, **3**, 205.
[3] Grace and Symons, *J.*, 1959, 958.
[4] Lefkovits, Fain, and Matsen, *J. Chem. Phys.*, 1955, **23**, 1690.
[5] Symons, *J.*, 1957, 387.
[6] Lind and Livingston, *J. Amer. Chem. Soc.*, 1933, **55**, 1036.

and the corresponding diols, are given in Table 1. The procedure for preparing stable solutions of carbonium ions was as described previously,[2,3] concentrations being generally less than 10^{-3}M.

Spectra.—Spectrophotometric measurements were made with a Unicam S.P. 500 quartz spectrophotometer and S.P. 700 recording spectrophotometer, 1 cm. stoppered cells being used whenever possible. Typical spectra are given in the Figures, and relevant details listed in Table 1. Intense bands obtained from solutions of dienes in sulphuric acid were fully developed within the time required for measurement (about 1 min.), but increased in intensity at measurable rates when solutions of hydroxy-compounds and halides were studied. However, after a period of about 3 days all spectra of dilute solutions remained constant, and data in the Table refer to such solutions.

TABLE 1. *Details of the ultraviolet absorption spectra of compounds thought to give allylic carbonium ions in sulphuric acid* (98%).

Compound	Probable ion	$\lambda_{max.}$ (mμ)	$10^{-3}\varepsilon$	$\Delta_{\frac{1}{2}}$ (cm.$^{-1}$)	Rate
$CH_2{:}CH{\cdot}CH_2{\cdot}OH$	$CH_2{:}CH{\cdot}CH_2^+$	273 [a]	4·7	4400	Slow
		272			
$CH_2{:}CH{\cdot}CH_2Cl$	,,	273	4·5	4900	,,
$CH_2{:}CH{\cdot}CH_2Br$	,,	275	4·2	5500	,,
$CH_3{\cdot}C_2H_3O$ *	,,	272	3·7	4400	V. slow
$CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$	,,	273	3·8	4700	,,
$HO{\cdot}[CH_2]_3{\cdot}OH$	,,	271	3·7	5300	,,
$CH_2{:}C{:}CH_2$	,,	*ca.* 275	*ca.* 3·0	5600	Fast
$CH_2{:}CH{\cdot}CH{:}CH_2$	$CH_3{\cdot}\overset{+}{C}H{\cdot}CH{:}CH_2$	290	3·0	4500	Fast
$CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}OH$	,,	290	*ca.* 0·2	4300	V. slow
$CH_3{\cdot}CH(OH){\cdot}CH(OH){\cdot}CH_3$	,,	285	*ca.* 0·2	4700	,,
$HO{\cdot}[CH_2]_4{\cdot}OH$	,,	291	*ca.* 0·2	4500	,,
$CH_3{\cdot}CH{:}CH{\cdot}CH_2{\cdot}OH$	,,	290	2·5	5300	Slow
$CH_2{:}CMe{\cdot}CH_2{\cdot}OH$	$CH_2{:}CMe{\cdot}CH_2^+$	256	1·25	5300	Slow
$CH_3{\cdot}CH{:}CH{\cdot}CH{:}CH_2$	$CH_3{\cdot}CH{:}CH{\cdot}\overset{+}{C}H{\cdot}CH_3$	290	2·5	5000	Fast
$CH_3{\cdot}CH(OH){\cdot}CMe_2{\cdot}CHMe{\cdot}OH$	$CH_3{\cdot}CH{:}CMe{\cdot}\overset{+}{C}H{\cdot}CH_3$	305	2·5	4000	Slow
$CH_2{:}CMe{\cdot}CH{:}CH_2$	$CH_2{:}CH{\cdot}\overset{+}{C}Me_2$	300	2·3	6400	Fast
$CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CMe_2{\cdot}OH$	$CH_3{\cdot}CH{:}CH{\cdot}\overset{+}{C}Me_2$	302	3·6	4500	Slow
$CH_3{\cdot}CH{:}CH{\cdot}CMe{:}CH_2$	,,	305	3·5	7000	Fast
$CMe_2(OH){\cdot}CMe_2{\cdot}OH$	$\overset{+}{C}Me_2{\cdot}CMe{:}CH_2$	290	1·2	5500	V. slow
$CMe_2{:}CH{\cdot}CMe{:}CH_2$	$CMe_2{:}CH{\cdot}\overset{+}{C}Me_2$	303	4·0	4600	Fast

* *I.e.*, epoxypropane.

