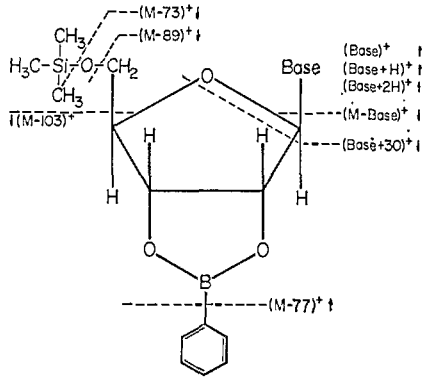


Figure 1. Fragmentation of nucleoside phenylboronate trimethylsilyl ethers.

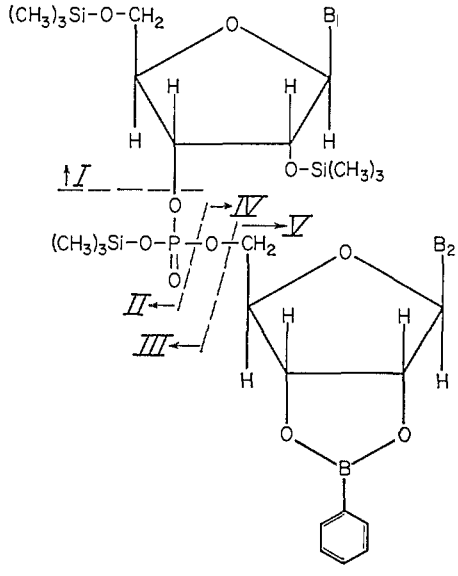


Figure 2. Fragmentation of silylated phenylboronates of dinucleoside phosphates.

fragment ions is sufficient to characterize each of the dinucleoside phosphates and, in particular, this information unequivocally differentiates between sequence isomers such as ApU and UpA. Figure 3 represents a possible fragmentation pattern to account for the ions observed. Ion I results from cleavage of the PO–C3′ bond, and ion V from cleavage of the PO–C5′ bond with charge retention on the carbon atom in each case.

Table I. Characteristic Fragment Ions of Silylated Phenylboronates of Dinucleoside Phosphates

Compd	Fragment *m/e* M+	I	II	III[a]	IV	V	Relative intensity[b]
ApA	1042	466	618	636	424	408	85:59:9:75:100
UpU	996	443	595	613	401	385	53:78:25:72:100
ApU	1019	466	618	636	401	385	66:75:7:38:100
UpA	1019	443	595	613	424	408	10:34:4:52:100
UpC	995	443	595	613	400	384	55:53:21:93:100
CpU	995	442	594	612	401	385	60:54:12:84:100

[a] Fragmentation of trialkyl phosphates with charge retention on the oxygen is accompanied by transfer of two hydrogens to form a protonated phosphate ion.[2] [b] The most abundant of the five ions = 100.

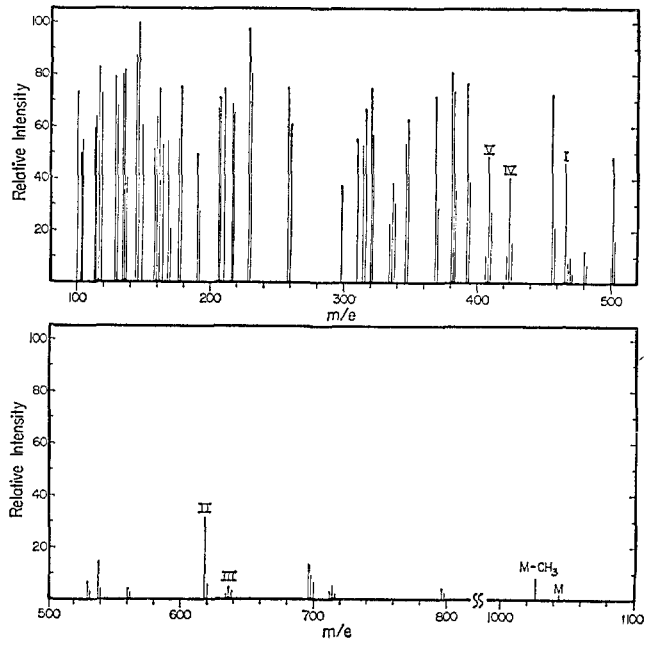


Figure 3. Mass spectrum of trimethylsilylated adenylyl-(3′–5′)-adenosine phenylboronate.

Ion III includes the structure of ion I with the addition of the phosphate–trimethylsilyl moiety. The same addition to ion V did not produce a prominent ion. However, cleavage of the P–O bond at the 5′ position of the nucleoside containing base B_2 yields ion IV. This same type of cleavage also results in ion II which includes base B_1. The key fragment ions for some dinucleoside phosphates are presented in Table I.

