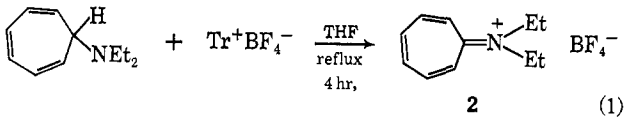
piperidino) has been prepared,[3] by the bromination–dehydrobromination route.[4] The present research utilizes a net hydride abstraction from 7-tropenylamines by tropenylium fluoroborate for the immonium salt syntheses. Where applicable, the latter salts were converted to the corresponding imines by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

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



2 (1)

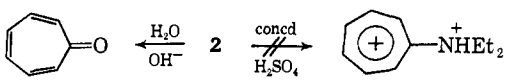
solvent and extraction of nonpolar organics into ether afforded the crude salt. Chromatography on Florisil (elution of impurities for 2 hr by THF, then elution of salt with 10% MeOH–THF)[6] furnished a 35% yield of pure **2** as yellow crystals, melting point approximately ambient. The salt is highly 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)		

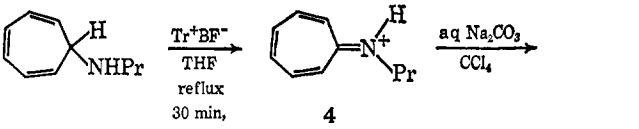
[a] The methyl derivatives have essentially identical properties. [b] All spectra in ethanol except tropenylium, which is in water. [c] KBr. [d] CCl_4. [e] We are unable to make a specific assignment to the C=N absorption.

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**).

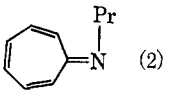


3

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-



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*-propyltropenylideneimine (**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.

(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.

(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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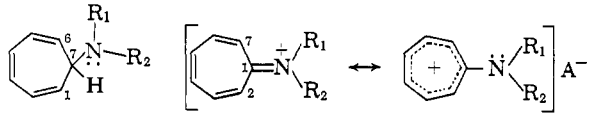
Synthesis and Properties of Tropenylidenimmonium (8-Azatroponium) Salts

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)).

chlorate (**2a**), was prepared by Jutz[2a] by the bromination–dehydrobromination procedure of Doering and Knox.[2b] We wish to report the synthesis of the parent tropenylidenimmonium ion (**2d**) and its N-methyl (**2e**) and N,N-dimethyl (**2b**) derivatives by the other general tropenylium[3] ion preparative method of hydride ion abstraction[4] from the related 7-tropenylamines (**1**), combined with facile solvolytic detropenylation of N-tropenyl derivatives for obtaining the less highly alkylated members.



1 **2′** **2″**

1a, $R_1 = R_2 = CH_3$; **b**, $R_1 = C_7H_7$; $R_2 = H$; **c**, $R_1 = C_7H_7$; $R_2 = CH_3$

2a, $R_1 = R_2 = -(CH_2)_5-$; $A = Br^-$; **b**, $R_1 = R_2 = CH_3$; $A = BF_4^-$, Br^-, etc.; **c**, $R_1 = C_7H_7$; $R_2 = H$; $A = BF_4^-$; **d**, $R_1 = R_2 = H$; $A = BF_4^-$; **e**, $R_1 = H$; $R_2 = CH_3$; $A = BF_4^-$

N-Alkylation of amines, even of the vinylic 1-N,N-dimethylamino-1,3,5-cycloheptatriene (thermal isomerization product of the 7-amino),[5] by stable carbonium ions is the dominant reaction course.[6] Nevertheless hydride ion abstraction[4b] from the ionogenic 7-alkylaminocycloheptatrienes (**1**) by the very stable tropenylium cation ($C_7H_7^+$) provides a simple, convenient route to these tropenylidenimmonium compounds for adventitious reasons: reversible N-quaternization by tropenylium ion to effectively regenerate the initial reactants and nullify the usual dominant quaternization reaction, and the greater stability of the immonium cation (cryptocarbonium ion) product than tropenylium cation reactant.[7] Ready detropenylation of N-tropenylimmonium systems on neutral alcoholysis is attributable to enhanced ionogenic character of the covalent N-tropenyl bond in such immonium compounds.

