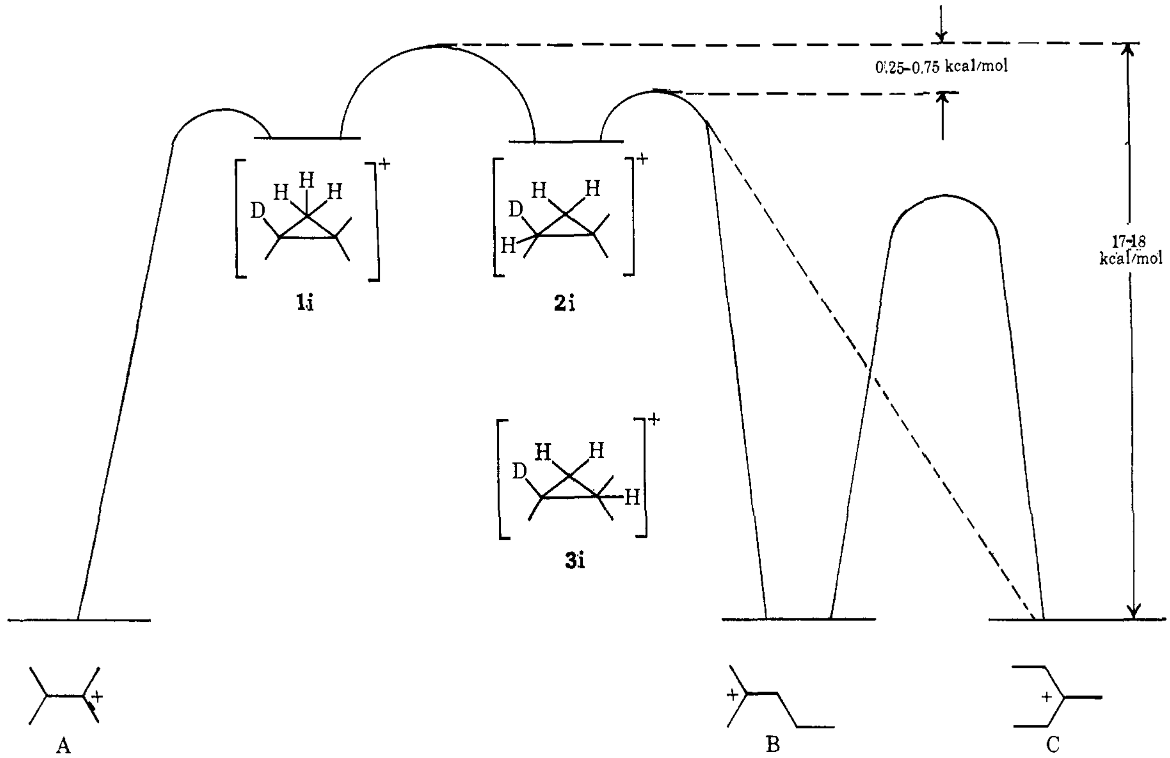
Scheme I



tert-butyl-d_9 chlorides[11] and for equilibruim β-deuterium isotope effect in cations.[12] The agreement is improved by assuming a small γ-deuterium isotope effect on the cationic center as reported for several solvolysis experiments.[13]

The kinetics of the rearrangement of 3-deuterio-2,3-dimethyl-butyl-2-ium ion (A) gave new information about the energy surface involving the three *tert*-hexyl ions A, B, and C.[2,4] It is postulated[14] that the reaction A $\rightleftarrows$ B and C proceeds through a corner- or edge-protonated cyclopropane intermediate in which protons migrate from corner to corner yielding the transition states or intermediates **1i**, **2i**, and **3i** (see Scheme I). Strong evidence for the involvement of similar intermediates is gathered from *tert*-amyl,[16] methylcyclopentyl,[17] *sec*-butyl,[5] isopropyl, and *tert*-butyl[18] cations.

At −40° we found the rate of rearrangement of A into B and C to be three–ten times faster than the rate of deuterium–hydrogen scrambling in A yielding $\mathrm{I_D} \rightleftarrows \mathrm{II_D}$. Therefore the energy barrier for the process **2i** (or **3i**) $\rightleftarrows$ **1i** $\rightleftarrows$ A is 0.25–0.75 kcal/mol higher than the energy barrier for the ring opening of **2i** (or **3i**) giving B and C.

