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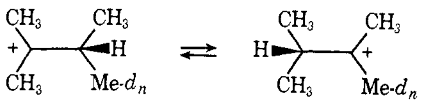
Equilibrium Deuterium Isotope Effects in Systems Undergoing Rapid Rearrangements. Methyl Interchange in Dimethylisopropylcarbonium Ion

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 ($\mathrm{I} \rightleftarrows \mathrm{II}$) 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- ($\mathrm{I}_3 \rightleftarrows \mathrm{II}_3$), 41% 1,1-dideuterio- ($\mathrm{I}_2 \rightleftarrows \mathrm{II}_2$), 13% 1-deuterio-2,3-dimethylbutyl-2-ium ion ($\mathrm{I}_1 \rightleftarrows \mathrm{II}_1$), 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 $\mathrm{I}_n \rightleftarrows \mathrm{II}_n$.



$\mathrm{I}_n, n = 0,1,2,3$ $\qquad$ $\mathrm{II}_n, K_n = [\mathrm{I}_n]/[\mathrm{II}_n]$

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 ($\mathrm{I}_n \rightleftarrows \mathrm{II}_n$; $n = 3, 4, 5, 6$).

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, $H_{\mathrm{II}_n} - H_{\mathrm{I}_n}$ 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.

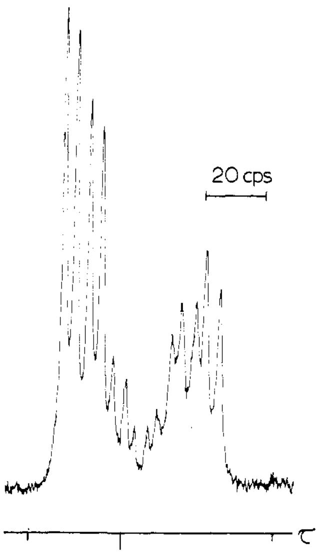


Figure 1. 100-MHz nmr spectrum of $\mathrm{I}_n \rightleftarrows \mathrm{II}_n$; $n = 0, 1, 2, 3$, in $\mathrm{SO_2ClF{-}SbF_5}$ at −96°.

The nonlinearity of the $H_{\mathrm{II}_n} - H_{\mathrm{I}_n}$ 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 $\mathrm{I}_n \rightleftarrows \mathrm{II}_n$. 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 $\mathrm{I}_n \rightleftarrows \mathrm{II}_n$ 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.

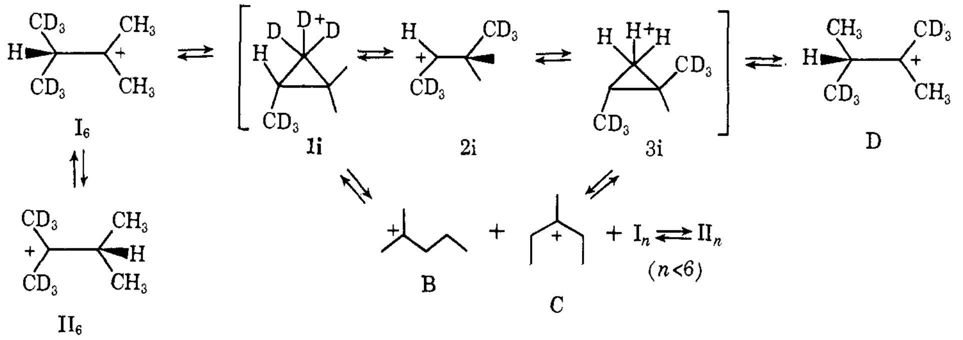
(3) M. Saunders and E. L. Hagen, *J. Amer. Chem. Soc.*, **90**, 2436 (1968).

(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.



ion $I_I \rightleftarrows II_I$ and unlabeled ion. The nmr spectrum of $I_1 \rightleftarrows II_1$ underwent temperature-dependent changes due to the methyl interchange process between −30 and +10°. A nmr line-shape analysis was performed to find the rate constant. The activation energy of the methyl interchange process was found to be 12.4–13.5 kcal/mol, log A = 12.5–13.5. In the nmr spectrum of $(I_6 \rightleftarrows II_6) \rightleftarrows D$ at equilibrium the measured area of the doublet at τ 7.07 ppm for D was 1.8 + 0.1 times the area of the doublet of the unsymmetrical ion $(I_6 \rightleftarrows II_6)$ at $T = -60$ to $-90°$.