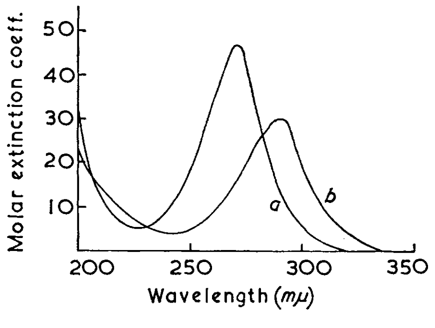


FIG. 1. *Ultraviolet absorption spectra of* (a) *allyl alcohol and* (b) *buta*-1,3-*diene in sulphuric acid.*

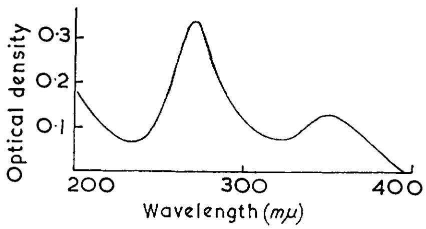


FIG. 2. *Ultraviolet absorption spectrum of a concentrated solution of allyl alcohol in sulphuric acid.*

Spectra from dilute solutions of allyl alcohol, chloride and bromide, 1,2-epoxypropane, and propane-1,2- and -1,3-diol had identical values of $\lambda_{max.}$ within experimental error, and the overall shape of the spectra were very similar to that shown in Fig. 1 for allyl alcohol. Molar extinction coefficients were all within the limits $4{\cdot}2 \pm 0{\cdot}5 \times 10^3$. The results for allene were more scattered and it was not possible to obtain a precise value for the extinction coefficient. However, in general, the results agreed fairly closely with those for the other compounds.

Spectra of solutions more concentrated than about 10^{-3}M changed markedly with time, and a new band in the 350 mμ region generally appeared. Such a spectrum is shown in Fig. 2. No explanation for this phenomenon is offered at this stage, but whenever such a band appeared, the solutions were rejected.

Other Solvents.—Addition of dilute oleums to solutions of allyl alcohol in sulphuric acid had no effect on their spectra. The bands were also well developed when 72% perchloric acid was used as solvent, but the apparent extinction coefficients were smaller than usual.

Possibility of Oxidation.—If the carbonium ion postulate is wrong, then the spectra recorded are most probably due to oxidation products. These could have been formed by oxidation by solvent, to give sulphur dioxide, by reaction with dissolved oxygen, or by disproportionation.

Sulphur dioxide can be ruled out as a major constituent of these solutions since it has an intense band in the 200 mμ region whose long-wavelength edge should have been observed.[2] In fact, most of the spectra recorded are relatively transparent in the 200—200 mμ region and we deduce that, if sulphur dioxide is present at all, its concentration is less than 0·1 equiv.

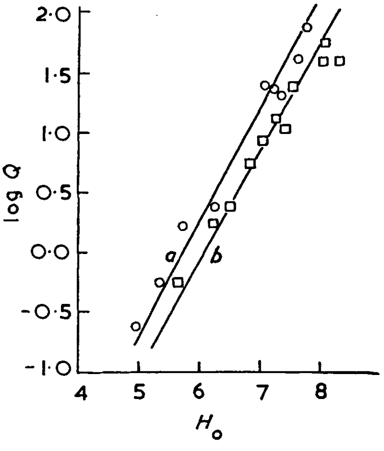


FIG. 3. *The concentration of allylic carbonium ions as a function of acidity.*

(a) *Allyl alcohol in sulphuric acid.*
(b) *Butadiene in sulphuric acid.*

Q is defined in the text. H_0 is Hammett's acidity function. The lines drawn have unit slope.

