pared readily from VIa without protection of the 3-keto group by ketalization. Reaction of VIa with ethylene glycol and *p*-toluenesulfonic acid furnished mainly the Δ^6-3-ketal VIIa, m.p. 143–144°; $[\alpha]_D$ + 152°; $\tau_{6,7\text{H}}$ 4.34 (two proton singlet) and the Δ^5-3-ketal, m.p. 150–151°; $[\alpha]_D$ + 25°; $\tau_{6\text{H}}$ 4.18 (single proton, triplet J = 3.5 c.p.s.). The 5-hydrogen in VIIa is β since its hydrogenation product IIIh[13] (Pd/C in ethanol), m.p. 189–190° and 208–209°; $[\alpha]_D$ + 67°; on hydrolysis with 80% acetic acid at room temperature, conditions which do not isomerize the *trans*-ketone IIIb, yielded the *cis*-ketone IIIc. Hydrolysis of VIIa with 80% acetic acid gave the Δ^6-3-ketone VIIb, m.p. 171–174°; $[\alpha]_D$ + 300°; no absorption at 240 mμ; $\tau_{6\text{H},7\text{H}}$ 4.13, 4.31; which with N HCl in methanol at room temperature isomerized to VIa.

Hydrolysis of VIIa with N KOH in methanol under helium gave the Δ^6-ketal acid VIIc,[14] m.p. 176–177°; $[\alpha]_D$ + 150°; $\tau_{6,7\text{H}}$ 4.33 (2 proton singlet); The acid chloride, m.p. 140–150°; prepared from VIIc with oxalyl chloride in benzene was converted to the diazoketone and the latter with excess HI into the 21-methyl ketone VIe, m.p. 203–204°; $[\alpha]_D$ + 28°; $\lambda_{\max}^{\text{alc}}$ 240 mμ (ϵ = 8,100); and with HCl in chloroform to the 21-chloro ketone VIf, m.p. 218–219°; $[\alpha]_D$ + 1°; $\lambda_{\max}^{\text{alc}}$ 241 mμ (ϵ = 8,700). Treatment of VIf with potassium acetate and iodide in acetone gave the 21-acetoxy ketone VIg, m.p. 160–161°; $[\alpha]_D$ 0°; $\lambda_{\max}^{\text{alc}}$ 240 mμ (ϵ = 9,300).

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[13] This product was identical with the product of direct ketalization of IIIb or IIIc.

[14] Similar hydrolysis of the Δ^5-ketal methyl ester VIb gave the Δ^5-ketal acid VIc, m.p. 237–238°; $[\alpha]_D$ +20°; $\tau_{6\text{H}}$ 4.18 (single proton). Deketalization of VIc and VIIc with boiling 0.05 N H_2SO_4 in methanol for 2 hours gave the Δ^5-3-keto acid VId, m.p. 296–299°; $\lambda_{\max}^{\text{alc}}$ 240 mμ (ϵ = 9400).

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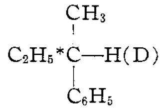
INTRAMOLECULAR PROTON TRANSFER IN A BASE-CATALYZED ALLYLIC REARRANGEMENT

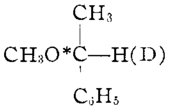
Sir

In earlier work, hydrogen–deuterium isotope effects that ranged from 0.3 to 3.0 were observed for the base-catalyzed racemization and isotope exchange reactions of I,[1a] II[1a] and III.[1b]



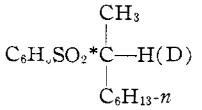
$$\mathrm{C_2H_5{*}}\overset{\mathrm{CH_3}}{\underset{\mathrm{C_6H_5}}{\mathrm{C}}}\mathrm{—H(D)}$$

I



$$\mathrm{CH_3O{*}}\overset{\mathrm{CH_3}}{\underset{\mathrm{C_6H_5}}{\mathrm{C}}}\mathrm{—H(D)}$$