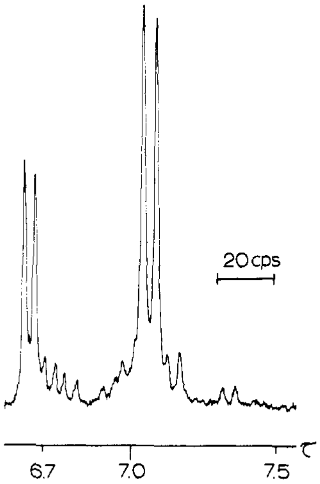


Figure 2. 100-MHz nmr spectrum of $I_6 \rightleftarrows II_6 \rightleftarrows D$ in SO_2ClF–SbF_5 at −60°. Due to incomplete labeling some $I_5 \rightleftarrows II_5$ and $I_4 \rightleftarrows II_4$ are present.

The deviation from the expected statistical ratio of 2 can be understood by considering that the isomer I_6, which has the six deuterium atoms away from the positive charge, is favored over II_6 ((I_6/II_6) = 2.584 at −79°). The average energy of the equilibrium mixture is lower than that of the symmetrical structure D. Introduction of this factor using a computer program written for this purpose yielded a predicted ratio of 1.8. We believe that this is the first observation of an equilibrium constant which is significantly affected by an isotope effect between isomers interconverted by a much more rapid process on one side of the equilibrium. This discrepancy from the statistical factor provides an independent method for obtaining the isotope effect. In this instance, it is less accurate than the use of isotopic splitting in the nmr spectrum, but in other cases it might be the only tool available.

No exchange between methyl and methine hydrogens was observed at $T < -50°$. On warming to −40°, the nmr peaks for the ions B and C appeared at a comparable rate as peaks at the positions of $I_5 \rightleftarrows II_5$ and $I_1 \rightleftarrows II_1$, and later at the positions of $I_4 \rightleftarrows II_4$ and $I_2 \rightleftarrows II_2$. This is consistent with a process accomplishing an overall pairwise interchange of the methine hydrogen with a hydrogen of *one* methyl group.[1] More deep-seated rearrangement could lead directly from $I_6 \rightleftarrows II_6 \rightleftarrows D$ to *any* isomer $I_n \rightleftarrows II_n$, $n < 6$. The mechanisms discussed would require two changes in branching level of the alkyl chain[8] where hydrogens from *two* methyl groups are converted to methylene and methine protons and scrambled before return to the starting material.

The observation that interchange of methyl groups $(I_6 \rightleftarrows II_6 \rightleftarrows D)$ is more rapid than any other process by a factor of 10–500 (at 0°) may be *most simply* explained by the supposition that the corner-protonated cyclopropane geometry **1i** or **3i** which is achieved in the course of methyl interchange is prevented from undergoing corner-to-corner proton migration by a barrier of several kilocalories/mole. This point of view suggests that the edge-protonated cyclopropane geometry may be less stable than the corner-protonated cyclopropane in this case.

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

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[8] M. Saunders and J. Rosenfeld, *J. Amer. Chem. Soc.*, **91**, 7756 (1969); H. Hogeveen and C. J. Gaasbeek, *Recl. Trav. Chim. Pays-Bas*, **88**, 1305 (1969); D. M. Brouwer, *ibid.*, **88**, 9 (1969).

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Cycloaddition Reactions of Alkenylidenecyclopropanes

Sir:

Several examples of the participation of the strained σ bonds of cyclopropane derivatives in cycloaddition reactions have been recently reported.[1-3] Bicyclo[1.1.0]butanes[2] and bicyclo[2.1.0]pentanes[1] react with reactive dienophiles in $_\sigma2 + _\pi2$ cycloaddition reactions *via* diradical intermediates. Examples of the participation of strained σ bonds of a cyclopropane in 4 + 2 cycloaddition reactions are less well known. α-Cyclo-

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[1] P. G. Gassman and G. D. Richmond, *J. Amer. Chem. Soc.*, **92**, 2090 (1970); **90**, 5637 (1968); *Chem. Commun.*, 1630 (1968); P. G. Gassman and K. T. Mansfield, *J. Amer. Chem. Soc.*, **90**, 1524 (1968); *Chem. Commun.*, 391 (1965); P. G. Gassman, K. T. Mansfield, and T. J. Murphy, *J. Amer. Chem. Soc.*, **91**, 1684 (1969).

[2] A. Cairncross and E. P. Blanchard, Jr., *ibid.*, **88**, 496 (1966); M. Pomerantz, G. W. Gruber, and R. N. Wilke, *ibid.*, **90**, 5040 (1968).

[3] C. D. Smith, *ibid.*, **88**, 4273 (1966).