Acknowledgment. We wish to acknowledge support of the work by the National Science Foundation and by the "Stiftung Fuer Stipendien auf dem Gebiete der Chemie, Basel, Switzerland."

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[11] J. C. Evans and G. Y.-S. Lo, *J. Amer. Chem. Soc.*, **88**, 2118 (1966).

[12] T. Koenig and R. Wolf, *ibid.*, **91**, 2569 (1969).

[13] V. J. Shiner, Jr., R. D. Fisher, and W. Dowd, *ibid.*, **91**, 7748 (1969); W. M. Schubert and P. H. LeFevre, *ibid.*, **91**, 7746 (1969); J. P. Schaefer, M. J. Dagani, and D. S. Weinberg, *ibid.*, **89**, 6938 (1967); K. T. Leffek, T. A. Llewellyn, and R. E. Robertson, *ibid.*, **82**, 6315 (1960); A. Streitwieser, Jr., and H. S. Klein, *ibid.*, **85**, 2759 (1963).

[14] The energy barrier (~15 kcal/mol) for the methide migration interconverting ions B and C is lower than that of the rearrangement of A into B and C.[15]

[15] D. M. Brouwer, *Recl. Trav. Chim. Pays-Bas*, **88**, 9 (1969).

[16] M. Saunders and E. L. Hagen, *J. Amer. Chem. Soc.*, **90**, 2436 (1968).

[17] M. Saunders and J. Rosenfeld, *ibid.*, **91**, 7756 (1969).

[18] E. L. Hagen, Ph.D. Thesis, Yale University, 1969.

[19] Fellow of the Alfred P. Sloan Foundation.

Martin Saunders,* [19] Mark H. Jaffe, Pierre Vogel
Department of Chemistry, Yale University
New Haven, Connecticut 06520

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Equilibrium Deuterium Isotope Effects in Systems Undergoing Rapid Rearrangements. Dimethyl-*tert*-butylcarbonium Ion and Cyclopentyl Cation

Sir:

In previous communications[1,2] we have shown that deuterium substitution in molecules undergoing rapid degenerate rearrangements can lift the degeneracy giving rise to nonstatistical equilibrium constants between the isomers and leading to additional splitting in the spectra. This occurs when the processes occurring *do not* rapidly mix all equivalent groups. If a group of hydrogens and deuteriums was *completely* scrambled by a rapid process (*i.e.*, all possible isomers rapidly achieved), then each proton would experience *the same* average environment and therefore all protons would have an identical chemical shift and yield only a single averaged peak. However, in spite of the fact that no additional splitting is expected, deuterium–hydrogen isotope effects can disturb the statistical probability of protons residing in the chemically different environments and thus produce a net chemical shift. In order to observe such a shift accurately, it is desirable to include, in the same sample, some of the undeuterated

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[1] M. Saunders, M. H. Jaffe, and P. Vogel, *J. Amer. Chem. Soc.*, **93**, 2558 (1971).

[2] M. Saunders and P. Vogel, *ibid.*, **93**, 2561 (1971).

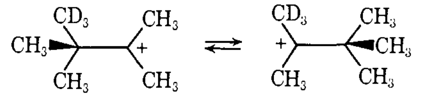
Table I[a]

	Temp, ±2°C			
	−92.7	−80	−68.5	−53
D, Hz	5.2 ± 0.1	4.8 ± 0.1	4.5 ± 0.2	4.1 ± 0.2
K (for $\Delta\omega = 210$ Hz)	1.55 ± 0.016	1.494 ± 0.013	1.455 ± 0.028	1.404 ± 0.026
At $T = -92°$	$(H_C - H_B)/3 = 52 \pm 2$ cal/mol			

[a] If $\Delta\omega$ were different, $H_C - H_B$ would be affected. $\Delta\omega = 190$ Hz yields 58 cal/mol and $\Delta\omega = 230$ Hz yields 47 cal/mol.

substance. We wish to report the first case of such an effect.

