accounted for by the 2,4-dimethylpentenyl bands and was prepared by addition of the diene from a simple eye dropper. This spectrum was chosen for presentation because there was a moderate amount of diene added, the 2.95 and 2.97 bands were well resolved, and the spectrum shows the nature of the other material formed during the process of solution.

If the diene is simply added dropwise with slow stirring to 96% H_2SO_4 at 25°, none of the hydrogens present are those of the 2,4-dimethylpentenyl cation. Since the diene is 99.5% pure (see Experimental), it is clear that dimerization (and perhaps further polymerization and rearrangement) are taking place during the process of dispersing the diene into the acid. Since the monomeric cation is stable for at least minutes, it is also clear that it should be possible to obtain a spectrum in which the 2,4-dimethylpentenyl cation bands account for 100% of the hydrogen if the diene could be introduced in a sufficiently attenuated form. This has not as yet been achieved.

Carbonium Ions. XII. The Direct Observation of Rearrangement and Hydrogen–Deuterium Exchange in Cycloalkenyl Cations[1]

BY N. C. DENO, NORMAN FRIEDMAN, JAMES D. HODGE, AND JOHN J. HOUSER

Such generally accepted principles as the greater stability of tertiary over secondary carbonium ions, the increasing stability of carbonium ions with increasing α-hydrogens, and the increasing stability of alkenes with increasing alkyl substitution can be observed in a most direct way from n.m.r. spectra of cycloalkenyl cations. The rate of hydrogen–deuterium exchange into such ions is base-catalyzed so that the rate is much slower in 96% H_2SO_4 than in more dilute acids. The rearrangement of 1,3,4,4,5- to 1,2,3,4,4-pentamethyl-cyclopentenyl cation is also base-catalyzed, but the rearrangement of 1,3,4,4,5,5- to 1,2,3,4,4,5-hexamethyl-cyclopentenyl cation is not.

The properties of aliphatic carbonium ions have in the past been inferred from the rate constants and the products produced in reactions believed to proceed via such carbonium ions as unstable intermediates. The preparation of stable solutions of these aliphatic carbonium ions now enables the direct observation of some of these properties.

Experimental

The n.m.r. spectra were recorded as described in the preceding paper.[2] The D_2SO_4–D_2O solutions were prepared by combining General Chemical Co. Sulfan (SO_3 containing an unknown polymerization inhibitor) with D_2O. Several methods of effecting the combination were tried, but since none were entirely satisfactory, they are not described in detail. The problem centers around solidification of the SO_3 in the presence of small amounts of D_2O. Subsequently, Miss Josephine de Luis and Dr. P. S. Skell at Penn State slowly distilled liquid Sulfan into D_2O (stirred). This would appear to be the method of choice because the SO_3 is kept warm and liquified.

In the fast hydrogen–deuterium exchanges, some temperature control was attained by adding the dienes to the D_2SO_4–D_2O at 35°, loading the n.m.r. tube, and immediately inserting the tube into the probe. Since the probe temperature held at 35 ± 2°, the reactions were approximately thermostated. Slow exchanges were simply held at 25° except for short periods of measurement.

The identification of the cations are presented in the preceding paper,[2] as are the methods of calibrating and reporting the n.m.r. spectra.

Discussion

Rearrangements.—Addition of 3-methylene-1,4,4,-5,5-pentamethylcyclopentene (I) to 96% H_2SO_4 would give on initial protonation the 1,3,4,4,5,5-hexamethyl-cyclopentenyl cation, II. The first spectrum observed,


I   II   III
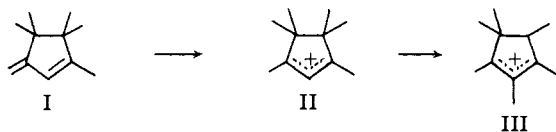
1–2 min. after mixing, is that of II and this spectrum is shown in Fig. 1. The single hydrogen on C-2 at 7.49

p.p.m. is definitive[2] as are the six hyperconjugated hydrogens at 2.90 p.p.m.

Already in Fig. 1, the incipient conversion to a new cation is apparent from the small band at 2.15 p.p.m. which is characteristically narrow and is definitive for methyl at C-2.[2] As time progresses, the band at 2.15 p.p.m. continues to grow concomitant with the gradual disappearance of the band at 7.49 p.p.m. This shows that the hydrogen at C-2 is being replaced by methyl. After about 1 hr., a stable n.m.r. spectrum is attained. A spectrum measured 3 hr. after mixing is shown in Fig. 2. This spectrum is entirely in accord with structure III.[2] The predominance of III over II at equilibrium may be associated with relief of steric repulsions and possibly with the fact that III has one more hyperconjugation hydrogen than II. The conversion of II to III takes place at the same rate in 70% H_2SO_4 as in 96% H_2SO_4. The rate of conversion of II to III is about the same in 0.1 M solution, measured by n.m.r. spectra, as in 10^{-5} M solution, measured by ultraviolet spectra, showing that the rate of conversion is first order in II.