Similarly, we conclude that oxidation by dissolved oxygen is insignificant, since the bands are developed at comparable rates in the presence or absence of oxygen.

Had disproportionation occurred, the most likely reaction would have the form:

$$\mathrm{CH_2{:}CH{\cdot}CH_2^+ + CH_2{:}CH{\cdot}CH_2{\cdot}OH \longrightarrow CH_2{:}CHMe + CH_2{:}CH{\cdot}CH(OH)^+} \quad . \quad . \quad . \quad . \quad (1)$$

We found acraldehyde in sulphuric acid to have $\lambda_{\text{max.}}$ 238 mμ (ε 9400), and tetrahydro-2-methylfuran (which probably gives an ion $\mathrm{CHMe{:}CH{\cdot}CHMe^+}$) in this acid to have $\lambda_{\text{max.}}$ 288 mμ (ε 380: $\Delta_{\frac{1}{2}}$ 4500) whereas oxiran, ethane-1,2-diol, butan-2-one, dibutyl ether, methyl t-butyl ether, pivalaldehyde, and tetrahydrofuran had no strong absorption above 220 mμ. The significance of these results is outlined in the Discussion.

Acidity Functions.—A solution of allyl alcohol in sulphuric acid was stored in the dark, until there was no further change in the spectrum. Aliquot parts were withdrawn and diluted with aqueous sulphuric acids, the composition of the solutions being determined by measuring their densities and comparing them with standard tables. The spectra of these solutions were measured and the results are shown in Fig. 3, as a plot of the acidity function [7] H_0 against log Q, where Q is defined by the equation

$$Q = [\text{Carbonium}]/[\text{Olefin}] = \varepsilon_{\text{exp.}}/(\varepsilon_{\text{max.}} - \varepsilon_{\text{exp.}}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$\varepsilon_{\text{exp.}}$ is the apparent extinction coefficient at 272 mμ for a given H_0 value, and $\varepsilon_{\text{max.}}$ is the extinction coefficient in 98% sulphuric acid.

The results follow a line of unit slope fairly closely. Reacidification of solutions in dilute aqueous sulphuric acid with 98% sulphuric acid resulted in an immediate and quantitative reappearance of the band at 272 mμ.

---

[7] Deno, Jaruzelski, and Schreisheim, *J. Amer. Chem. Soc.*, 1955, **77**, 3044.

From these results and equation (2) tentative pK values have been estimated.

$$pK_A = H_0 + \log Q \qquad (2)$$

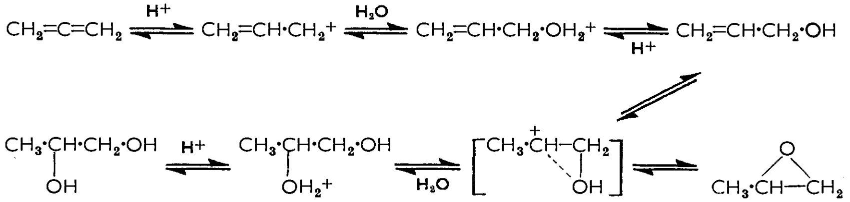
Similar results were obtained with buta-1,3-diene. The peak at 290 mμ was used to follow the spectral changes and typical results are shown in Fig. 3. Only the initial stages of deprotonation were followed since in the regions of lower acidity ($<70\%$ H_2SO_4) results were irreproducible, and a subsidiary band in the 250—260 mμ region was often found. At higher acidities, the spectral changes were reversible, and an isosbestic point appeared in the 230 mμ region. In addition a broad maximum in the 215—220 mμ region appeared, which was probably due to unprotonated butadiene. The extinction coefficient at 217 mμ, estimated on the assumption that only butadiene and its conjugate acid were present, was $1{\cdot}9 \times 10^4$: the accepted value is $2{\cdot}1 \times 10^4$. These results lend weight to the postulate that the pK values estimated from the results given in Fig. 3 are correctly assigned, namely: Me_3C^+ (ref. 2) — 3·0; $CH_2\dot{:}CH{\cdot}CH_2^+$ — 5·5; $CH_2\dot{:}CHMe^+$ — 5·9.