It may be noted that the elemental composition (indicating the presence of boron) of ion V would always yield unambiguous information as to which base is at the 3′ terminus of a particular oligonucleotide, and, furthermore, would also establish that the compound is not phosphorylated at this position. The significance of this type of information will become increasingly apparent when attempts are made to order the bases in the more complex tri- and tetranucleotides.

Acknowledgment. We thank Dr. P. T. Gilham for informative discussions and Dr. J. H. Beynon for valuable advice on interpretation of spectra. The able technical assistance of Miss Penny Schuber and Mr. Wilford Perry is gratefully acknowledged.

(6) Author to whom correspondence should be addressed.

J. J. Dolhun, J. L. Wiebers[6]
Department of Chemistry, Purdue University
Lafayette, Indiana 47907
Received October 14, 1969

A New Rearrangement Process in Methylcyclopentyl and *t*-Amyl Cations

Sir:

A reaction which interchanges the three methyl groups of *t*-amyl cation has recently been studied using nmr.[1–3] We now report an additional, slower process

(1) M. Saunders and E. Hagen, *J. Am. Chem. Soc.*, 90, 2436 (1968).
(2) D. M. Brouwer and E. L. Mackor, *Proc. Chem. Soc.*, 147 (1964).
(3) D. M. Brouwer, *Recueil*, 87, 210 (1968).

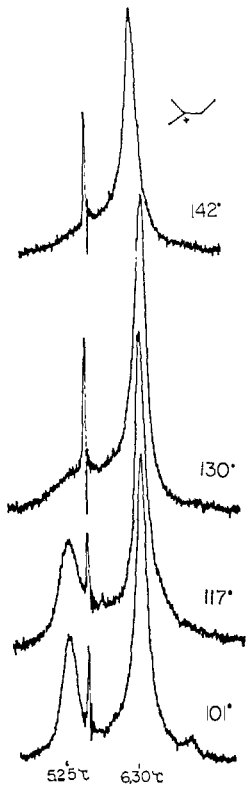


Figure 1.

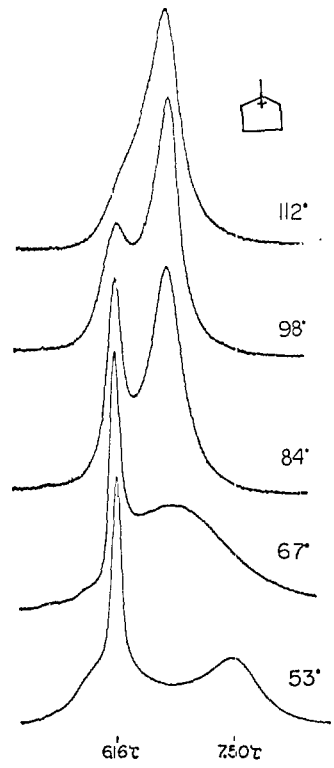


Figure 2.

which exchanges the two methylene protons with the nine methyl protons, resulting in a single nmr peak for all 11 hydrogens at high temperature.[4] Methylcyclopentyl cation has also been found to exchange ring and methyl protons at high temperature.

The cations were prepared from *t*-amyl chloride and cyclohexyl chloride in excess antimony pentafluroride and SO_2ClF in the manner previously reported,[1] the isomerization of cyclohexyl to methylcyclopentyl having been previously noted. Spectra agreed with those in the literature.[6]

Spectra of *t*-amyl cation (Figure 1) on heating above 100° revealed gradual loss of structure of the methylene multiplet followed by coalescence of the methylene and methyl lines above 130°, all completely reversible. The experimental spectra were processed with previously reported methods[7] using the values obtained[1] for the methyl shift process. The resulting values for the new reaction based on the mechanism given below were $E_a = 18.8 \pm 1$ kcal/mol, $\log A = 13.2 \pm 0.5$.[8]

(4) Olah and coworkers have reported[5] that *t*-amyl cation solutions in SbF_5 give a single peak at room temperature and suggest an unspecified "exchange" process as the cause. However, our work and that of Brouwer and coworkers[2,3] report no such findings in studies of this cation in similar media and in HF–SbF_5 solutions. At 70° we find no detectable change in the methylene peak although the methyls have coalesced to a very broad singlet. From traces published by Olah, the most reasonable explanation seems to be viscosity broadening until only the downfield methyl peak was visible. It may be significant that, in the broadened traces which they show, all peaks are affected about equally contrary to what would be expected for exchange broadening.

(5) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastein, *J. Am. Chem. Soc.*, **86**, 1360 (1964); G. A. Olah and C. U. Pittman, Jr., *Advan. Phys. Org. Chem.*, **4**, 305 (1966).

(6) G. Olah, J. Bollinger, C. Cupas, and J. Lukas, *J. Am. Chem. Soc.*, **89**, 2696 (1967).