A similar type of rearrangement takes place when 3,4,4,5,5-pentamethyl-2-cyclopenten-1-ol (IV) is dissolved in 96% H_2SO_4. The initially formed cation, V, was not observed. The n.m.r. spectrum after 1–2 min. is shown in Fig. 3 and approximates that expected for cation VI. The comparison of observed and calculated n.m.r. band areas has already been presented.[2] It is of interest that the rearrangement from the secondary to the tertiary carbonium ion is so rapid.

IV   V   VI   VII
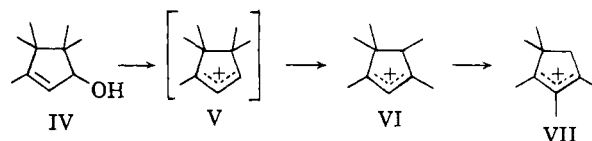
The spectrum of VI is not permanent, but continues to change leading to the stable n.m.r. spectrum shown in Fig. 4. The identification of this spectrum as that due to VII has been presented.[2] This conversion of VI to VII requires about 1 hr. for completion in 96% H_2SO_4.
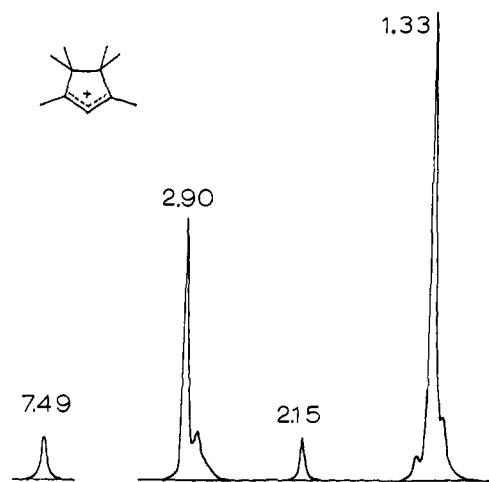
Fig. 1.—N.m.r. spectrum of II recorded 1–2 min. after adding I to 96% H_2SO_4. From the area of the band at 2.15 p.p.m. relative to the area of the band at 7.49, it is estimated that about 25% of II has already progressed to III.
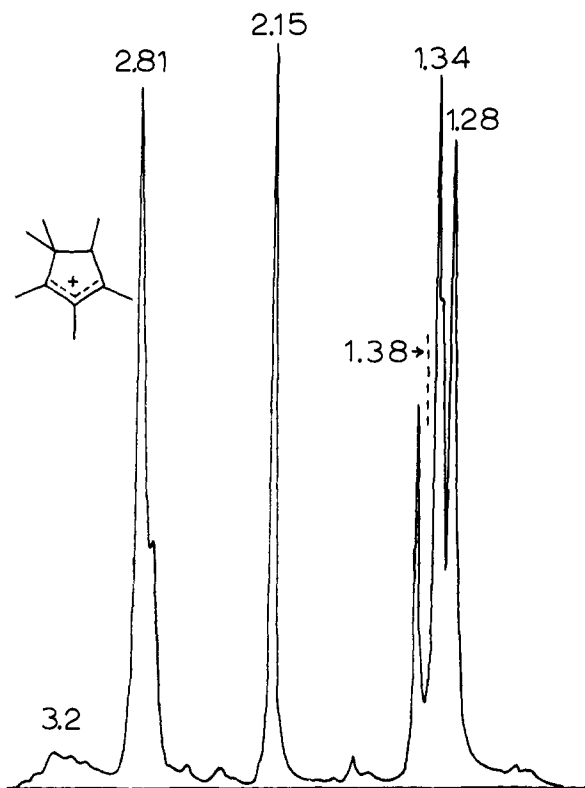

Fig. 2.—N.m.r. spectrum of III recorded 3 hr. after addition of the diene I to 96% H_2SO_4. The intermediate cation II has disappeared.

Fig. 3.—N.m.r. spectrum of VI recorded 1–2 min. after adding the alcohol IV to 96% H_2SO_4. From the areas of the bands at 2.15 and 7.62 p.p.m., it is estimated that about 27% of VI has progressed to VII.

Fig. 4.—N.m.r. spectrum of VII recorded 3 hr. after addition of the alcohol IV to 96% H_2SO_4. The intermediate cation VI has disappeared.

