have produced cystine, tyrosine, and phenylalanine. No such fragments were found, though the cleavage of peptide chains undoubtedly occurred. The fragments separated from the digestion products and containing all the amino acids of lysine-vasopressin and the one fragment that had no phenylalanine corresponded in principle to the expected (theoretical) cleavage products of the antiparallel dimer.

The results of chymotryptic hydrolyses are thus compatible with a cylic antiparallel structure. Structural studies (J. Meienhofer, Deutsches Wollforschungsinstitut, Aachen, Germany) using a C^{14}-labeled cross-linking reagent, 1,5-difluoro-2,4-dinitrobenzene (FFDNB),[12] gave inconclusive results. A negligible content of 2,4-dinitrophenylene-1,5-bis-Nϵ-lysine[13] among the products of the reaction followed by total hydrolyses pointed to antiparallel structure. Other reaction products[13] of cross linking with FFDNB were identified but offered no arguments in favor of parallel or antiparallel structure due to the difficulty in estimating distances between reactive centers and possibilities of "folding-back" of the tripeptide side chain at the proline residue.

(12) H. Zahn, H. D. Weigmann, and E. Nischwitz, *Kolloid-Z.*, 179, 49 (1961).
(13) H. Zahn and J. Meienhofer, *Makromol. Chem.*, 26, 126 (1958).

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Carbonium Ion Salts. X. Hydroxytropenium Iodide Monohydrate[1]

Sir:

Many carbonium ion salts react rapidly with moisture. Some deliquesce with decomposition as do the tropenium halides,[2-4] and most of the less stable ones react irreversibly to form carbinols or olefins. The three carbonium ion hydrates reported to date[5-7]

(1) This work was supported by the Petroleum Research Fund and the National Science Foundation.
(2) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, 76, 3203 (1954).
(3) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *ibid.*, 79, 4557 (1957).
(4) K. M. Harmon, F. E. Cummings, D. A. Davis, and D. J. Diestler, *ibid.*, 84, 3349 (1962).
(5) M. Gomberg and H. R. Snow, *ibid.*, 47, 198 (1925), report a dihydrate of 4,4',4''-trihydroxytriphenylcarbonium chloride.
(6) M. E. Vol'pin, Yu. D. Korsehkov, and D. N. Kursanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 560 (1959), report a monohydrate of diphenylhydroxycyclopropenium bromide.

are all of salts of hydroxy cations; this suggests that hydrogen bonding from the substituent hydroxyl to hydrate water may play an important role in the formation of such hydrates, but no spectral nor thermodynamic evidence for such hydrogen bonding has been reported.

Hydroxytropenium iodide is prepared in 73.5% yield by treatment of tropone with anhydrous hydrogen iodide in methylene chloride as brilliant red microneedles, m.p. 151–152°. *Anal.* Calcd. for C_7H_7IO: $C_7H_6OH^+$, 45.77; I^-, 54.23. Found: $C_7H_6OH^+$, 45.9; I^-, 54.24. The red iodide quickly turns yellow in moist air and with excess moisture deliquesces to form a red solution; this solution on standing dries to red or yellow crystals depending on the moisture content of the atmosphere. These observations strongly suggested the formation of a stable yellow hydrate.

A portion of the red iodide was sealed in a vacuum system at 30.00° and water vapor admitted. Uptake of water commenced at a pressure of 6.15 mm., and a pressure plateau was maintained until 0.6 mole of water had been consumed; after this point water uptake slowed to an impractical rate. This was attributed to conversion of the surface of the crystals to the hydrate with concurrent shielding of the crystal center from water vapor.

To obviate this difficulty, an oxygen-free glove box was converted to a humidistat by inclusion of a saturated solution of calcium chloride hexahydrate, and a solution of the iodide in water was allowed to evaporate under 8 mm. of water vapor. This gave a quantitative yield of hydroxytropenium iodide monohydrate as bright yellow needles. *Anal.* Calcd. for $C_7H_9IO_2$: $C_7H_6OH^+$, 42.50; I^-, 50.75. Found: $C_7H_6OH^+$, 42.4; I^-, 50.71. At 30° the vapor pressure of water over this compound was 6.15 mm., identical with the pressure plateau found above. The hydrate seems stable indefinitely as long as the pressure of water is slightly above this value.

