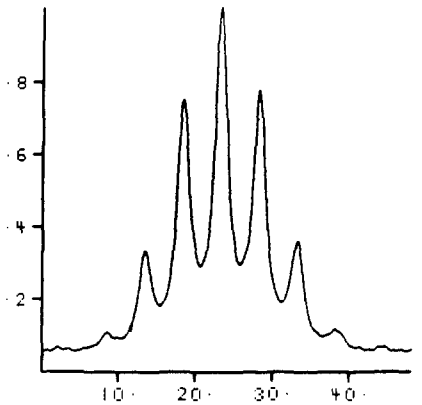


Figure 1. Experimental isopropyl cation septet at −11°.

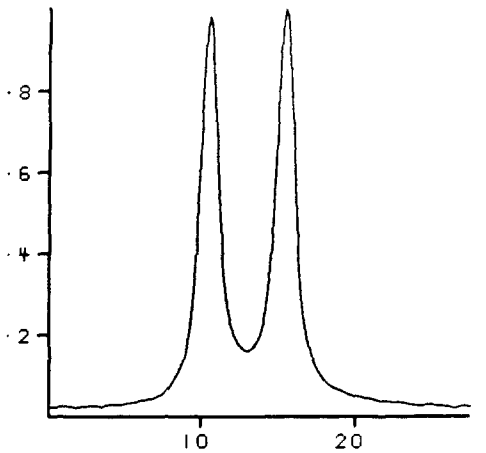


Figure 2. Experimental isopropyl cation doublet at −5°.

changed in a manner indicating interchange between the two types of protons present. The simplest mechanism for this interchange is reversible rearrangement to *n*-propyl cation. This mechanism leads to the matrix of transition probabilities[4]

$$\begin{vmatrix} & 1/4 & 1/4 \\ 1/12 & & 5/24 \\ 1/12 & 5/24 & \end{vmatrix}$$

where the matrix elements are the probabilities that a proton at the *i*th frequency will go to the *j*th frequency when a single step of the reaction considered occurs. Site 1 is all of the lines of the downfield multiplet taken together, and sites 2 and 3 are the frequencies of the methyl doublet. For example, the matrix element $^5/_{24}$ arises from the product of factors $^1/_2$, $^5/_6$, and $^1/_2$ originating from the probabilities that a *different* proton returns from the center carbon of *n*-propyl than the one which migrated there, that the proton considered is one of the five methyl protons which did *not* interchange with the proton which had been in the center, and that the proton which exchanged places with the central proton had a *different* spin orientation, respectively. Broadening due to natural line width was introduced into the calculated spectra using the digitally recorded sharpest spectrum of the upfield doublet. The downfield half of the downfield peak and the upfield half of the upfield peak were combined, and a convolution[1,5] was performed on the calculated curve with this composite line shape. Calculated curves for the doublet agreed satisfactorily with the experimental spectra over the temperature range examined. We could not fit the observed spectra with mechanisms involving intermolecular hydrogen exchange with intermediate olefin formation. Olefin formation would also be expected to lead rapidly to the stable hexyl ions by addition of more cation. Fitting the rates obtained to the Arrhenius equation gave $E_a = 16.4 \pm 0.4$ kcal/mol and $\log A = 13.2 \pm 0.3$, where errors reported are standard deviations.

Using the proposed mechanism, the interpretation of the observed activation energy is the enthalpy difference between isopropyl and *n*-propyl ions plus E_a for the reverse reaction. In a similar way the 15.3-kcal/mol activation energy obtained from studying the rearrangement of *t*-amyl cation[1] was assigned to the energy difference between secondary and tertiary ions, plus E_a for the secondary–secondary Wagner–Meerwin shift rearrangement. From what is known, both the exothermic primary–secondary and degenerate secondary–secondary processes have low barriers. Therefore, within the uncertainties of the barriers for these rapid steps, it may be concluded that the energy difference between simple primary and secondary ions is approximately the same as that between secondary and tertiary ions.