II

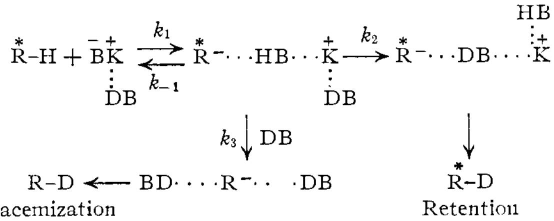


$$\mathrm{C_6H_5SO_2{*}}\overset{\mathrm{CH_3}}{\underset{\mathrm{C_6H_{13}\text{-}\mathit{n}}}{\mathrm{C}}}\mathrm{—H(D)}$$

III

The low values and certain aspects of the stereochemical course of the reactions led to postulation of a mechanism embodied in equation (1). With solvents in which $k^{\text{H}}/k^{\text{D}} < 1$, then $k_{-1} > k_2$ or k_3. If $k_{\text{obs.}}{}^{\text{e}}$ is the observed rate constant for isotopic exchange and $k_{\text{obs}}{}^{\alpha}$ for racemization, then equations (2) and (3) can be written, which provide isotope effects associated only with an equilibrium constant and the exchange of one hydrogen bonded carbanion for another.

(1)

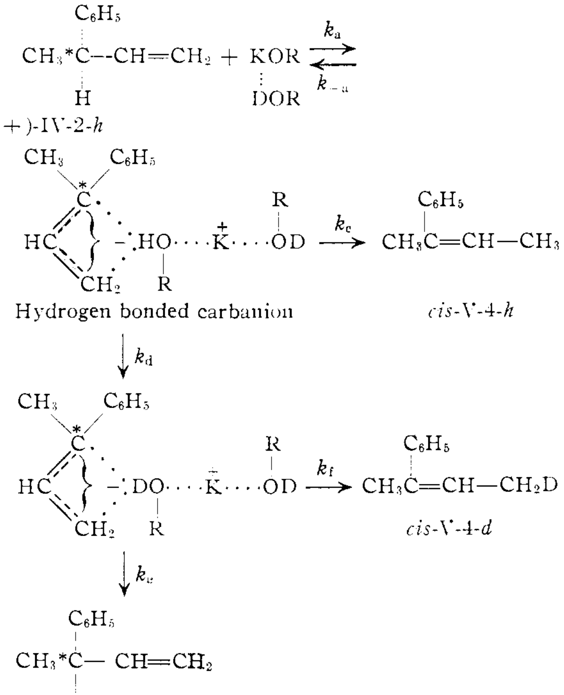


$$\text{(2)}\quad k^{\text{e}}{}_{\text{obs}} = \frac{k_1}{k_{-1}}\,(k_2 + k_3) = K(k_2 + k_3)$$

$$\text{(3)}\quad k^{\alpha}{}_{\text{obs}} = \frac{k_1}{k_{-1}}\,k_3 = Kk_3$$

A clear implication of $k_{-1} > k_2$ or k_3 is that in a system such as IV with a driving force for rearrangement, an intramolecular base-catalyzed proton transfer is a distinct possibility. Such a process has been observed in *tert*-butyl alcohol-O-D (98% deuterated) with potassium *tert*-butoxide as catalyst.

(4)



Optically active (+)-IV-2-h^2 was dissolved in *tert*-butyl alcohol-O-D (0.386 M) which was 0.409 M in potassium *tert*-butoxide, and the solution was heated at 75° for 257 min. The olefin was recovered (75%) through pentane extraction, olefins IV and *cis*-V[2] were separated from one another by preparative vapor phase chromatography, and analyzed for deuterium and optical activity. Compound IV was completely free of deuterium,[3] and exhibited the same rotation as the starting material, $\alpha^{25}{}_D$ + 3.25° (l 1 dm., neat). Compound V contained only 0.46 of one atom of deuterium per molecule.[3] The nuclear magnetic resonance spectrum of *cis*-V indicated that most of this deuterium was at C-4. Clearly a *minimum* of 54% of the re-

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[1] (a) C. J. Cram, C. A. Kingsbury and B. Rickborn, *J. Am. Chem. Soc.*, **83**, 3688 (1961); (b) D. J. Cram, D. A. Scott and W. D. Nielsen, *ibid.*, **83**, 3696 (1961).

