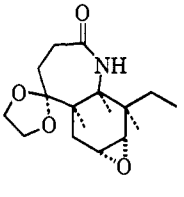
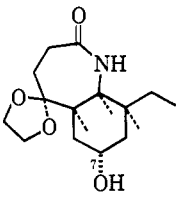
Because the Beckmann rearrangement proceeds with *anti* migration the structure of V retrospectively verified the stereochemistry of the *anti*-oxime IV and the assigned structure of the *cis*-monoketal III.

The double bond of V survived all the transformations and was available at this point to introduce a C_7-oxygen function into the molecule. Perbenzoic acid attacked mostly from the *convex* face[12] of the molecule, leading to the oxide VI in 65% yield; mp 170–172°; ν_{max}^{KBr} 3.17, 3.28 (–NH–), 6.02 μ (–*CO*–NH–). A selective lithium aluminum hydride reduction of VI furnished the C_7-*axial* hydroxy lactam VII (85%); mp 181–183°; ν_{max}^{KBr} 2.98 (–NH–), 3.07 (–OH), 6.13 μ (–*CO*–NH). During the next step the lactam group protected the nitrogen

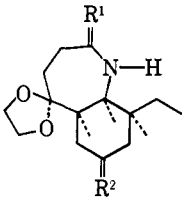


VI

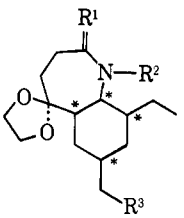


VII

function from oxidation. Thus, a Sarett oxidation of VII produced the C_7-ketone VIII in 90% yield; mp 220°; ν_{max}^{KBr} 3.0, 3.14, 3.28 (–NH–), 5.84 (>C=O), 6.03 μ (–*CO*–NH). A Wittig reaction transformed the ketone lactam VIII to the *exo*-methylene derivative IX (82%); mp 196–197°; ν_{max}^{KBr} 3.1 (–NH–), 3.3 (>C=CH_2), 6.03 μ (–*CO*–NH–); nmr δ 4.72 ppm (>C=CH_2, singlet). Hydroboration attacked the double bond on the *convex* face of IX, creating an *equatorial* hydroxymethyl derivative, X (90%); ν_{max}^{neat} 3.0 (–OH), 6.0 μ (–*CO*–NH–). A lithium aluminum hydride reduction of X produced the amino alcohol XI (90%); ν_{max}^{neat} 3.0 μ (–OH); the mass spectrum showed the molecular ion at *m/e* 269 and the most intense peak at *m/e* 168. The N-carbobenzoxylated amino alcohol XII [ν_{max}^{neat} 3.0 (–OH), 6.0 μ (>N–*CO*–)] was tosylated to XIII; ν_{max}^{neat} 5.92 (amide), 7.35, 8.50 μ (–SO_2–).



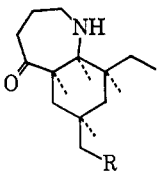
VIII, $R^1 = R^2 = O$
IX, $R^1 = O$; $R^2 = >CH_2$



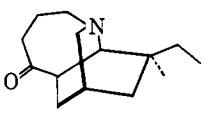
X, $R^1 = O$; $R^2 = H$; $R^3 = OH$
XI, $R^1 = H_2$; $R^2 = H$; $R^3 = OH$
XII, $R^1 = H_2$; $R^2 =$ Cbz; $R^3 = OH$
XIII, $R^1 = H_2$; $R^2 =$ Cbz; $R^3 = OTs$

The ketal and N-carbobenzoxy groups of XIII were then cleaved with HBr–AcOH and the hydrobromide of the amino ketone XIV was isolated in good yield; mp 150°; ν_{max}^{KBr} 3.7 (>NH_2^+), 5.88 (ketone), 7.60, 8.40 μ (–SO_2–). The mass spectrum of the hydrobromide salt of XIV interestingly showed peaks at *m/e* 379 (M – HBr) and another molecular ion at *m/e* 287, 289 corresponding to XV. A large peak at *m/e* 208 suggested the formation of the protonated tricyclic ketone system (XV → XVI).

The preparative equivalent of the above mass spectroscopic cyclization of XIV to *dl*-9-ethyloctahydro-1,7-methano-1H-benzazepin-5(4H)-one (XVI) was carried out in refluxing isoamyl alcohol in good yield. The tricyclic ketone XVI was successfully transformed by Fischer indolization to the racemic ibogamine (Ia); mp 128–131° (lit.[6] mp 129–132°).