A further process which might be considered is rearrangement of the intermediate *n*-propyl cation to protonated cyclopropane before return to isopropyl. Proton scrambling in protonated cyclopropanes is well documented, so complete mixing could result before return to *n*-propyl.[6,7] The protonated cyclopropane might be formed *via* *n*-propyl cation or conceivably directly from isopropyl by simultaneous ring closure and hydride shift. Complete proton scrambling *via* this mechanism predicts line shapes identical with those of the first mechanism proposed since the elements in the probability matrix are the same except that they are all multiplied by a factor of $^{12}/_7$. Alteration of the preexponential term in the Arrhenius equation by this factor would not be experimentally noticeable, and the activation energy would be unaffected.

Acknowledgment. We thank the National Science Foundation for support of this work.

(4) M. Saunders in "Magnetic Resonance in Biological Systems," A. Ehrenberg, Ed., Pergamon Press, Ltd., Oxford, 1967, p 85.
(5) C. S. Johnson, Jr., *Advan. Magnetic Resonance*, **1**, 33 (1965).
(6) R. L. Baird and A. A. Aboderin, *J. Am. Chem. Soc.*, **86**, 252 (1964).
(7) C. C. Lee and L. Gruber, *ibid.*, **90**, 3775 (1968).
(8) Fellow of the Alfred P. Sloan Foundation.
(9) National Institutes of Health Predoctoral Fellow

Martin Saunders,[8] Edward L. Hagen[9]
Yale University
New Haven, Connecticut 06520
Received September 3, 1968

Rearrangement Reactions of Secondary Carbonium Ions. Protonated Cyclopropane Intermediates Formed from *sec*-Butyl Cation

Sir:

Protonated cyclopropane intermediates undergoing rapid rearrangements have been invoked in accounting

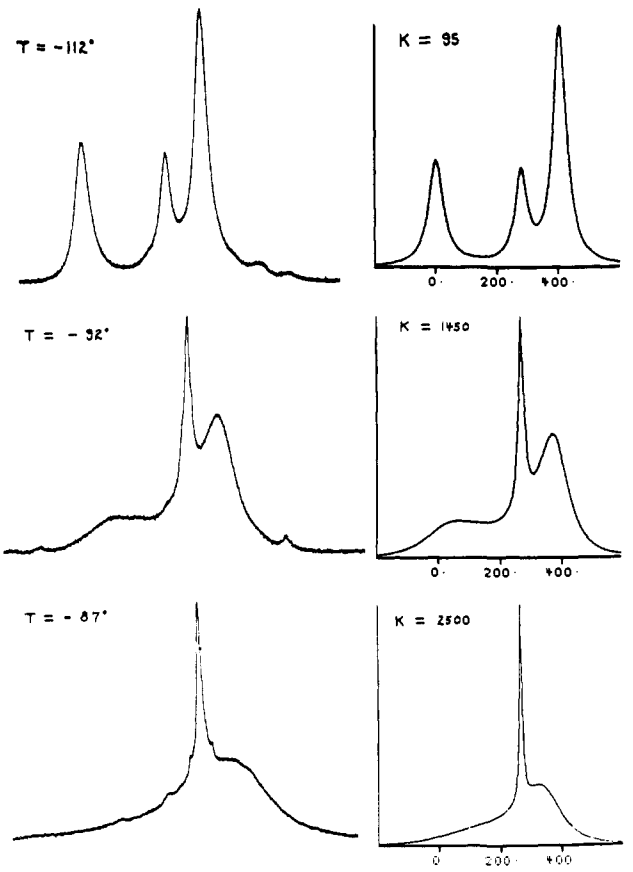


Figure 1. Experimental (left) and calculated (right) line shapes for *sec*-butyl cation. The *t*-butyl peak (center) was added to the calculated shapes to make comparison easier. The temperatures and rate constants are shown.

for hydrogen–deuterium scrambling on solvolysis of cyclopropane in deuterio acid.[1] We should like to report evidence obtained by direct observation of stable solutions of *sec*-butyl cation for intermediacy of such species in carbonium ion rearrangements.