Hydride ion abstraction[4] from 7-N,N-dimethylamino-1,3,5-cycloheptatriene (**1a**)[8a] by tropenylium fluoroborate[4c] (1 equiv) in dry acetonitrile under nitrogen in the dark at 46° for 24 hr followed by addition into excess ether gave, along with cycloheptatriene in the ether solution, a yellow-brown, semisolid crude salt precipitate which yielded on recrystallization (EtOH) 78–82% N,N-dimethyl-2,4,6-cycloheptatrienylidenimmonium fluoroborate (**2b**) [*Anal.* Found: C, 49.03; H, 5.43; N, 6.37; B, 4.74; F, 34.66], brilliant yellow needles, mp 110°, completely air stable and nonhygroscopic, soluble in polar and insoluble in nonpolar solvents, stable in water at pH ≦ 7. This compound was hydrolyzed in aqueous sodium bicarbonate (1 equiv) at 25° in 24 hr with continuous ether extraction to yield 97% tropone, hydrogenated (4.0 moles, Pd–C, EtOH) to dimethylcycloheptylammonium fluoroborate (the melting point and mixture melting points were identical with those of authentic picrate and picrylsulfonate salts), and selectively reduced by excess sodium borohydride (MeOH, −80 to −30°) to 72% of about equal amounts of 7-N,N-dimethylamino- and 7-methoxycycloheptatriene (from the solvolytic equilibrium mixture).[10] Alternatively, dropwise addition of bromine (2 equiv) to a stirred acetonitrile solution of **1a** at 0° and addition of the concentrated product solution into absolute ethanol gave a 30% yield of N,N-dimethyl-2,4,6-cycloheptatrienylidenimmonium tribromide (**2b**), orange plates, mp 102–104°, which was transformed on warming with excess ethanolic cyclohexene, precipitation with ether, and recrystallization ($MeCN–Et_2O$) into the monobromide salt **2b**, yellow needles, mp 122–124° [*Anal.* Found: C, 50.35; H, 5.77; N, 6.66; Br, 37.43] or mp 156° [*Anal.* Found: C, 50.35; H, 5.72; N, 6.64; Br, 37.29]. The fluoroborate **2b** on treatment with bromine in a hydroxylic solvent gave the same tribromide salt, and with aqueous sodium tetraphenylborate gave quantitative precipitation of the yellow tetraphenylborate salt **2b**, mp 233° (1 EtOH:1 MeCN).

Similar dehydrideation of di-7-tropenylamine[8b] (**1b**) by tropenylium fluoroborate (1 equiv) on brief reflux (12 min) of an acetonitrile solution, evaporation, ether precipitation, and recrystallization (EtOAc–MeCN) yielded 59% N-(7-tropenyl)-2,4,6-cycloheptatrienylidenimmonium fluoroborate (**2c**), yellow-brown crystals, mp 109°, nmr identification. Solvolytic detropenylation of this labile secondary immonium salt (**2c**) by reflux (15 min) of an absolute ethanol solution and recrystallization (1 EtOH:4 EtOAc) of the ether-precipitated crude product afforded 66% tropenylidenimmonium (2,4,6-cycloheptatrienylidenimmonium) fluoroborate (**2d**), white plates [*Anal.* Found: C, 43.73; H, 4.31; N, 7.14; B, 5.51; F, 39.26], mp 188–192°, air stable with only slow yellow coloration with time, stable in neutral aqueous solution for at least several hours, other solubilities similar to **2b**.

Treatment of di-7-tropenylmethylamine[8c] (**1c**) with tropenylium fluoroborate (1 equiv) in acetonitrile (10-min reflux), hydrolytic aqueous extraction of the ether-diluted solution to effect detropenylation, and addition of aqueous sodium tetraphenylborate precipitated the yellow-orange N-methyl-2,4,6-cycloheptatrienylidenimmonium tetraphenylborate, mp 247–248°; addition of silver fluoroborate to an acetonitrile solution of this

(2) (a) C. Jutz, *Chem. Ber.*, **97**, 2050 (1964); (b) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **76**, 3203 (1954).

(3) The semicommon name of tropenylium for the 2,4,6-cycloheptatrienylium ion ($C_7H_7^+$) is in greater accord with accepted nomenclature rules (*Pure Appl. Chem.*, **11**, 64 (1965)) as more descriptive and practically adaptable (tropenylium ($C_7H_7^+$), tropenyl ($C_7H_7\cdot$), tropenide ($C_7H_7^-$), bitropenyl (C_7H_7–C_7H_7)) and will minimize confusion with members of the tropane heterobicyclic series. Use of this name for the ($C_7H_6^+$)– group in a substitutive name is incompatible with accepted practices (*cf. J. Am. Chem. Soc.*, **86**, 5036 (1964); **88**, 4093 (1966)).