[2] D. J. Cram, *ibid.*, **74**, 2141 (1952).

[3] Combustion and falling drop method.

arrangement involved *intramolecular* proton transfer from C-2 to C-4. The possibility exists that some of the 0.46 atom of deuterium was incorporated in *cis*-V after it was formed. These observations indicate that in scheme (4), $k_c \gtrless k_d$, and that if any deuterium was incorporated into *cis*-V during the rearrangement (as distinct from after), then $k_f >> k_e$ and $k_c >> k_{-a}$.

Although in recent years a number of intramolecular rearrangements involving carbonium ion–anion ion pairs have been reported, to the author's knowledge this is the first example of an intramolecular carbanionic process. This phenomenon may be rather general, and the scope and intimate mechanistic details are under active investigation.[4]

[4] This research was sponsored by the U. S. Army Research Office (Durham).

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CARBONIUM ION SALTS. VI. TROPENIUM HYDROGEN DIHALIDES AND AN IMPROVED ROUTE TO TROPENIUM CHLORIDE[1]

Sir:

Recent theoretical studies of the hydrogen dichloride anion[2] indicate considerable interest in this novel type of hydrogen-bonded species. We wish to report the preparation of tropenium hydrogen dichloride and hydrogen dibromide whose ease of preparation and marked stability may render them more amenable to physical chemical studies than previously reported[3] salts of these anions, and to describe a synthesis of tropenium chloride which in yield and quality of product is superior to any yet reported.

Tropenyl methyl ether[4] was added to a saturated solution of hydrogen chloride in ether under a stream of dry hydrogen chloride gas[5]; an immediate precipitate formed which when dried *in vacuo* gave 86.1% tropenium hydrogen dichloride as white microcrystals, ultraviolet spectrum (96% sulfuric acid)[7] λ_{max} 268 (sh), 274 (4350), 280 mμ. *Anal.* Calcd. for $C_7H_8Cl_2$: $C_7H_7^+$, 55.89; Cl, 43.49. Found: $C_7H_7^+$, 55.8; Cl, 43.23, 43.32. Use of hydrogen bromide in the above reaction gave a white precipitate containing excess hydrogen bromide which upon adiabatic removal of solvent *in vacuo* gave 78.0% tropenium hydrogen dibromide as small light yellow needles, ultraviolet spectrum (96% sulfuric acid)[7] λ_{max} 268 (sh), 274 (4310), 280 mμ. *Anal.* Calcd. for $C_7H_8Br_2$: $C_7H_7^+$, 36.17; Br, 63.42. Found: $C_7H_7^+$, 35.9; Br, 63.45, 63.21. Both salts dissolve instantly in water to give colorless solutions which neutralize two moles of base per mole of salt; qualitative ultraviolet spectra of such solutions showed the presence of tropenium ion (λ_{max} 275, 280 (sh) mμ)[4] and no covalent species. Infrared spectra[8] confirm the presence of tropenium ion in these salts. The hydrogen dichloride does not show a discrete melting point, but decomposes slowly over 100°; the decomposition temperature is a function of rate and temperature of initial heating. The hydrogen dibromide is converted to the brilliant yellow bromide on warming to 100°. Both compounds are reasonably hygroscopic and were handled in the glove box at all times. The stability of these compounds is demonstrated by storage *in vacuo* under continuous pumping at 1 mm. for 18 hours which gave a 1% increase in tropenium ion concentration in the hydrogen dichloride and a 4% increase in the case of the dibromide. The vapor pressure of hydrogen halide over primary and secondary ammonium hydrogen dihalides is quite high[3a] and cesium hydrogen dichloride is reported to be unstable at temperatures greater than 0°.[3d] Even tetramethylammonium hydrogen dichloride[2c] has a vapor pressure of 2 mm. at room temperature, which suggests that this salt would be destroyed under these conditions.