An attempt was made to measure the pK value for 2-methylpenta-1,3-diene, but in this case a band at about 260 mμ appeared as soon as the band at 305 mμ had diminished appreciably, and reacidification gave a spectrum similar to that of Fig. 2. We do not know what compound is responsible for these bands, but one can deduce from the results that the pK value must be considerably larger than that of butadiene.

DISCUSSION

Nature of the Species with a Band at 273 mμ.—The fact that ethylene oxide and ethylene glycol do not give this species in sulphuric acid means that certain obvious explanations need not be considered. The relative rates of reaction are also significant: that olefins react very rapidly, allylic compounds at a measurable rate, and diols very slowly is in accord with the postulate that the absorbing species is, in each instance, an allylic carbonium ion (cf. Table 1), and would be difficult to explain by any other hypothesis. In this sense, these compounds resemble simple tertiary alcohols and their corresponding olefins.[1,2] Examples of the reactions postulated are summarized in Scheme 1.

Scheme 1.



Also in accord with the carbonium ion postulate are the estimated pK values, the fact that the dependence of the spectrum on acid concentration follows H_0, and the energy and intensity of the absorption band. These points are discussed in more detail below.

The most probable alternative to the carbonium-ion hypothesis, that some oxidised species is responsible for the new band, has been found (p. 3) to be unlikely.

Methyl Substitution.—Similar reasoning to that given above is applicable to the other compounds listed in Table 1, and we therefore postulate that in all cases the species responsible for the ultraviolet absorption bands are allylic carbonium ions. We conclude that methyl substitution in the β-position gives a band of slightly higher energy, whereas methyl in the α- or γ-position gives a band of lower energy, although further α- or γ-substitution has little effect.

For simplicity, the carbonium-ion postulate is accepted as correct in the following discussion.

Nature of the Electronic Transition for Allylic Carbonium Ions.—The ion, $CH_2\dot{:}CH{\cdot}CH_2^+$, which should be planar, has C_{2v} symmetry, and the first allowed transition is expected to be the transition, ${}^1A_2 \longleftarrow {}^1B_1$, which, in terms of the scheme given by Walsh for bent triatomic molecules BAB, can be written [8]

$$\ldots(b_1'')^2 \longrightarrow \ldots(b_1'')(a_2'')$$

The b_1'' level is a π molecular orbital covering all three carbon atoms: if one assumes that each carbon has sp^2-hybridization, with the directed orbitals lying in the xy plane, then the b_1'' level is built up by the in-phase overlap of the p_z-orbitals on the three carbon atoms. However, the excited a_2'' orbital is built up from out-of-phase overlap of p_z-orbitals on the two outer carbon atoms (α and γ) and is thus largely confined to these atoms. That this is the case can be seen by considering electron-spin resonance results from the allyl radical.[9] These results can be rationalised if one assumes that the unpaired electron lies almost entirely on the α- and γ-carbon atoms.[10]

We conclude that, on excitation, there will be transfer of negative charge from the β- towards the α- and γ-carbon atoms. This leads to the prediction, found to be satisfactory in another context,[3] that α- or γ-methyl substitution should lead to a strong shift of the ${}^1A_2 \longleftarrow {}^1B_1$ transition to shorter wavelengths, since the stabilising effect of methyl is greater, the greater the electron deficiency on the carbon to which it is attached. Similarly, we would expect β-methyl to stabilise the excited state somewhat more than the ground state, and thus shift the band slightly to longer wavelengths. These predictions are the reverse of what is observed.

If the carbonium-ion postulate is correct, then this simple viewpoint must be modified. An alternative approach would be to use data from gas-phase experiments. The ionisation potentials (in ev) for the corresponding 17-electron radicals are 8·16 for allyl,[11] 8·03 for 2-methylallyl, and 7·71 for 1-methylallyl.[12] Thus, if we correlate the energy of the ${}^1A_2$ excited state of the carbonium ion with the radical, we predict a steady trend (small for 2- and large for 1-methylallyl) to high energy for the ${}^1A_2 \longleftarrow {}^1B_1$ transition. This is now in accord with experiment for β-methyl substitution.