The spectrum of secondary butyl cation has not previously been described. Olah, *et al.*, have reported that attempted preparation from 2-fluorobutane with SbF_5,[2] *n*-butane with SbF_5–HSO_3F,[3] or butanol-2 with SbF_5–HSO_3F,[4] led directly to *t*-butyl cation. We have found that, if the reaction is performed at −110° on the vacuum line, the spectra shown in Figures 1 and 2 are obtained as a function of temperature. The center peak is *t*-butyl cation which is formed in the preparation. We assign the two remaining peaks at low temperatures to the 2 and 3 and 1 and 4 protons of *sec*-butyl cation averaged by very rapid 3,2-hydride shifts. The similar hydride shift in 2,3-dimethyl-2-butyl cation has, so far, been too rapid to measure.[5] A lower limit of 200,000 sec^{-1} on the 3,2-hydride shift rate at −112° leading to an approximate upper limit of 6 kcal/mol on E_a can be

$$CH_3\overset{+}{C}HCH_2CH_3 \rightleftharpoons CH_3CH_2\overset{+}{C}HCH_3$$

assigned by using predicted peak frequencies for the 1, 2, 3, and 4 hydrogens based on those in isopropyl

(1) R. L. Baird and A. A. Aboderin, *J. Am. Chem. Soc.*, **86**, 252 (1964).
(2) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *ibid.*, **86**, 1360 (1964).
(3) G. A. Olah and J. Lukas, *ibid.*, **89**, 2227 (1967).
(4) G. A. Olah, J. Sommer, and E. Namanworth, *ibid.*, **89**, 3576 (1967).
(5) G. A. Olah and J. Lukas, *ibid.*, **89**, 4739 (1967).

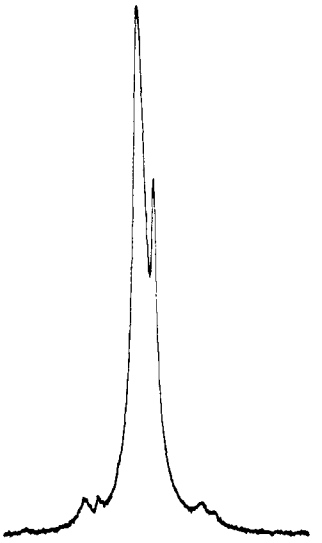


Figure 2. Nmr spectrum of the *sec*-butyl cation at about −55° showing the two low-temperature peaks totally coalesced. The peak on the right is that of *t*-butyl cation.

and *t*-amyl[2] and employing a normal value for log *A*. These frequencies also predict the shift between the upfield and downfield lines to be 4.1 ppm, agreeing well with the experimental 4.02 ppm. As the sample is warmed from −110 to −40°, the changes which are shown occur in the spectrum. The *t*-butyl peak is unchanged over this temperature range except that it is broadened by the viscosity of the solvent at lower temperatures. Above −40° fairly rapid conversion of *sec*-butyl cation to *t*-butyl cation occurs.

The rapid process which coalesces the two peaks in *sec*-butyl might be ascribed to reversible rearrangement to the primary ion, one of the possible mechanisms for isopropyl.[6] However, this mechanism provides no explanation for the barrier here being so much lower. An alternative mechanism, which we favor, is cyclization to a protonated methylcyclopropane intermediate (either edge or corner protonated), followed by proton scrambling rearrangement and reopening to *sec*-butyl cation. A similar rearrangement process has been suggested by Brouwer[7] to explain the acid-induced carbon interchange process observed in *n*-butane. Simultaneous hydrogen shift and ring opening, if it occurred readily in protonated methylcyclopropane, would give the *t*-butyl cation leading to rapid conversion of *sec*-butyl cation to the more stable tertiary ion and therefore must be prevented by a substantial activation barrier. The rate observed for conversion of *sec*-butyl to *t*-butyl at −41° would lead to a barrier of roughly 18 kcal/mol assuming a normal log *A*. The similarity of this value to the E_a for proton interchange in isopropyl cation is consistent with the view that both processes pass through a similar transition state, either one leading to a primary ion or the simultaneous process considered here.

We have been able to calculate line shapes for *sec*-butyl as a function of rate assuming protonated methylcyclopropane intermediates (Figure 1). Proton scrambling in the protonated methylcyclopropane might be

(6) M. Saunders and E. L. Hagen, *ibid.*, **90**, 6881 (1968).
(7) D. M. Brouwer and J. M. Oelderik, Abstracts of Papers, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, No. R58.

complete or incomplete before reopening to *sec*-butyl ion, but the maximum effect on the rate constants resulting from this difference is a factor of $^3/_2$, and therefore only an insignificant change in the log A term would result. Assuming complete mixing and fitting the rates to the Arrhenius equation yielded $E_a = 7.5 \pm 0.1$ kcal/mol and log $A = 12.3 \pm 0.1$, where errors reported are standard deviations.