XIV, R = OTs
XV, R = Br



XVI

The mass spectrum of the synthetic product was identical with that of the naturally occurring ibogamine; all the characteristic "ibogamine peaks"[13] were exhibited, including the significant peaks at *m/e* 280 (M^+), 265 (M – 15), 195, and 156 and those of other fragments which arise from the isoquinuclidine moiety[13] at *m/e* 122, 124, 135, 136, and 149. In addition, the synthetic product showed R_f values in three different solvent systems identical with those of ibogamine.

This synthesis provides the first preparative proof that the ethyl side chain of the iboga alkaloids has a cis configuration with respect to the N_6 function.[14]

Acknowledgments. The author is much indebted to the Analytical Department of Wyeth Laboratories. He especially wishes to thank Dr. Stephen Shrader for the invaluable determination and interpretation of the mass spectroscopy data, Dr. Charles Hetzel for the determination of the nuclear magnetic resonance spectra, and Dr. Norbert Neuss of Eli Lilly Company, who kindly provided the samples of natural ibogamine and epiibogamine.

(12) R. B. Woodward, F. E. Bader, H. Bickel, A. J. Frey, and R. W. Kierstead, *Tetrahedron*, **2**, 1 (1958).

(13) K. Biemann and M. Friedmann-Spiteller, *J. Am. Chem. Soc.*, **83**, 4805 (1961).

(14) See numbering in ref 2c.

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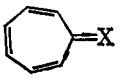
Received October 5, 1967

Tropenylidenimmonium Salts and Tropenylidenimines

Sir:

We wish to describe syntheses for, and some of the salient properties of, several members of the two classes of compounds **1**, X = R_2N^+= and RN̈=. The imines to be described have no previous direct precedent, although the related oxime and phenylhydrazone[1] of



1

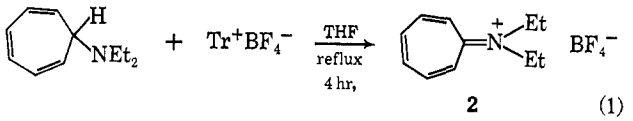
tropone have been reported (**1**, X = HON= and NHPhN=), and diazatropolones have been synthesized.[2] A single tropenylidenimmonium salt (**1**, X =

(1) T. Mukaki, *Bull. Chem. Soc. Japan*, **33**, 238 (1960).

(2) (a) T. Nozoe, *et al.*, *Proc. Japan Acad.*, **29**, 565 (1953); (b) W. R. Brasen, H. E. Holmquist, and R. E. Benson, *J. Am. Chem. Soc.*, **82**, 995 (1960).

piperidino) has been prepared,[3] by the bromination–dehydrobromination route.[4] The present research utilizes a net hydride abstraction from 7-tropenylamines by tropenylium fluoroborate for the immonium salt syntheses. Where applicable, the latter salts were converted to the corresponding imines by base treatment.

N,N-Diethyltropenylidenimmonium fluoborate (**2**) was prepared as indicated in eq 1.[5] Evaporation of the



2 (1)

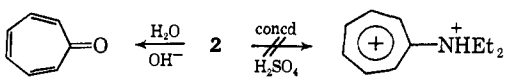
solvent and extraction of nonpolar organics into ether afforded the crude salt. Chromatography on Florisil (elution of impurities for 2 hr by THF, then elution of salt with 10% MeOH–THF)[6] furnished a 35% yield of pure **2** as yellow crystals, melting point approximately ambient. The salt is highly water soluble and quite insoluble in nonpolar organics. Like tropone, and in contrast to tropylidene, **2** has a structured singlet (ss) nmr absorption representing the six ring protons (τ 2.3 compared to τ 3.1 for tropone). The ethyl protons absorb at τ 6.1 (2 H, q) and 8.6 (3 H, t). The similarity between **2** and tropone is further evident in their infrared and visible–ultraviolet spectra (Table I). Though **2**

Table I

Compound	Nmr, τ	Visible–ultraviolet, mμ[b]	Infrared, cm^{-1}
Tropenylium	0.6	275	
Hydroxy-tropenylium	1.3		
2	2.3	234, 328	1635[c]
4[a]	2.3	239, 327 (s), 333	1638[c]
Tropone	3.1	215, 218, 222, 302, 312	1645[d]
5[a]	3.7	234, 300 (s), 310	1570, 1602, 1642[e]
Tropylidene	3.5–4.7 (m)		

[a] The methyl derivatives have essentially identical properties. [b] All spectra in ethanol except tropenylium, which is in water. [c] KBr. [d] CCl_4. [e] We are unable to make a specific assignment to the C=N absorption.