A 1:3 mixture of 2,2,3-trimethylbutyl-3-ium ion (A) and 98.3% deuterated 1,1,1-trideuterio-2,2,3-trimethylbutyl-3-ium ion (B ⇄ C) was prepared by distilling the corresponding chloride mixture into a solution of SbF_5 in SO_2ClF cooled to −100°. At $T < -40°$ the nmr spectrum[3] of this ion mixture displayed two singlets having the expected area ratio of 1:2.4 situated at τ 7.3 and separated by the temperature-dependent value D

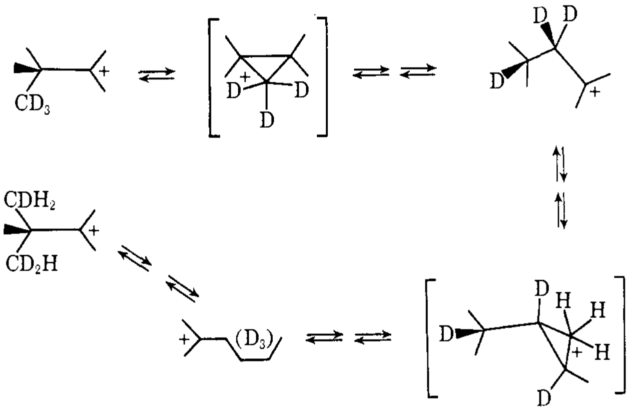


B C

(see Table I). The peak for B ⇄ C occurring at lower field than the peak for A indicates a ($\beta - \gamma$) differential deuterium isotope effect such that B is more stable than C. By measuring D, $K = {}^2/_3([B]/[C])$ can be calculated with the relation $K = (3\Delta\omega + 20D)/(3\Delta\omega - 30D)$ where $\Delta\omega$ is the chemical-shift difference between the different methyl groups in the absence of the rapid rearrangement. The methide shift that interconverts B and C is extremely fast even at low temperature;[4] thus $\Delta\omega$ cannot be measured directly. By using a $\Delta\omega$ value equal to the observed chemical-shift difference in *tert*-amyl cation[4,5] we obtained K and $H_C - H_B = RT \ln K$ values (see Table I) comparable to those measured for the dimethylisopropylcarbonium ion.[1,2] Thus it appears that the differential isotope effect for interchange of H and D between methyls with C–H's β and γ to tertiary cationic carbons is approximately the same in these two open-chain compounds (50–60 cal/mol per H–D pair). We have preliminary indications that analogous differential isotope effects in cyclic ions may be quite different.[6] Assuming the γ-deuterium isotope effect small[7] our values are comparable to those obtained in solvolysis experiments for open alkyl systems going through classical carbonium ion intermediates.[8]

The cyclopentyl cation is another case where complete mixing of the protons occurs.[9] Tetradeuteriocyclopentyl cation was prepared from the corresponding chloride *via* reduction of 2,2,5,5-tetradeuteriocyclopentanone[10] and examined in a mixture with undeuterated material. No resolution of the nmr singlets for the unlabeled and deuterated ions due to the combination of α-, β-, and γ-deuterium isotope effects on the carbonium ion has been observed between −92 and 0°. If the α-deuterium isotope effect had the same sign and comparable magnitude as the β-deuterium isotope effect[7a,d,11] the difference of chemical shifts between the monodeuterated and the unlabeled ions would be small. Strong evidence for the hyperconjugative origin of secondary kinetic β-deuterium isotope effects[12] has been gathered. In addition, the conformational dependence of these effects has been established.[13] Therefore a more appropriate model than open-chain alkyl ions is necessary for the ($\beta - \gamma$) deuterium isotope effects in the cyclopentyl cation.

By warming 1,1,1-trideuterio-2,2,3-trimethylbutyl-3-ium ion (B ⇄ C) to −30° the other six isomeric tertiary ions were formed.[4] At a somewhat slower rate, the amplitude of the nmr peak of B ⇄ C decreased relatively to the nondeuterated ion A. This can be explained by a scrambling process among protons from different methyl groups yielding, in the case of the system containing deuterium, ions having one dideuteriomethyl and one monodeuteriomethyl or three monodeuteriomethyl groups. These isomers would be expected to yield complex spectra in contrast to the singlet of B ⇄ C. In order to account for this H–D mixing the following mechanism can be drawn.



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[3] Nmr spectra were taken with a Varian HA-100 spectrometer; external TMS was used as lock signal and reference.