Attempted formation of a secondary amyl cation from either 2-chloropentane or 1-chloropentane under the same conditions has so far led only to *t*-amyl cation. Cyclization of the initial secondary ion to protonated dimethylcyclopropane here could, after proton shifts, lead to a species which could open to the 3-methyl-2-butyl cation, an isomeric secondary ion only a single hydride shift away from the *t*-amyl cation.[8] The methylcyclopropane intermediate can lead to the *t*-butyl cation by a similar opening, only by first forming the high-energy primary isobutyl cation.

Acknowledgment. We thank the National Science Foundation for support of this work.

(8) M. Saunders and E. L. Hagen, *J. Am. Chem. Soc.*, **90**, 2436 (1968).
(9) Fellow of the Alfred P. Sloan Foundation.
(10) National Institutes of Health Predoctoral Fellow.

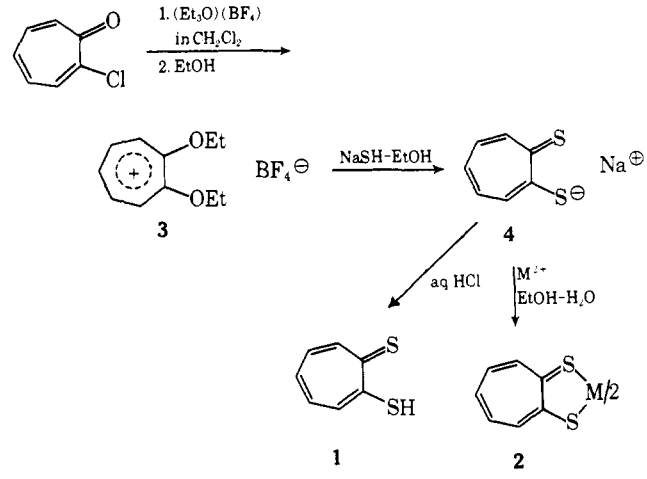
Martin Saunders,[9] Edward L. Hagen,[10] Jerold Rosenfeld[10]
Yale University
New Haven, Connecticut 06520
Received September 3, 1968

Dithiotropolone (2-Mercaptocycloheptatrienethione) and Its Metal Complexes

Sir:

The preparation of tropolone in 1950[1] has been followed by the synthesis of a variety of monoprotic, chelating, 1,7-disubstituted 1,3,5-cycloheptatrienes, *viz.*, the aminotropones,[2] aminotroponeimines,[2b,3] aminothiotropones,[3b,4,5] and 2-mercaptotropone.[6] These compounds, of much interest in their own right, form stable metal complexes[2b,7] whose structural and electronic properties are of considerable current significance.[7] This information, together with continuing research on sulfur-bonded chelates with nonclassical electronic ground states,[8] renders dithiotropolone (**1**) and its complexes attractive synthetic objectives. We report here the synthesis of hitherto unknown **1** and a series of its bis complexes **2**.

2-Chlorotropone,[2a] obtained from tropolone,[9] was treated with 1 equiv of triethyloxonium tetrafluoroborate in dichloromethane solution for 20 hr at ~25°. Removal of solvent followed by refluxing of the resultant solid in absolute ethanol for 2 hr and recrystallization of the product from THF yielded 1,2-diethoxytropylium tetrafluoroborate[10] (**3**) (65%): mp 115–116°, nmr ($CDCl_3$) τ 8.18 (triplet, 6, CH_3), 5.17 (quartet, 4, CH_2), 1.33 (multiplet, 5, ring-H). Treatment of **3** with 2 equiv of sodium hydrosulfide in ethanol followed by 15 min of stirring at ~25° and removal of solvent afforded sodium dithiotropolonate (**4**) as a reddish brown solid which was not further purified. Anaerobic reaction of **4** with dilute aqueous hydrochloric acid and slow sublimation (35°, 10^{-4} mm) of the impure product gave deep red-brown, crystalline **1**[11] in low yield: mp 72–73°; nmr ($CDCl_3$) τ 2.95 (multiplet, 3, ring-H), 1.57 (multiplet, 2, ring-H), 0.76 (1, SH); mass spectrum (70 eV) *m/e* (relative intensity) 154 (100, P), 153 (86), 121 (55), 110 (35), 90 (32), 89 (31), 77 (52). Dithiotropolone is



less stable than tropolone and should be handled in the absence of air.