The result can be rationalised in terms of the correlation diagram given by Walsh.[8] We should expect that replacement of β-hydrogen by methyl would tend to decrease the apex angle. This, in turn, would lead to a *decrease* in the energy of the b_1'' level, since it is weakly bonding between the outer atoms, but an *increase* in the energy of the upper a_2''-orbital since it is antibonding between the outer atoms. If this factor is more important than the one discussed above, then a shift of the band to high energy would result.

However, all considerations show that α- or γ-substitution should give a strong shift to high energies. We therefore postulate either that the shift to low energies is a solvent effect or, more probably, that the band observed is *not* the ${}^1A_2 \longleftarrow {}^1B_1$ transition at all, but a transition involving the C–H bonding electrons of the substituent. The possible effect of solvent can be understood in the following way: for the allyl carbonium ion, the solvent will be organised to stabilise partial positive charges on the end carbon atoms and thus the ground state will be stabilised and the excited state destabilised relatively to the ion in the gas phase. If we consider the 1,3-dimethylallyl (1-methylbut-2-enyl) carbonium ion, the effect of solvent will be weaker, since close approach is sterically hindered, and thus, other things being equal, the band should shift to lower energies.

The alternative would be that the ${}^1A_2 \longleftarrow {}^1B_1$ band is, in fact, on the high-energy side of the band for the allyl ion, say in the 200 mμ region, and that the bands for α- or γ-methyl-substituted ions in the 300 mμ region are due to " hyperconjugation " transitions from the methyl group(s) of a type postulated already to explain the band at 293 mμ assigned to trimethyl carbonium ions, for which ordinary π–π transitions are impossible.[2]

Anomalous Extinction Coefficients.—Values of apparent extinction coefficients (ε) for

---

[8] Walsh, *J.*, 1953, 2266.

[9] Matheson and Smaller, *J. Chem. Phys.*, 1958, **28**, 1169.

[10] Symons, *J.*, 1959, 277.

[11] Lossing, Ingold, and Henderson, *J. Chem. Phys.*, 1954, **22**, 621.

[12] McDowell, Lossing, Henderson, and Farmer, *Canad. J. Chem.*, 1956, **34**, 345.

bands derived from the butanediols are far smaller than those for the bands from the corresponding dienes. These bands develop very slowly, and, in general, we consider that important alternative reactions occur to give, irreversibly, compounds that have no strong bands above about 210 mμ in sulphuric acid. There are many possibilities, but the following suggestions may be relevant.

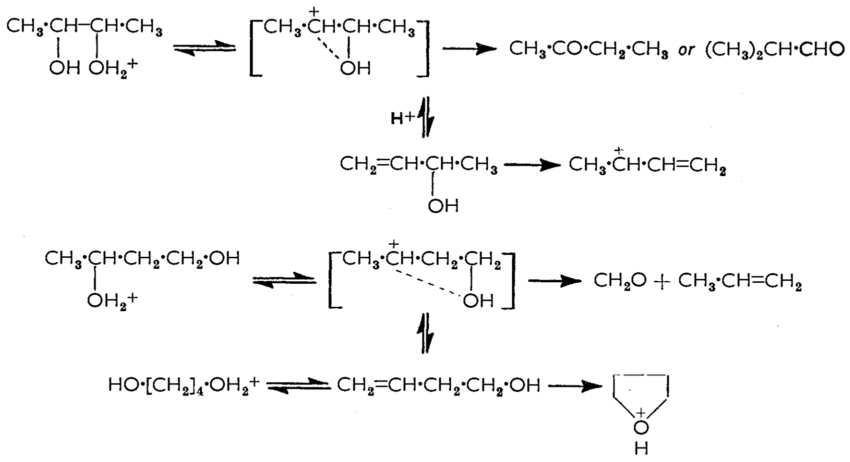
(i) Butane-1,4-diol probably gives tetrahydrofuran. Separate experiments showed that this ether does not give any band above 200 mμ even after several days in sulphuric acid. That a weak band at 291 mμ is obtained from this diol means that conversion into tetrahydrofuran is not the only reaction of significance. One reason for this could be that, in sulphuric acid, both hydroxyl groups are protonated. This would inhibit cyclisation far more than elimination. Some or all of the reactions of scheme (2) may be important.

