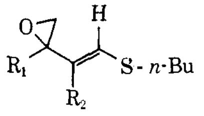
butyllithium in hexane. After standing 15 min at $-20°$ this pale yellow mixture was cooled to $-70°$ and was treated with a solution of 1.49 g (5×10^{-3} mol) of **5** in 15 ml of anhydrous DME. After 1 hr at $-70°$ the yellow mixture was treated with 200 ml of water and extracted with four portions of ether. The ethereal extracts were dried over sodium sulfate, filtered, and evaporated, and the residue was then allowed to stand at room temperature for 24 hr. After this time the product was dissolved in 20 ml of ether and stirred vigorously with 1.30 g of mercuric sulfate for 30 min. This mixture was dried, filtered, and evaporated to afford a black residue which was dissolved in 5 ml of pentane and filtered through 40 g of Florisil. The Florisil was eluted with an additional 300 ml of pentane. Evaporation of the pentane eluents afforded 0.860 g (78%) of 3-*n*-hexyl-4-*n*-pentylfuran (**6**) as a clear oil [ir (film) 8.7, 9.5, and 11.4 μ; uv max 216 nm (ϵ 3300); nmr (CCl_4) 0.8–1.8 (m, 20), 2.2–2.5 (t, 4), 7.0 (s, 2)]. Further elution with 50 ml of ether afforded <1% of starting material **5** and ~12% of unidentified, dark, oily material.

In most instances the product furan is accompanied by considerably more (~20–30%) unreacted *n*-butylthiomethylene derivative as the principal and only recognizable contaminant. Despite extensive efforts we have as yet been unable to find a method to ensure complete reaction. Aside from this unresolved difficulty the furan synthesis is quite clean.

The reaction of *n*-butylthiomethylene ketones with $CH_2S(CH_3)_2$ very probably proceeds by way of intermediates **7** and **8**, analogous to those proposed by Harris[3] in the case of enol ethers of 1,3-dicarbonyl compounds. The product initially formed, before standing for 24 hr, has been found in case V to exhibit nmr spectral properties [nmr (CCl_4) 5.4 (d, J = 15 Hz) and 6.2 ppm (d, J = 15 Hz)] consistent with an intermediate epoxide **7** ($R_1 = CH_3(CH_2)_8$; R_2 = H). If the final treatment with mercuric sulfate is omitted, dihydrofuran derivatives **8** have been detected spectrally, and **9** has been isolated as a pure oil by preparative tlc (ir (film) 5.80 (w), 5.95 (w), and 9.9 μ (s); nmr (CCl_4) 0.7–2.3 (m, 21), 2.47 (t, 2), 4.38 (br s, 2), and 5.65 ppm (br s, 1); M^+ (*m/e*) 266.1706 (calcd 266.1704)].



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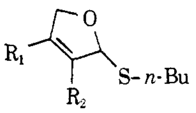

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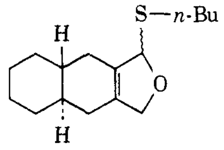

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Intramolecular Hydride Shifts in Carbonium Ions

Sir:

Rapid 1,2-hydride shifts are commonly accepted in explanation of a number of rearrangement reactions and in accounting for nmr spectra of several stable carbonium ions. Besides these steps 1,3, 1,4, and 1,5 hydride shifts have also been invoked in a variety of reactions.[1] We wish to report the observation of the nmr spectra of the 2,4-dimethyl-2-pentyl (I), the 2,5-dimethyl-2-hexyl (II), and the 2,6-dimethyl-2-heptyl (III) cations which provide the first *direct* and *quantitative* data on the occurrence of these shifts in the ions themselves.

The ions were each prepared *in vacuo* by forming molecular beams of the corresponding alkyl chloride and antimony pentafluoride and impinging them on a surface cooled to liquid nitrogen temperature.[2] The resulting mixture was dissolved in SO_2ClF at $-115°$ and was transferred to nmr tubes which were then sealed.