The variation of water vapor pressure over the hydrate with temperature was investigated in the range 26–47°. These data fit an excellent straight line of the form $\ln P_{atm} = -a/T + b$, where $a = 7288$ and $b = 19.24$. From these constants the thermodynamic values at 25° are calculated as $\Delta F° = 3.09$ kcal./mole, $\Delta H° = 14.48$ kcal./mole, and $\Delta S° = 38.22$ e.u. for the reaction

$$(C_7H_6OH^+I^- \cdot H_2O)(s) = (C_7H_6OH^+I^-)(s) + H_2O(g)$$
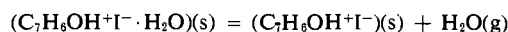
Consideration of the infrared spectra of hydroxytropenium iodide and its hydrate casts considerable doubt on the previous assignment[8] of the O–H stretching frequency of the hydroxytropenium ion. In the region 1700–3700 cm.$^{-1}$, the anhydrous iodide shows a single broad peak centered at 2600 cm.$^{-1}$ (Figure 1); in the hydrate this peak shifts to 1830 cm.$^{-1}$ and a new intense absorption appears at 3250 cm.$^{-1}$. We have assigned the 2600-cm.$^{-1}$ band in the iodide to the O–H stretch of the hydroxytropenium ion for the following reasons: (1) hydroxytropenium bromide and fluoroborate also show only a single, very similarly shaped

(7) R. van Helden, A. P. ter Borg, and A. F. Bickel, *Rec. trav. chim.*, 81, 599 (1962), report a dihydrate of (4-hydroxy-3,5-dimethylphenyl)-tropenium chloride.
(8) B. W. Zaitsev, Yu. D. Koreshkov, M. E. Vol'pin, and Yu. N. Sheinker, *Dokl. Akad. Nauk SSSR*, 139, 1107 (1961).
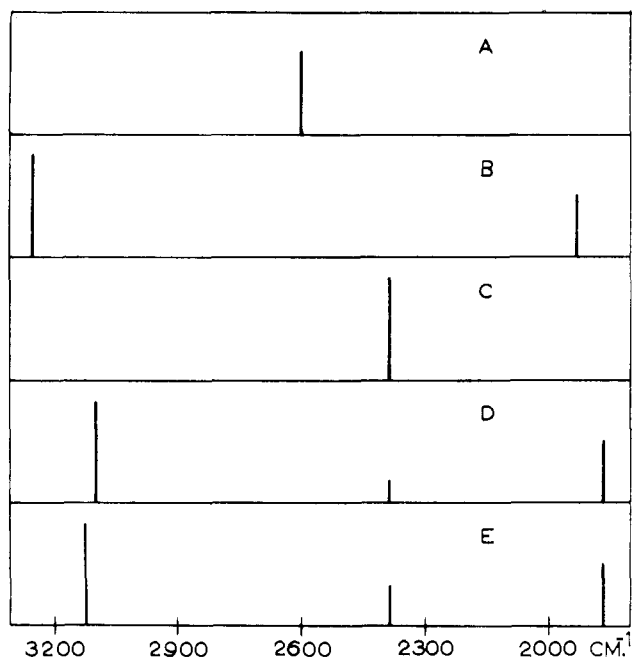
Figure 1. Schematic representation of infrared absorptions of (A) anhydrous hydroxytropenium iodide, (B) hydroxytropenium iodide monohydrate, (C) anhydrous hydroxytropenium bromide, (D) partially hydrated hydroxytropenium bromide, and (E) previously reported "hydroxytropenium bromide."[8]

band in this region at 2390 and 2410 cm.$^{-1}$, respectively; (2) in deuterioxytropenium bromide (prepared from tropone and dry deuterium bromide) the 2390-cm.$^{-1}$ band shifts to 1860 cm.$^{-1}$ for a ν_H/ν_D ratio of 1.28[9]; and (3) methoxytropenium fluoroborate[3,11] shows no absorption in this region.[12]

Vol'pin, et al.,[8] report that hydroxytropenium bromide shows a strong band at 3125 cm.$^{-1}$ and medium broad bands at 2387 and 1876 cm.$^{-1}$; they assign the 3125-cm.$^{-1}$ band to O–H stretch in the cation and the other two bands to O–H–Br hydrogen bonding. We have prepared anhydrous hydroxytropenium bromide as light yellow plates (Anal. Calcd. for C_7H_7BrO: $C_7H_6OH^+$, 57.27; Br$^-$, 42.72. Found: $C_7H_6OH^+$, 56.9; Br$^-$, 42.91) and find that it shows only the broad band at 2390 cm.$^{-1}$. When the yellow bromide is exposed to moist air it turns white, and it will deliquesce with excess moisture to form yellow solutions. Evaporation of such solutions leaves white needles which show a strong absorption at 3100 cm.$^{-1}$, a medium broad band at 1870 cm.$^{-1}$, and a weak band at 2390 cm.$^{-1}$. We believe this latter band to be due to unhydrated bromide present, and the other two bands to be hydrate absorptions.