The conversion of VI to VII would appear to be closely related to the conversion of II to III, particularly since the rates of conversion are nearly equal at 25° in 96% H_2SO_4. However, whereas the conversion of II to III has the same rate in 70% as in 96% H_2SO_4, the conversion of VI to VII in 70% H_2SO_4 is complete within the 2 min. required for the first n.m.r. measurement. This base catalysis suggests that the conversion of VI to VII involves a proton removal step.

Hydrogen–Deuterium Exchanges.—A most notable fact about the n.m.r. spectra of the various alkenyl cations is that every hydrogen appears. This immediately proves that none of the hydrogens are exchanging with half-lives of less than 0.01 sec., for that would have led to hybridization of the bands with those of the sol-
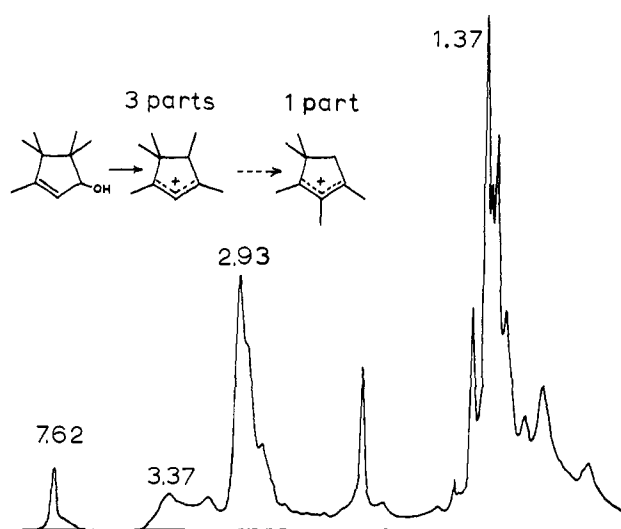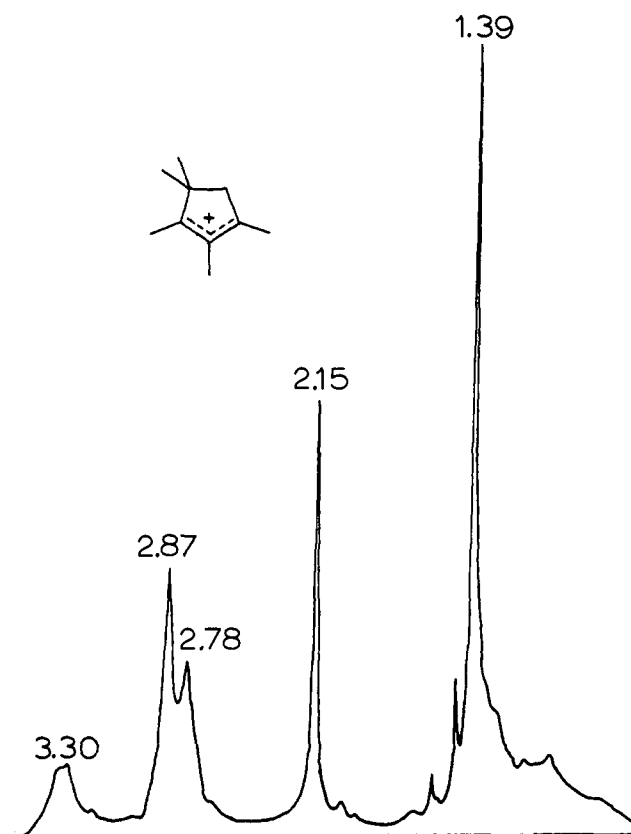
vent sulfuric acid and the contributions from such hydrogens would have been included in the solvent band. This conclusion was completely supported by n.m.r. spectra taken in 94% D_2SO_4. Table I lists approximate times for half-exchange. The absolute values are not very precise because of the lack of temperature control, but the relative rates for hydrogens at different positions in a particular ion are of good precision.

Hydrogen–deuterium exchange occurred only on carbon atoms α to the allylic cation system. The hydrogen at C-2 does *not* exchange. The mechanism

TABLE I

HALF-LIVES OF HYDROGEN–DEUTERIUM EXCHANGE AT EACH POSITION IN SEVERAL CYCLOPENTENYL AND CYCLOHEXENYL CATIONS, ~25°, 94% D_2SO_4

Cation	H on ring carbons (α to the allylic system)	CH₃ at C-1 or C-3	$-CH_2CH_3$	$-CH(CH_3)_2$
		Time, sec., for half-exchange[a]		
VIIIa	5.8 × 10⁵	None (200 hr.)	...	...
VIIIb	3.8 × 10⁵	1.4 × 10⁶	9.0 × 10⁴	...
VIIIc	3.8 × 10⁵	3.5 × 10⁶	...	1.8 × 10³
IXa	(4.0 × 10³)[b]	(2.8 × 10³)[b]	...	...
IXb	(2.4 × 10³)[b]	(1.9 × 10³)[b]	10[b]	...
IXd	4.5 × 10⁵ (3.26 band) 8.5 × 10⁴ (2.77 band)	5.7 × 10⁴	...	...
IXd in 85% D₂SO₄	(2.8 × 10³)[b] (3.26 band) (6.4 × 10³)[b] (2.77 band)	(6.0 × 10²)[b]	...	...