Addition of hydrogen chloride gas to the brilliant yellow solution of tropenium chloride in methylene chloride gives a colorless solution in which the broad tailing of the tropenium peak from chloride charge-transfer[9] is lost and a new C–T band (λ_{max} 314 mμ (1700)) appears. When hydrogen bromide is passed into the deep orange solution of tropenium bromide in methylene chloride the color becomes light yellow and the bromide C–T band (λ_{max} 402 mμ (1380))[9] is replaced by a new band (λ_{max} 356 mμ (1300)). This apparent shift in the C–T spectra[10] to shorter wave lengths shows the presence of anions with higher ionization potentials than the corresponding halides[11] as would be expected if the hydrogen dihalides were formed.

Tropenium chloride is a difficult compound; it is implacably hygroscopic, and we find—once having overcome the moisture problem enough to tell—that it is also extremely sensitive to light. Diffuse sunlight rapidly darkens the chloride through Pyrex glass, and a sunlamp destroys it completely in minutes to give several as yet un-

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[1] Supported by the Petroleum Research Fund and the National Science Foundation.

[2] (a) T. C. Waddington, *J. Chem. Soc.*, 1708 (1958); (b) D. W. A. Sharp, *ibid.*, 2558 (1958); (c) S. Chang and E. F. Westrum, Jr., *J. Chem. Phys.*, **36**, 2571 (1962).

[3] (a) F. Kauffler and E. Kunz, *Ber.*, **42**, 385, 2482 (1909); (b) R. West, *J. Am. Chem. Soc.*, **79**, 4568 (1957); (c) H. F. Herbrandson, R. T. Dickerson, Jr., and J. Weinstein, *ibid.*, **76**, 4046 (1954); (d) R. E. Valleé and D. H. McDaniel, *ibid.*, **84**, 3412 (1962).

[4] W. von E. Doering and L. H. Knox, *ibid.*, **76**, 3203 (1954).

[5] This method was suggested by our observation that when tropenium chloride is prepared by passing hydrogen chloride over an ethereal solution of tropenyl methyl ether[6] an excess of hydrogen chloride gives products with low tropenium ion content.

[6] Method suggested by H. J. Dauben, Jr., and L. R. Honnen, private communication.

[7] H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon and D. L. Pearson, *J. Am. Chem. Soc.*, **79**, 4557 (1957), report λ_{max} 268 (sh), 273.5 (4350), 280 mμ for tropenium ion in this solvent.

[8] We wish to thank Dennis J. Diestler who determined the infrared spectra of the salts by the potassium bromide disk technique.

[9] K. M. Harmon, F. E. Cummings, D. A. Davis and D. J. Diestler, *J. Am. Chem. Soc.*, **84**, 120, 3349 (1962).

[10] Our placement of the chloride C–T band at 299 mμ[9] is based on the assumption that subtraction of the spectrum of tropenium fluoroborate from that of tropenium chloride of equivalent concentration would give a measure of the chloride C–T absorption; the fact that the chloride to hydrogen dichloride shift produces a peak at 314 mμ and also a loss of color makes us question the validity of this subtraction. Although a value of 299 mμ (33,500 cm.$^{-1}$) gives a reasonably straight line when the energies of the tropenium halide C–T bands are plotted against halide ion ionization potentials, a true straight plot calls for a value of 31,200 cm.$^{-1}$, which lies to longer wave lengths than the hydrogen dichloride C–T band.

[11] S. P. McGlynn, *Chem. Rev.*, **58**, 1113 (1958).