(ii) Scheme 2 includes also the postulated reactions of butane-1,3-diol to give the carbonium ion. Again, this is a subsidiary reaction for this diol, which, in the main, reacts in other ways. We tentatively suggest that the main reaction in this instance is acid-catalysed carbon–carbon bond cleavage to give formaldehyde and propene.[13]

(iii) Similarly, butane-2,3-diol can either follow Scheme 2 to give the allylic carbonium ion or undergo rearrangement to give isobutyraldehyde or ethyl methyl ketone.

It is noteworthy that more highly substituted diols appear to give higher yields of carbonium ions. This suggests that carbonium-ion formation is facilitated by such substitution, relative to rearrangements of the type under consideration.

Scheme 2.



Significance to Reaction Mechanisms.—If our postulate is correct, then the spectral information should be of use in any studies of mechanism in which allylic carbonium ions are thought to be involved. The extinction coefficients are quite large, so that with appropriate cells it might be possible to measure the stationary concentrations of such ions during the course of reaction.

The results with epoxides are thought to be significant in connection with the question of ring opening. Ingold,[14] and Long, Pritchard, and Stafford,[15] have concluded that, at least for some epoxides in the presence of acids, carbonium ions of the type $HO{\cdot}CR_2{\cdot}CR_2^+$ are important intermediates (*A*-1 mechanism).

---

[13] Cf. Newman's "Steric Effects in Organic Chemistry," Wiley and Sons, New York, p. 375, for relevant references.

[14] Ingold, "Structure and Mechanism in Organic Chemistry," Bell & Sons Ltd., London, 1953, p. 344.

[15] Long, Pritchard, and Stafford, *J. Amer. Chem. Soc.*, 1957, **79**, 2362.

However, evidence from kinetic studies on solutions of epoxides under high pressure strongly suggests that even the acid-catalysed hydrolysis of isobutene oxide is a bimolecular substitution of the conjugate acid (*A*-2 mechanism).[16] Our results lend some support for the latter mechanism, in that there is no spectrophotometric evidence for the formation of carbonium ions of the above type which should have a spectrum rather different from those of the corresponding saturated carbonium ions.[2] Indeed, with an unprotonated hydroxyl group so close to the positive carbon atom, it is very hard to understand how cyclisation to the conjugate acid of the oxide could be avoided. Koskikallio and Whalley concluded that the Zucker–Hammett hypothesis fails in this instance.[16] Parker and Isaacs[17] have marshalled other evidence in favour of the *A*-2 mechanism, and suggest that most of the apparent discrepancies can be resolved if the transition state for ring opening involves a high degree of bond breaking.

Many of these arguments are relevant to the mechanism of pinacol–pinacolone rearrangements, and it seems probable that the structure of the intermediate involved will more closely resemble a protonated epoxide than a simple carbonium ion.

p*K Values*.—Since the decrease in intensity of the ultraviolet bands with decrease in acidity of the medium follows Hammett's acidity function, H_0, we conclude that the equilibrium involves gain and loss of a proton. A tentative allocation of p*K* values for various carbonium ions is given on p. 7. We assume that greater conjugation in the olefin accounts largely for the smaller basicity of butadiene than of isobutene and allene.

Thanks are offered to the D.S.I.R. for a maintenance grant (to J. R.).

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHAMPTON,
SOUTHAMPTON.

[*Received, May* 16*th*, 1960.]

[16] Koskikallio and Whalley, *Trans. Faraday Soc.*, 1959, **55**, 815.

[17] Parker and Isaacs, *Chem. Rev.*, 1959, **59**, 737.