[4] G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, **89**, 4739 (1967); D. M. Brouwer, *Recl. Trav. Chim. Pays-Bas*, 87, 210 (1968).

[5] M. Saunders, E. L. Hagen, and J. Rosenfeld, *J. Amer. Chem. Soc.*, 90, 6882 (1968).

[6] Unpublished observations in this laboratory by D. Cox and C. Khoury.

[7] (a) V. J. Shiner, Jr., R. D. Fisher, and W. Dowd, *J. Amer. Chem. Soc.*, **91**, 7748 (1969); (b) W. M. Schubert and P. H. LeFevre, *ibid.*, **91**, 7746 (1969); (c) K. T. Leffek, J. A. Llewellyn, and R. E. Robertson, *ibid.*, **82**, 6315 (1960); (d) J. P. Schaefer, M. J. Dagani, and D. S. Weinberg, *ibid.*, **89**, 6938 (1967); (e) A. Streitwieser, Jr., and H. S. Klein, *ibid.*, **85**, 2757 (1963).

[8] M. Nikoletic, S. Borcic, and D. E. Sunko, *Tetrahedron*, **23**, 649 (1967); K. L. Servis, S. Borcic, and D. E. Sunko, *ibid.*, **24**, 1247 (1968).

[9] G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, **90**, 933 (1968); G. A. Olah and A. M. White, *ibid.*, **91**, 3954 (1969).

[10] We wish to thank Mr. Christopher Khoury for preparation of this sample.

[11] A. Streitwieser, Jr., and G. A. Dafforn, *Tetrahedron Lett.*, 1263 (1969).

[12] E. A. Halevi, *Progr. Phys. Org. Chem.*, **1**, 109 (1963); G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *J. Amer. Chem. Soc.*, **86**, 1360 (1964); P. Laszlo and Z. Welvart, *Bull. Soc. Chim. Fr.*, 2412 (1966); J. W. Timberlake, J. A. Thompson, and R. W. Taft, *J. Amer. Chem. Soc.*, **93**, 274 (1971).

[13] V. J. Shiner, Jr., and J. G. Jewett, *ibid.*, **86**, 945 (1964); **87**, 1382 (1965); V. J. Shiner, Jr., and J. S. Humphrey, Jr., *ibid.*, **85**, 2416 (1963); A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *ibid.*, **80**, 2326 (1958).

One change of branching level in the alkyl chain converts the hydrogens of a single group to methylene and methine protons.[1,2] On return from such a process *no* scrambling of hydrogen will have occurred. Therefore *two* reversible changes in branching level are necessary for any interchange of the H and D of two methyl groups. We therefore have evidence that this system can go through the numerous steps necessary to convert it to the singly branched level and then return.

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Martin Saunders,* Pierre Vogel
Department of Chemistry, Yale University
New Haven, Connecticut 06520

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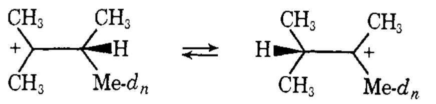
Equilibrium Deuterium Isotope Effects in Systems Undergoing Rapid Rearrangements. Methyl Interchange in Dimethylisopropylcarbonium Ion

Sir:

In the previous communication[1] we reported that substitution of a deuterium on a methyl group of the dimethylisopropylcarbonium ion gives rise to new splitting in the nmr spectrum resulting from lifting of the degeneracy between the two isomers (I ⇄ II) related by hydride transfer. We now report the preparation and observation of ions of the same structure containing two, three, four, five, and six deuterium atoms leading to the discovery of a hitherto unreported degenerate rearrangement.

By adding Grignard reagent made from 76% deuterated methyl iodide to 3-methyl-2-butanone we obtained the starting material for an ion mixture containing 44% 1,1,1-trideuterio- ($I_3 \rightleftarrows II_3$), 41% 1,1-dideuterio- ($I_2 \rightleftarrows II_2$), 13% 1-deuterio-2,3-dimethylbutyl-2-ium ion ($I_1 \rightleftarrows II_1$), and 2% unlabeled ion.[2]

The nmr spectrum (see Figure 1) of this ion mixture displays pairs of doublets separated by different temperature-dependent D_n values for the different isomers $I_n \rightleftarrows II_n$.