[a] The reaction is first order only in the early stages because of a statistical factor introduced when CH₃ is successively converted to CH₂D and CHD₂. The half-lives were computed from observations before half-exchange had taken place. [b] These rates were actually measured at 35° and corrected to 25° by assuming that the rate constant increases by a factor of 2 between 25 and 35°.

for these exchanges is undoubtedly loss of H⁺ to form the diene and readdition of the proton to go back to the original cation. In accord with this mechanism, the rates of exchange greatly increase as the concentration of D₂SO₄ is lowered, a result of the increasing activity of D₂O.

The rate of exchange on the cyclohexenyl cations were about 100 times faster than on the cyclopentenyl cations. The rate of exchange on the linear 2,4-dimethylpentenyl cation (time for half-exchange at 25° was 6.0 × 10² sec., estimated as explained in footnote b of Table I) was about a factor of 10 faster than on the cyclohexenyl cations. The thermodynamic stability of the cations decreases in the order cyclopentenyl, cyclohexenyl, linear alkenyl (presented in the following paper). We thus come to realize that rates of proton abstraction are inversely proportional to the carbonium ion stability. That is, the less stable the ion, the more rapidly is H⁺ lost. This principle is identical with that found in hydride transfer reactions where the less stable the cation, the more rapidly it abstracted hydride.[3]

Hydride transfers between Lewis acids (of which carbonium ions are exemplary) and proton transfers between bases have more than the above principle in common. In both phenomena, the moiety transferred does not exist as an isolated particle and in fact both reactions can be viewed as displacement on hydrogen. Hydride transfer would be electrophilic (S_E) displacement and proton transfer would be nucleophilic (S_N) displacement. We foresee that every aspect of acids and bases associated with proton transfers will find their counterpart in hydride transfers.

Turning back to the H–D exchanges, the comparable exchange rates for endocyclic CH₂ (at C-4 and C-5 in the VIII series and at C-4 and C-6 in the IX series) and the exocyclic CH₃ at C-3 shows that two isomeric dienes are formed at comparable rates. This fact was already evident from the n.m.r. spectra of the diene

(3) N. Deno, G. Saines, and M. Spangler, J. Am. Chem. Soc., 84, 3295 (1962).

mixtures obtained when the dienes of the IX series were first prepared.[2]

VIIIa, R = CH₃
    b, R = CH₂CH₃
    c, R = CH(CH₃)₂

IXa, R = CH₃
    b, R = CH₂CH₃
    c, R = CH(CH₃)₂
    d, R = C₆H₅

The relatively rapid exchange on $-CH_2CH_3$ of VIIIb and IXb and on $-CH(CH_3)_2$ of VIIIc is a direct demonstration of the well known propensity of carbonium ions to deprotonate to the more highly alkylated olefin
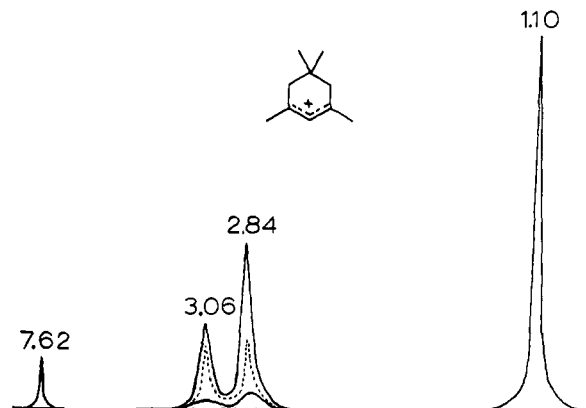

Fig. 5.—A typical H–D exchange experiment. The cation is 1,3,5,5-tetramethylcyclohexenyl (IXa) and the data are recorded for 0, 10, and 180 min. in 94% D₂SO₄.

or diene. The complete failure to exchange on $-CH_2-CH_3$ or $-CH(CH_3)_2$ demonstrated that the unconjugated alkyl cations, such as X and XI, were not formed.

X

XI