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), $k_c \gtrsim k_d$, 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]

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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).

identified compounds. No route yet reported[4,7,12] has given tropenium chloride of high quality in good yield with consistency. The hygroscopic nature of the compound renders recrystallization difficult, and since the chloride is thermally unstable sublimation results in extensive decomposition.

These difficulties are obviated by use of tropenium hydrogen dichloride as starting material. A sublimer is charged with the hydrogen dichloride in the glove box, wrapped in foil, and sublimation carried out at 70° and 0.1 mm. for three to five hours to yield 100% tropenium chloride as colorless, hard, free-flowing prisms, ultraviolet spectrum (96% sulfuric acid)[7] λ_{max} 268 (sh), 274 (4340), 280 mμ. *Anal.* Calcd. for C_7H_7Cl: $C_7H_7^+$, 71.99. Found: $C_7H_7^+$, 71.9. The chloride is handled at all times in the glove box where it is stable to the atmosphere for about 24 hours; complete liquidation occurs in 30 seconds on removal to the room. All operations are carried out in a darkened room under red-orange light. Trituration of the hydrogen dichloride with ether gave slightly darkened, less stable tropenium chloride (71.2% tropenium ion) which melted at 101–102° (reported,[4] 101°); however, the sublimed prisms do not show any change under 115° and slowly decompose over 125°.

Studies on carbonium ion hydrogen diiodides are in progress.

[12] D. Bryce-Smith and N. A. Perkins, *J. Chem. Soc.*, 1339 (1962).

[13] National Science Foundation and Petroleum Research Fund Scholar, 1962.

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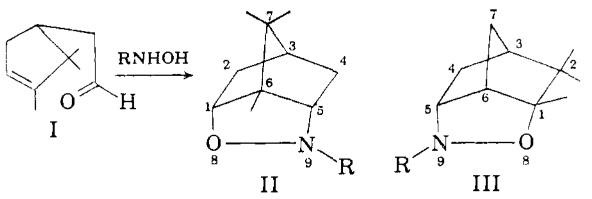
RING CLOSURE TO BRIDGED BICYCLIC SYSTEMS BY THE INTRAMOLECULAR NITRONE-OLEFIN CONDENSATION

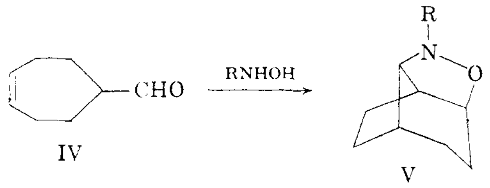
Sir:

In the course of our investigations of the scope and utility of the intramolecular addition of nitrones to olefins,[1,2] we have observed recently an apparent qualitative relationship between the formation of cyclic products obtained in the condensations of N-alkylhydroxylamines with a 3-cyclopentenylacetaldehyde or 4-cycloheptenylcarboxaldehyde and the reported anchimerically assisted solvolysis of five and seven-membered cycloalkenyl esters to give bridged bicyclic products.[3,4,5] Although these reactions seem to be of widely different nature, we feel that this relationship has some bearing on the mechanism of the intramolecular nitrone–olefin and, perhaps, other 1,3-dipolar additions.

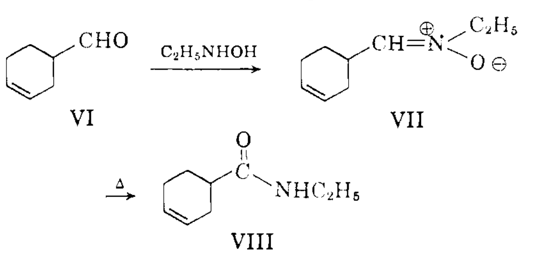
Acetolysis of esters of β-(Δ³-cyclopentenyl)-ethanol gave high yields of *exo*-norbornyl acetate.[4,5] The condensation of campholenic aldehyde (I) with N-methyl or N-isopropylhydroxylamines afforded, after distillation, a mixture of the tricyclic isoxazolidines II and III (70–80% yield), in the ratio (determined by gas chromatography) of approximately 2:3, respectively. These isomers were separated by careful fractionation. The bornane derivative II (R = CH_3)[6] had b.p. 97° (10 mm.), $n^{25}D$ 1.4858, *picrate* m.p. 198–199° dec., *methiodide* m.p. 149–150° dec. The structure of II was supported by the n.m.r. spectrum which showed (60 mc., CCl_4, TMS) bands at δ = 0.87 and 0.93 (*gem*-diMe), 1.14 (C_6-Me), 2.64 (N-Me), 2.95 broad doublet, J = 8 c.p.s. C_5–H) and 3.95 p.p.m. (broad doublet, J = 7.4 c.p.s., C_1–H). Hydrogenolysis of the isoxazolidine gave an amino alcohol, m.p. 58–59°. The lower boiling camphene compound III (R = CH_3) had b.p. 96° (10 mm.), $n^{25}D$ 1.4830, *picrate* m.p. 216–218° dec., *methiodide* m.p. 169–170° dec. Hydrogenolysis of the isoxazolidine gave an amino alcohol melting at 78.5–79°. The n.m.r. spectrum of III was very similar to that of II, except that the methyl peaks were slightly shifted and no low field hydrogen resonance (**H**–C–O) was observed.



When 4-cycloheptenecarboxaldehyde (IV) was condensed with N-methylhydroxylamine, a single product V was obtained in 60% yield. The tricyclic isoxazolidine structure V (b.p. 118–120° at 25 mm., $n^{25}D$ 1.5002, *methiodide* m.p. 190.0–190.5° dec.) was consistent with infrared and n.m.r. spectral data, and hydrogenolysis could be effected.



Several groups have reported the lack of double-bond participation and the failure to isolate bicyclic products from the solvolyses of 3-cyclohexenylcarbinyl esters.[3,7,8] When 3-cyclohexene carboxaldehyde (VI) reacted with N-ethylhydroxylamine, only the corresponding nitrone (VII) was



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[1] N. A. LeBel and J. J. Whang, *J. Am. Chem. Soc.*, **81**, 6334 (1959).

[2] N. A. LeBel and J. J. Whang, to be submitted.

[3] G. LeNy, *Compt. rend.*, **251**, 1526 (1960).

[4] R. Lawton, *J. Am. Chem. Soc.*, **83**, 2399 (1961).

[5] P. D. Bartlett and S. Bank, *ibid.*, **83**, 2591 (1961).

[6] Satisfactory analyses have been obtained for all new compounds described herein.

[7] R. S. Bly, Jr., and H. L. Dryden, Jr., *Chem. and Ind.*, 1287 (1959).

[8] C. F. Wilcox, Jr., and S. S. Chibber, *J. Org. Chem.*, **27**, 2332 (1962).