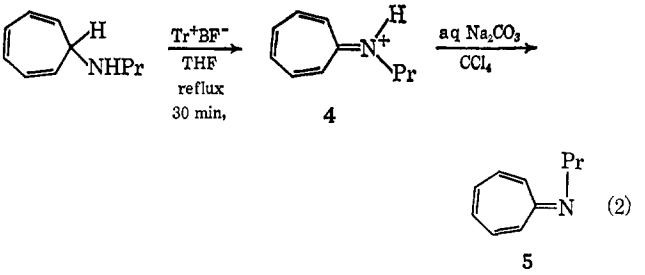
is quite stable in acidic and neutral aqueous media, it is hydrolyzed rapidly and in high yield to tropone upon dissolution in dilute sodium hydroxide. Interestingly, **2** is not protonated (nor rapidly decomposed) even in concentrated sulfuric acid, though a reasonable dicationic structure can be written (**3**).



3

N-*n*-Propyltropenylidenimmonium fluoroborate (**4**) was obtained in like manner to **2**, but starting with tropenyl-*n*-propylamine[7] (eq 2). The work-up pro-

(3) C. Jutz, *Chem. Ber.*, **97**, 2050 (1964).
(4) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **76**, 3203 (1954).
(5) W. von E. Doering and L. H. Knox, *ibid.*, **79**, 352 (1957). The diethyl compound used in our work had bp 57–59° (1.5 mm).
(6) A second salt was eluted afterwards, apparently diethylammonium fluoroborate.



4 **5** (2)

ceeded as before, but purification could be effected by recrystallization from 2-propanol (mp 93–95°, 60% yield). **4** has nmr absorptions at τ 2.3 (6 H), 6.4 (2 H, t), 8.1 (2 H, m), and 8.9 (3 H, t). Other physical properties of **4** are given in Table I. The corresponding N-methyl salt was prepared in a similar way:[8] τ 2.3 (6 H), 6.8 (3 H, s), 60% yield.

The conjugate base of **4** (N-*n*-propyltropenylidenimine (**5**)) was obtained by dissolving **4** in water, adding CCl_4 to give a two-phase system, and then adding saturated sodium carbonate solution. Inside a few minutes the organic layer became yellow-orange and was separated and condensed *in vacuo* to obtain an ~20% solution. The nmr spectrum of the latter shows it to contain only the desired imine: τ 3.7 (6 H, ss), 6.85 (2 H, t), 8.35 (2 H, m), and 9.05 (3 H, t). Other physical properties are given in Table I. Extraction of the imine into D_2O–D_2SO_4 regenerates the immonium salt precursor (nmr). The imine is moderately stable in solution, a 20% solution undergoing no appreciable decomposition after 24 hr under refrigeration. However complete evaporation of the solvent leads to immediate polymerization of the imine, after which the conjugate acid can no longer be regenerated. The N-methylimine was obtained similarly: τ 3.7 (6 H, ss) and 6.97 (3 H, s). A mass spectrum of this imine was obtained in 50% ether solution and exhibited a parent peak (*m/e* 119). Catalytic hydrogenation gave N-methylcycloheptylamine.

Acknowledgment. We wish to thank the National Institutes of Health and the Robert A. Welch Foundation for support.

(7) Obtained from tropenylium fluoroborate and excess *n*-propylamine, bp 73–76° (3 mm), τ 3.44 (2 H, m), 3.9 (2 H, m), 4.8 (2 H, m), 7.38 (3 H, t, congruent CH_2 adjacent to N and methine at the 7 position), 8.5 (2 H, m), 8.67 (1 H, s), 9.1 (3 H, t).
(8) Tropenylmethylamine (bp 51–52° (5 mm)) was prepared from tropenylium fluoborate and excess aqueous methylamine. The amine was then refluxed in THF for 1 hr with 1 equiv of the cation; the salt was recrystallized from 2-propanol, mp 76–79°.
(9) Alfred P. Sloan Fellow.

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Received March 16, 1967

Synthesis and Properties of Tropenylidenimmonium (8-Azatroponium) Salts

Sir:

The first immonium analog of tropone,[1] N,N-pentamethylene-2,4,6-cycloheptatrienylidenimmonium per-

(1) 2-Aminotroponimines (nitrogen analogs of tropolone) have been reported earlier by T. Nozoe, M. Sata, R. Matsui, and T. Masuda (*Proc. Japan Acad.*, **29**, 565 (1953)) and by W. R. Brasen, H. E. Holmquist, and R. E. Benson (*J. Am. Chem. Soc.*, **82**, 995, 5948 (1960); **83**, 3125 (1961)).