(7) M. Saunders in "Magnetic Resonance in Biological Systems," A. Ehrenberg, Ed., Pergamon Press Ltd., Oxford, 1967, pp 85–99.

(8) All quoted errors are standard deviations.

Brouwer has reported broadening of the α and β hydrogen peaks in methylcyclopentyl cation at about +20°[3] and has suggested a series of hydride and methide shifts analogous to the mechanism proposed for methyl interchange in *t*-amyl.[1] Interchange of the α and β hydrogens occurred rapidly at 75°, and interchange of the methyl and ring hydrogens at higher temperatures. Final coalescense to a singlet at about 110° was observed (Figure 2). Again, all spectral changes were reversible. The line shapes were analyzed considering processes analogous to those employed with the *t*-amyl case. The Arrhenius parameters for the two reactions were found to be $E_a = 15.4 \pm 0.5$ kcal/mol, $\log A = 13.0 \pm 0.3$ and $E_a = 18.2 \pm 0.1$, $\log A = 13.6 \pm 0.1$ for the low and high temperature processes.

Interchange of the methylene and methyl hydrogens in both cases might occur *via* hydride shifts to one of several primary ions. However, the corresponding E_a should then be at least the difference in energy between tertiary and primary ions which has been estimated to be about 30 kcal/mol.[9] An analogous process would be expected to scramble deuterium and hydrogen in (1,1,1,2,2,2)-hexadeuterio-*t*-butyl cation. Since the barrier for this process has been shown to be more than 28 kcal/mol,[10] such a mechanism is unlikely for the new reaction.

The reversible dimerization *via* elimination to olefin suggested by Karabatsos[11] would account for mixing of the methylene protons. However, observation of the hexadeuterio-*t*-butyl cation[10] indicates that, with tertiary aliphatic ions, in this medium, elimination has a minimum barrier of 28 kcal/mol, again far above that observed.

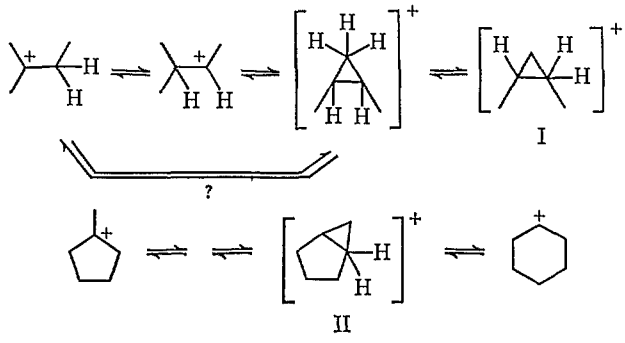
(9) A. G. Evans, "The Reactions of Organic Halides in Solution," The Manchester University Press, Manchester, England, 1946, p 15.

(10) Unpublished results of M. Saunders and E. L. Hagen.

(11) G. Karabatsos and F. Vane, *J. Am. Chem. Soc.*, **85**, 729 (1963).

Processes involving protonated cyclopropane intermediates should have lower activation energies. In the *sec*-butyl cation,[12] a process with an E_a of 7.5 kcal/mol is accounted for on the basis of a transition from a secondary ion to a protonated cyclopropane. In the tertiary ion *t*-amyl such a process might require an additional 12 or 13 kcal/mol, *i.e.*, an E_a of approximately 20 kcal/mol, a value close to that observed. The mechanism might be represented as in Scheme I.

Scheme I



The rearrangement finds analogy in the mechanism proposed by Baird and Aboderin[13] for the reaction of cyclopropane in deuterio acid. Edge-protonated species might be intermediates rather than transition states as proposed here, but we have no direct evidence on this point. We also cannot rule out direct formation of protonated cyclopropanes from tertiary ions by simultaneous hydride shift and closure. A complicating factor in the case of the methylcyclopentyl cation is the likelihood that the two angular protons in II are sterically nonequivalent, in contrast to the situation in I, and therefore hydrogen exchange might not occur. A further shift around the three-membered ring or pseudorotation might get around this difficulty.

Another possibility we considered was that protonated cyclopropanes might open reversibly to cyclohexyl or *sec*-pentyl cations, making the hydrogens in question equivalent. The probability matrices[6] were not sufficiently different to distinguish these possibilities by line-shape analysis; however carbon labeling could. Interchange of methyl hydrogen and ring hydrogen might occur in the protonated cyclopropane, but only reversible isomerization to cyclohexyl cation can readily explain exchange of methyl *carbon* with ring carbon. To determine the relative rates of methyl hydrogen and carbon exchange with ring hydrogen and carbon, 1-methylcyclopentyl chloride was synthesized starting with equal amounts of $^{13}CH_3I$ (60% ^{13}C) and CD_3I (~95% D) *via* Grignard on cyclopentanone and converted to cations at low temperature. At about −25°, the ^{13}C methyl side bands rapidly decreased and the methyl peak grew, indicating that ^{13}C was *indeed* moving into the ring. Deuterium in the methyl group was simultaneously replaced by hydrogen from the ring. The rates at −33°, methyl carbon mixing with ring carbon, $5 \pm 2 \times 10^{-4}$ sec^{-1}, and methyl hydrogen mixing with ring hydrogens, $3 \pm 2 \times 10^{-4}$ sec^{-1}, were very close. We conclude that the protonated cyclopropane continues on to the cyclohexyl ion most of the time.