The nmr spectrum at $-114°$ for ion I is shown in Figure 1A and is similar to that described by Brouwer.[3] The methylene protons appear as a broad peak at τ 5.94, and the α- and γ-methyl protons give rise to a broadened singlet and doublet at τ 6.13 and 8.68, respectively. Spin decoupling showed the unresolved multiplet at τ 6.92 to be due (at least in part) to the methine proton. In addition, traces of *tert*-butyl (sharp singlet at τ 6.08) and 2,3-dimethylpentyl cation (peaks at τ 7.20, 7.35, and 8.45) were also present.

Upon warming, the methyl peaks of ion I broaden and at approximately $-90°$ coalesce to give a single peak centered near τ 7.4. In this temperature range, the methylene protons undergo no noticeable change. The reaction therefore cannot proceed *via* successive 1,2-hydride shifts. A complete line-shape analysis, assuming the 1,3-hydride shift, yields an activation energy of 8.5 ± 0.1 kcal/mol with a log A of 12.6 ± 0.1.

The spectrum of carbonium ion II (Figure 1B) at $-95°$ consists of peaks at τ 5.88 and 8.13 for the α- and β-methylene protons and τ 6.18 and 8.80 for the α- and δ-methyl protons. As reported by Brouwer,[3] line broadening due to hydride shifts was absent up to $-55°$. (Above this temperature, the spectrum becomes more complicated due to rearrangement to the isomeric tertiary cations.) However, by using the magnetization transfer technique,[4] it was shown that a 1,4-hydride shift does occur in the ion, and that the energy required for the transfer is in the vicinity of 12–13 kcal/mol. This

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[1] J. L. Fry and G. J. Karabatsos in "Carbonium Ions," Vol. 2, G. Olah and P. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, p 521.

[2] M. Saunders and D. Cox, "A Molecular Beam Technique for Preparing Carbonium Ions," submitted for publication, *J. Amer. Chem. Soc.*

[3] D. M. Brouwer and J. A. van Doorn, *Recl. Trav. Chim. Pays-Bas*, **88**, 573 (1969).

[4] R. A. Hoffmann and S. Forsen, *Progr. Nucl. Magn. Resonance Spectrosc.*, **1**, 15 (1966).

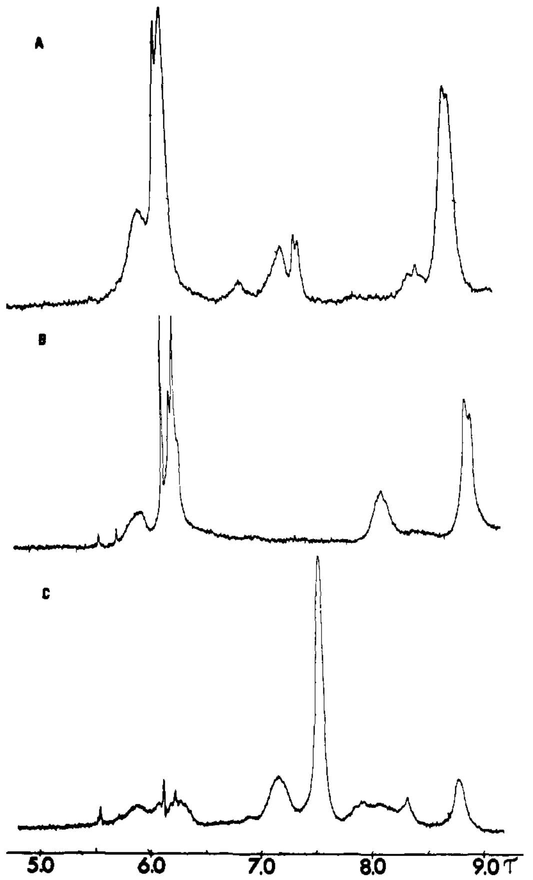

Figure 1. 100-MHz spectra of (A) 2,4-dimethyl-2-pentyl cation at -114°, (B) 2,5-dimethyl-2-hexyl cation at -95°, (C) 2,6-dimethylheptyl cation at -95°.

information was obtained by strong irradiation at -60° of the α-methyl resonance which caused a marked decrease in the intensity of the δ-methyl peak and *vice versa.*

Ion III was more difficult to obtain than ion I or II. Most of the attempts at preparation led to oxidation to the ditertiary cation. This dication is characterized by an intense peak at τ 5.9 and has previously been reported by Olah.[5] When ion I was successfully prepared its spectrum was less well resolved than those for the lower homologs. The interesting feature in the spectrum at -95° (Figure 1C) is the broad peak centered at τ 7.5 which is at the average of the shifts expected for the α and ϵ methyls. We take this as evidence for a rapidly occurring degenerate 1,5-hydride transfer in the ion with an activation energy of no more than 6 or 7 kcal/mol. Upon heating above -85°, this peak rapidly disappears with the appearance of the peak for the dication at τ 5.9.