$I_n, n = 0,1,2,3$ $\quad$ $II_n, K_n = [I_n]/[II_n]$

On adding partially deuterated methyl Grignard reagent to isobutyl isobutyrate, we obtained the starting material for a mixture of the hexa-, penta-, tetra-, and trideuterio-2,3-dimethylbutyl-2-ium ions ($I_n \rightleftarrows II_n$; $n = 3, 4, 5, 6$).

Figure 1. 100-MHz nmr spectrum of $I_n \rightleftarrows II_n$; $n = 0, 1, 2, 3$, in SO_2ClF–SbF_5 at −96°.

The isotopic separations D_n[4] were found to be 14.5 ± 0.5, 30 ± 0.5, 46 ± 0.5 Hz at −76 ± 2° for $n = 1, 2, 3$, and 62.3 ± 0.3, 77.9 ± 0.4, 92.8 ± 0.3 Hz at −79 ± 2° for $n = 4, 5, 6$. From the chemical shift between the different methyl groups (estimated from corresponding frequencies in *tert*-amyl[1,3]) $\Delta\omega = 210$ Hz, we calculated $K_n = (\Delta\omega + D_n)/(\Delta\omega - D_n)$. We obtained $K_n = 1.148 \pm 0.006$, 1.33 ± 0.011, 1.561 ± 0.016 for $n = 1$–3 at −76° and 1.844 ± 0.019, 2.18 ± 0.028, 2.585 ± 0.041[5] for $n = 4$–6 at −79°. From these data, $H_{II_n} - H_{I_n}$ values were calculated. The values, normalized by dividing by n, were found to be 54.2 ± 2, 56.2 ± 1.6, 58.3 ± 1.3, 58.8 ± 1, 59.6 ± 1, and 61.3 ± 1 cal/mol for $n = 1$–6.

The nonlinearity of the $H_{II_n} - H_{I_n}$ values with n appears to be slightly outside of experimental error. Similar observations have been reported in solvolysis studies of *tert*-butyl-d_1, -d_2, -d_3, -d_6, and -d_9 chlorides.[6] On irradiating the methine proton at τ 5.4 ppm, decoupling was obtained simultaneously for all the pairs of doublets of $I_n \rightleftarrows II_n$. These latest observations confirm the hypothesis used to explain the spectra of the monodeuterated ion.[1]

The hexadeuterated ion enabled us to observe the interchange, invisible in unlabeled ion, of pairs of nonequivalent methyl groups (*via* secondary ion **2i**). The isomers D related by the rapid hydride shift are once more degenerate and therefore *one* doublet is observed at the position (τ 7.07 ppm) of the nondeuterated ion.

The nmr spectra (see Figure 2) of a hexadeuterio-2,3-dimethylbutyl-2-ium ion prepared by using a 98.3% deuterated starting material[7] showed that the methyl interchange occurred to equilibrium during the preparation of the ion at $T = -90°$. A similar observation was made with the ion mixture containing $I_n \rightleftarrows II_n$ with $n = 3, 4, 5$, and 6 deuterium atoms in which the nmr spectrum displayed very intense doublets at the positions of the 1-deuterio-2,3-dimethylbutyl-2-ium

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(1) M. Saunders, M. H. Jaffe, and P. Vogel, *J. Amer. Chem. Soc.*, **93**, 2558 (1971).

(2) The ion samples were prepared by using the corresponding chlorides according to the method described previously.[1,3] Nmr spectra were taken with a Varian HA-100 spectrometer; external TMS was used as lock signal and reference.

(3) M. Saunders and E. L. Hagen, *J. Amer. Chem. Soc.*, **90**, 2436 (1968).

(4) D_n is twice the separation between the low-field doublets and the doublet of the nondeuterated ion at τ 7.07 ppm.

(5) The reported errors on K take into account the uncertainty in the temperature (±2°).

(6) V. J. Shiner, Jr., B. L. Murr, and G. Heinemann, *J. Amer. Chem. Soc.*, **85**, 2413 (1963).

(7) We are grateful to Mr. M. Boni, summer student, for the preparation of the deuterated methyl iodide samples and to Mr. M. Steinberg for help in preparing some of the labeled compounds.