(12) M. Saunders, E. Hagen, and J. Rosenfeld, *J. Am. Chem. Soc.*, **90**, 6882 (1968).
(13) R. Baird and A. Aboderin, *ibid.*, **86**, 252 (1964).

Acknowledgment. This work was supported by a grant from the National Science Foundation.

(14) Fellow of the Alfred P. Sloan Foundation.
(15) National Institutes of Health predoctoral fellow.

Martin Saunders,[14] Jerold Rosenfeld[15]
Yale University
New Haven, Connecticut
Received August 11, 1969

Metal Ions and Hydrogen Peroxide.[1,2] Evidence for a Catalase-Like Activity of the *cis*-Diaquo Isomer of the Cu^{2+}–2,2′-Bipyridyl 1:2 Complex

Sir:

In a recent study[3] the catalytic activity of the Cu^{2+}–2,2′-bipyridyl system on the decomposition of H_2O_2 was investigated. The results obtained from the kinetic investigation of Cu^{2+}–2,2′-bipyridyl 1:1 mixtures can be summarized in eq 1, where v_0 is the initial rate of the decreasing concentration of H_2O_2

$$v_0 = -\frac{d[H_2O_2]}{dt} = k\frac{[Cu(bipy)][H_2O_2]^2}{[H^+]} \quad (1)$$

Increasing amounts of 2,2′-bipyridyl at constant concentrations of Cu^{2+} and H_2O_2 inhibit the catalytic activity; however, at higher pH values (>7), v_0 is still noticeable (Figure 3 in ref 3). Calculations on the basis of the concentration of the Cu^{2+}–2,2′-bipyridyl 1:1 complex, where the formation of $[Cu(bipy)OH]^{+}$ [4] or $[(Cu(bipy)OH)_2]^{2+}$ [5] was taken into account, lead to no satisfactory agreement between $v_{0,exptl}$ and $v_{0,calcd}$ at high pH with large excesses of 2,2′-bipyridyl. It was concluded that this is due to the formation of Cu^{2+}–peroxo-2,2′-bipyridyl complexes.[3] (The stability constants of such complexes are not known; hence, no calculations could be done.)[3] This conclusion was based on the observation that Cu^{2+} in aqueous solution usually has a square-planar (or strongly distorted octahedral) coordination sphere[6] and that Cu^{2+} complexes formed with cyclic tetradentate ligands are catalytically inactive.[7] Therefore, the Cu^{2+}–2,2′-bipyridyl 1:2 complex was also considered as inactive.[3]

In a recent esr and nmr study by Noack and Gordon[8] of the Cu^{2+}–2,2′-bipyridyl system, it was shown that the Cu^{2+}–2,2′-bipyridyl 1:2 complex exists as two isomers, one where the two hydrated coordination positions are *trans* and another where they are *cis*. In addition, strong evidence was given that the equilibrium between these two isomers in aqueous solution and at room tem-

(1) Part XXII of the series. This work was supported by a research grant from the Schweizerischen Nationalfonds zur Förderung der wissenschaftlichen Forschung.
(2) Part XXI: H. Erlenmeyer, C. Flierl, and H. Sigel, *J. Amer. Chem. Soc.*, **91**, 1065 (1969).
(3) H. Sigel, C. Flierl, and R. Griesser, *ibid.*, **91**, 1061 (1969).
(4) A. E. Martell, S. Chaberek, Jr., R. C. Courtney, S. Westerback, and H. Hyytiainen, *ibid.*, **79**, 3036 (1957).
(5) D. D. Perrin and V. S. Sharma, *J. Inorg. Nucl. Chem.*, **28**, 1271 (1966).
(6) D. D. Perrin, I. G. Sayce, and V. S. Sharma, *J. Chem. Soc., A*, 1755 (1967).
(7) H. Sigel, *Angew. Chem.*, **81**, 161 (1969); *Angew. Chem. Intern. Ed. Engl.*, **8**, 167 (1969).
(8) M. Noack and G. Gordon, *J. Chem. Phys.*, **48**, 2689 (1968); *cf.* also I. M. Procter and F. S. Stephens, *J. Chem. Soc., A*, 1248 (1969); C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 1362 (1955).