Dithiotropolonate metal complexes, $M(SST)_2$, are readily prepared from aqueous ethanol solutions of **4** and the appropriate metal salt. As a class the complexes are stable to air and moisture, intensely colored, very slightly soluble in noncoordinating solvents, and somewhat more soluble in pyridine and DMF. Complexes of Ni (black), Pd (violet), Pt (black), Cu (greenish black), Zn (red), and Cd (red-brown) have been obtained in 25–50% yield based on **3**. All are diamagnetic except for $Cu(SST)_2$ whose isotropic epr parameters ($\langle g \rangle = 2.041$, $\langle a \rangle = 78$ G (^{63}Cu), CH_2Cl_2 solution) are entirely typical of spin-doublet [Cu–S_4] complexes.[8b] The mass spectra of the Ni and Zn complexes evidence prominent parent ion peaks and rather similar fragmentation patterns leading to $MC_7H_5S_2^+$ and, like **1**, $C_7H_5S_2^+$, $C_7H_5S^+$, $C_7H_5^+$, and $C_6H_5^+$ among the major products.

That these complexes do possess the dithiotropolonate structure **2** rather than that of the analytically indistinguishable rearrangement products **5** has been demonstrated by comparison of certain properties with those of bisdithiobenzoate complexes, $M(dtb)_2$, which

(1) For a recent summary of tropolone chemistry, *cf.* D. Lloyd, "Carbocyclic Non-Benzenoid Aromatic Compounds," Elsevier Publishing Co., Amsterdam, 1966, Chapter VI.
(2) (a) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **74**, 5683 (1952); (b) W. R. Brasen, H. E. Holmquist, and R. E. Benson, *ibid.*, **83**, 3125 (1961); (c) N. Soma, J. Nakazawa, T. Watanabe, Y. Sato, and G. Sunagawa, *Chem. Pharm. Bull.* (Tokyo), **13**, 457 (1965).
(3) (a) H. Nakao, *ibid.*, **13**, 810 (1965); (b) N. Soma, J. Nakazawa, T. Watanabe, Y. Sato, and G. Sunagawa, *ibid.*, **13**, 819 (1965).
(4) W. R. Brasen and R. E. Benson, *J. Am. Chem. Soc.*, **83**, 3135 (1961).
(5) T. Nozoe and K. Matsui, *Bull. Chem. Soc. Japan*, **34**, 1382 (1961).
(6) T. Nozoe, M. Sato, and K. Matsui, *Proc. Japan Acad. Sci.*, **29**, 22 (1953); *Sci. Rept. Tohoku Univ., First Ser.*, **37**, 211 (1953).
(7) (a) E. L. Muetterties, H. Roesky, and C. M. Wright, *J. Am. Chem. Soc.*, **88**, 4856 (1966); (b) W. R. McClellan and R. E. Benson, *ibid.*, **88**, 5165 (1966); (c) D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *ibid.*, **85**, 397 (1963).
(8) (a) R. H. Holm, A. L. Balch, A. Davison, A. H. Maki, and T. E. Berry, *ibid.*, **89**, 2866 (1967), and references therein; (b) J. A. McCleverty, *Progr. Inorg. Chem.*, in press.
(9) H. C. Stevens, D. A. Reich, D. R. Brandt, K. R. Fountain, and E. J. Gaughan, *J. Am. Chem. Soc.*, **87**, 5257 (1965).
(10) All new compounds gave satisfactory elemental analyses except for **4**, whose purity was not assessed.
(11) *Anal.* Calcd for $C_7H_6S_2$: C, 54.51; H, 3.92; S, 41.57. Found: C, 54.51; H, 3.92; S, 41.56.