(4) (a) H. J. Dauben, L. R. Honnen, F. A. Gadecki, and D. L. Pearson, *ibid.*, **79**, 4557 (1957); (b) H. J. Dauben and K. M. Harmon, 134th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1958, Abstract 35P; (c) H. J. Dauben, L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).

(5) A. P. ter Borg, E. Razenberg, and H. Kloosterziel, *Rec. Trav. Chim.*, **84**, 1305 (1965); **85**, 774 (1966).

(6) R. Damico and C. D. Broaddus, *J. Org. Chem.*, **31**, 1607 (1966).

(7) H. J. Dauben and L. M. McDonough, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1962, Abstract 55Q.

(8) Prepared by the method of Doering and Knox[9] with minor modifications except for common use of tropenylium fluoroborate: (a) from anhydrous dimethylamine in dry acetonitrile at 25°, 70%, bp 63.5° (10 mm), colorless, pungent, irritating odor, moderately air sensitive; (b) from saturated aqueous ammonia at 25°, 60%, colorless, mp 30° (pentane); (c) from excess aqueous 40% methylamine at 25°, 74%, colorless methylditropenylamine [*Anal.* Found: C, 85.41; H, 8.10; N, 6.77], mp 70–71° (pentane).

(9) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **79**, 352 (1957).

(10) Ionogenic cycloheptatriene derivatives with heteroatom 7 substituents (S = R_2N, RNH, RO, and R_3N^+) undergo reversible solvolysis readily in protonic solvents (H–A = H–OR, H–NR_2, etc.), C_7H_7–S + H–A ⇌ C_7H_7–SH^+,A^- ⇌ C_7H_7–A + H–S, easily demonstratable by vpc analysis of a neutral methanolic solution of **1a**.

salt gave white insoluble silver tetraphenylborate and the crude yellow-brown immonium fluoroborate which, combined with a second crop from the mother liquors on repetition of the separation sequence, provided an 80% yield of N-methyl-2,4,6-cycloheptatrienylidenimmonium fluoroborate (**2e**), pale yellow micaceous crystals, mp 79–80° (*i*-PrOH), structure confirmation by ultraviolet, visible, and nmr spectra (Table I). (*Anal.* Found: C, 46.42; H, 4.87; N, 6.77; B, 5.22; F, 36.72.)

Table I

Immonium fluoroborate	R_1	R_2	λ_{max} (MeCN), mμ	τ (MeCN), area[a]
2d	H	H	234[b] (315 sh), 324	2.35 (scm)[c]
2e	H	CH_3	239[b] (324 sh), 331	2.35 (scm, 6 H);[c] 6.77, 6.87 (d) or 6.82 (s)[d] (3 H)
2c	H	C_7H_7	240, 330	2.35 (scm, 6 H);[c] 3.15 (t), 3.56 (q), 4.42 (q), 6.00[e] (t) (7 H)
2b	CH_3	CH_3	241, 335[f]	2.35 (scm, 6 H);[c] 6.47 (s, 6 H)

[a] TMS internal reference. Allowance made for very broad (τ 1–2 width) absorptions of N–H protons in the region of ring protons. [b] Centers of finely structured band. [c] Approximate center of strongly coupled multiplet (scm). [d] Time average of doublet ($J \simeq 5.5$ cps) seen on N–H proton exchange. [e] C-7 proton absorption shifted τ 1.5 to lower field by adjacent positive charge. [f] ϵ_{max} 15,000.

Tropenylidenimmonium ions (**2b,d,e**) are devoid of detectable basicity as their uv and nmr spectra are unchanged even in concentrated sulfuric acid solvent. Conjugate tropenylidenimine bases are formed readily on deprotonation of primary and secondary immonium ions (**2d,c**) by trimethylamine (MeCN), tropenylidenimine (λ_{max} (MeCN) 231, 297 mμ), and N-tropenyltropenylidenimine (λ_{max} (MeCN) 232, 295 mμ) and are fairly stable in low concentrations but readily polymerized in concentrated solutions.

Limited data available preclude accurate evaluation of the relative importance of immonium (**2′**) and amine (**2″**) canonical structures in the hybrid. Hydrolysis of N,N-dimethyltropenylidenimmonium fluoroborate (**2b**) to tropone occurs rapidly in aqueous sodium carbonate and slowly in aqueous sodium bicarbonate and is undectable for several hours in pure water, in sharp contrast to immediate hydrolysis of diphenylmethylidenimmonium chloride[11a,b] (pK_a = 6.82)[11c] in cold water to benzophenone. These facts suggest an appreciable contribution of the charge-migrated amine structure (**2″**) to the resonance hybrid (**2′** ↔ **2″**) and presumably more than the estimated 16% contribution[12a] of the charge-separated structure to the tropone hybrid (pK_a = −1.02).[12b,13]

(13) Partial support by the U. S. Army Research Office (Durham) and the National Science Foundation and technical assistance by Allen R. Banks are gratefully acknowledged.