The data presented herein clearly indicate that the O–H stretching frequency of the hydroxytropenium cation is a broad band in the 2300–2700-cm.$^{-1}$ region. The position of this band is anion dependent, which suggests O–H–X hydrogen bonding. This band under-

(9) This ratio, normally 1.35 for the shift of an O–H frequency on deuteration, is often slightly reduced in the solid state.[10]

(10) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, p. 111, and references therein.

(11) H. J. Dauben, Jr., and K. M. Harmon, unpublished work in Ph.D. Thesis of K. M. H., University of Washington, 1958.

(12) All of these salts show C–H absorptions in the vicinity of 3000 cm.$^{-1}$; these bands are small compared to the O–H bands under discussion and are easily distinguished from them.

goes a large shift to lower energies with hydrate formation indicative of strong hydrogen-bond formation,[10] and the O–H stretching band of the water of hydration appears as an intense absorption in the 3100–3300-cm.$^{-1}$ region with slight anion dependence. Vol'pin, et al.,[8] were dealing with a hydrate; this fact is supported by the published[8] infrared spectrum of their tropone starting material. This tropone was clearly wet, as it contains a strong band at 3400 cm.$^{-1}$ which is found in wet tropone, but not in material which has been rigorously dried.[13]

The above spectral and thermochemical data suggest that the water in hydrates of hydroxytropenium ion is strongly hydrogen bonded to the –OH on the cationic ring and that secondary hydrogen bonding of the hydrogens of water to halide ion is also probably present. Such hydrogen bonding could account for the
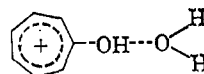
change in color of the iodide from red to yellow on hydration, since the net effect would be to increase the electron density of the ring and make it a poorer acceptor for the charge-transfer[4] transition which causes the color of such salts.

The observed enthalpy change represents the difference between the enthalpy of hydrogen-bond formation and the differential lattice enthalpy,[14] i.e., the change in enthalpy of the crystal lattice on hydrate formation. Since for the dissociation process $\Delta H°_{(L)}$ is almost surely negative, 14 kcal./mole would seem a reasonable lower limit for the strength of the hydrogen bond in hydroxytropenium iodide monohydrate.

(13) Y. Ikegami, Bull. Chem. Soc. Japan, 35, 967 (1962), gives the infrared spectrum of dried tropone. The last water is remarkably difficult to remove.

(14) K. M. Harmon, S. D. Alderman, K. E. Benker, D. J. Diestler, and P. A. Gebauer, J. Am. Chem. Soc., 87, 1700 (1965).

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A New Method for Halodecarboxylation of Acids Using Lead(IV) Acetate

Sir:

Synthetically, carboxylic acids are decarboxylated with halogens to alkyl halides through the agency of the dry silver salt,[1] or in modified procedures directly with mercuric oxide or lead acetate.[2] We wish to report a convenient method for the decarboxylation of acids with lead tetraacetate and ionic halide (particularly chloride) salts (MX).

The stoichiometry of the reaction as written in eq. 1 is suggested.

$$RCO_2H + Pb(OAc)_4 + MX \longrightarrow$$
$$RX + CO_2 + Pb(OAc)_2 + HOAc + MOAc \quad (1)$$
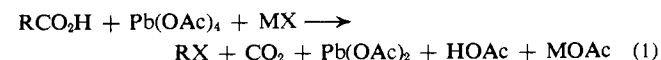
(1) (a) R. G. Johnson and R. K. Ingham, Chem. Rev., 56, 219 (1956); (b) C. V. Wilson, Org. Reactions, 9, 332 (1957).

(2) (a) S. J. Cristol and W. Firth, Jr., J. Org. Chem., 26, 280 (1961); 27, 2711 (1962); (b) J. A. Davis, et al., ibid., 30, 415 (1965); (c) D. H. R. Barton and E. P. Serebryakov, Proc. Chem. Soc., 309 (1962); (d) G. B. Bachman and J. W. Wittman, J. Org. Chem., 28, 65 (1963).