Several mechanisms for the 1,3-hydride shift can be imagined (Figure 2). Consecutive 1,2 shifts (Figure 2B) are inconsistent with the observed spectral changes as previously noted. The 1,3 shift could conceivably go *via* a protonated cyclopropane (Figure 2C). However, the occurrence of the 1,4- and 1,5-hydride transfers (the latter requiring *less* energy than the 1,3 shift) in ions where no such intermediate can be considered argues against this pathway. Furthermore, cases in which the intermediacy of such protonated cyclopropanes has been firmly established[6–8] indicate that the transition state for corner-to-corner migration in this kind of intermediate lies at least 15 kcal higher in energy than a tertiary ion. The process which converts the 2,4-dimethyl-2-pentyl cation into the 2,3,3-dimethyl-2-butyl cation requires 17 kcal of activation energy[9] and most likely involves a protonated cyclopropane.

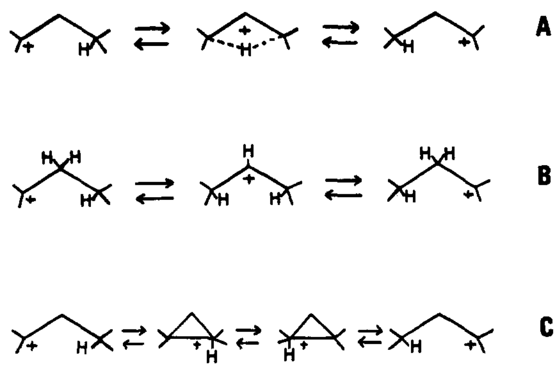

Figure 2. Mechanisms considered for the 1,3 hydride shift: (A) simple 1,3 shift, (B) consecutive 1,2 shifts, (C) hydride shift *via* protonated cyclopropane.

For these reasons, it seems likely that the process under observation in all of these ions is simply a hydride transfer between the two tertiary centers with no direct bonding between the carbons at these centers (Figure 2A).

The magnitude of the energy barriers for the hydride shifts (1,4 > 1,3 > 1,5) is likely a reflection of the steric and conformational factors operative in these systems. It is interesting that the order of rates found in these acyclic systems is the same as the order of rates for reaction involving hydride shifts in medium-sized rings which have been studied by other techniques.[10,11]

Acknowledgment. The stimulation for this work was the prepublication disclosure by Professor D. Arigoni of several reactions induced by polyphosphoric acid which were convincingly demonstrated to occur *via* 1,5 hydride shifts (see Q. Branca and D. Arigoni, *Chimia*, **23**, 189 (1969), and Q. Branca, Dissertation, Federal Institute of Technology, Zurich, 1970). This work was supported by a grant from the National Science Foundation.

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[5] J. M. Bollinger, C. A. Capas, K. J. Friday, M. L. Woolfe, and G. A. Olah, *J. Amer. Chem. Soc.*, **89**, 156 (1967).

[6] M. Saunders, E. Hagen, and J. Rosenfeld, *ibid.*, **90**, 6882(1968).

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

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

[9] D. M. Brouwer and J. M. Oelderich, *Recl. Trav. Chim. Pays-Bas*, **87**, 721 (1969).

[10] V. Prelog and J. G. Traynham in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Wiley-Interscience, New York, N. Y., 1963, p 593.

[11] A. E. Cope, M. M. Martin, and M. A. McKervey, *Quart. Rev., Chem. Soc.*, 20, 119 (1966).

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Circular Differential Raman Spectra of Carvone

Sir:

Recently, Bosnich, *et al.*,[1] reported the observation of Raman "circular dichroism" or circular differential

[1] B. Bosnich, M. Moskovits, and G. A. Ozin, *J. Amer. Chem. Soc.*, **94**, 4750 (1972).