(14) Visiting Professor, University of California at Los Angeles, spring quarter, 1967.

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Phenonium *vs.* Open Ions in Solvolyses of 3-Phenyl-2-butyl Tosylate and Its *p*-Nitro Derivative[1]

Sir:

This paper reports the dramatic differences in solvolytic behavior between the optically active stereomers of 3-phenyl-2-butyl tosylate (I-OTs) and those of the *p*-nitro derivative II-OTs. The nitro group is far removed from the reaction site and should seriously depress the tendency of phenyl to act as a neighboring group. Because of the identical structures of the two systems aside from the remote *para* substituent, II-OTs serves as a splendid stereochemical and kinetic model for open-chain behavior in the 3-phenyl-2-butyl system.

Nitration of the acid phthalate of optically pure L-*threo*-I-OH[2] gave product, hydrolysis of which gave L-*threo*-II-OH,[3] $[\alpha]^{25}D$ 39.2° (*c* 3, ethanol). Similarly, L-*erythro*-II-OH was prepared,[3] $[\alpha]^{25}D$ 15.6° (*c* 3, ethanol), from 94% optically pure L-*erythro*-I-OH.[2] Oxidation[4] of the optically pure L-*threo*-II-OH and the 94% optically pure L-*erythro*-II-OH samples under neutral conditions gave L-3-(*p*-nitrophenyl)-2-butanone[3] of rotations $[\alpha]^{25}D$ −192 ± 2° (*c* 1, chloroform) and −181 ± 2° (*c* 1, chloroform), respectively. Acetolysis at 100° of optically pure L-*threo*-II-OTs gave a 13% yield of secondary acetate (7% *threo* and 93% *erythro* by nmr analysis) and 68% olefin. Hydrolysis of the acetate and oxidation[4] of the alcohol to ketone gave material, $[\alpha]^{25}D$ −184 ± 2° (*c* 1, chloroform), or 4 ± 2% racemized. In formolysis at 50°, an 11% yield of secondary formate (30% *threo* and 70% *erythro*) and a 72% yield of olefin were formed. Hydrolysis of the formate and oxidation[4] of the alcohol gave ketone, $[\alpha]^{25}D$ −143 ± 2° (*c* 1, chloroform), or 25 ± 2% racemized. In acetolysis at 100°, 94% optically pure L-*erythro*-II-OTs gave a 9% yield of secondary acetate (10% *erythro*, 90% *threo*) and 57% olefin. Conversion of the acetate to the ketone gave $[\alpha]^{25}D$ −182 ± 2° (*c* 1, chloroform), or no detectable racemization. In formolysis of 94% optically pure L-*erythro*-II-OTs at 50°, a 9% yield of secondary formate (37% *erythro*, 63% *threo*) and 59% olefin was obtained. Conversion of the formate to ketone gave $[\alpha]^{25}D$ −183 ± 2° (*c* 1, chloroform), no detectable racemization. These results indicate that the racemized portion of ketone ultimately obtained from L-*threo*-II-OTs acetolysis arose

(11) (a) A. Hantzsch and F. Kraft, *Ber.*, **24**, 3516 (1891); (b) C. Moureu and G. Mignonac, *Ann. Chim.* (Paris) [9] **14**, 320 (1891); (c) J. B. Culbertson, *J. Am. Chem. Soc.*, **73**, 4818 (1951); *cf.* pK_a (cyclohexylidenimmonium ion) = 9.15 (M. Brězina and P. Zuman, *Chem. Listy*, 47, 975 (1953)).

(12) (a) H. Hosoya, J. Tanaka and S. Nagakura, *Tetrahedron*, **18**, 859 (1962); (b) H. Hosoya and S. Nagakura, *Bull. Chem. Soc. Japan*, 39, 1414 (1966).

(1) This research was sponsored by the U. S. Army Research Office, Durham, N. C. The authors extend their thanks.

(2) (a) D. J. Cram, *J. Am. Chem. Soc.*, 71, 3863 (1949); (b) D. J. Cram, *ibid.*, **74**, 2129 (1952).

(3) All new compounds gave carbon and hydrogen analyses within 0.3% of theory.

(4) K. E. Pitzner and J. G. Moffatt, *J. Am. Chem. Soc.*, **87**, 5670 (1965).