was examined, exchange did occur. The exchange was followed at 78.2° by observing changes in the n.m.r. spectrum of a sample of IV in deuteriotrifluoroacetic acid. Under these conditions, the half-lives for exchange of the hydrogens in the 2- and 5-positions of IV were 12 and 29 hr., respectively. Interestingly enough, the 4- and 6-hydrogens of IV and the hydrogens of the monoquaternary salt VI showed no measurable exchange after 80 hr. at 78.2°. We have also measured the half-life for exchange of the ring hydrogen in the tetrazolium salt VII[7,8] under our conditions and found it to be 6 hr. We made this measurement in order to relate our results to those of Olofson,[7] who reported that even in 2 N DCl VII undergoes rapid exchange involving base-catalyzed ylide formation.

VI   VII
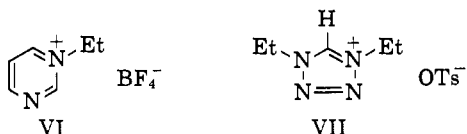
Our results are interesting in two respects. First, the 2-hydrogen of IV undergoes exchange, probably *via* the cation ylide VIII, at a rate not too different from that of the tetrazolium salt VII. Presumably a good part of the driving force for this exchange is stabilization of VIII by removal in its formation of an unfavorable charge interaction. Second, although the 4- and 6-hydrogens of IV do not exchange, the 5-hydrogen does exchange. Because any factor[9] favoring exchange of the 5-hydrogen by an ylide mechanism would certainly operate to an even greater extent to facilitate exchange of the 4- and 6-hydrogens, it follows that ylide formation cannot be involved in exchange of the 5-hydrogen. A reasonable explanation for the observed exchange of the 5-hydrogen is that it occurs *via* the intermediate IX, formed by 1,4 addition of trifluoroacetic acid to the dication.

VIII   IX
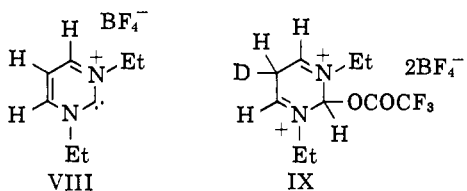
Our exchange results, although of a preliminary and incomplete nature, suggest that hydrogen exchange in heterocyclic systems occurs by at least two mechanisms, which operate in some cases with nearly equal facility.

We are actively pursuing further study of this interesting new class of substances and will report the results in future communications.

(7) R. A. Olofson, W. R. Thompson, and J. S. Michelman, *J. Am. Chem. Soc.*, **86**, 1865 (1964).

(8) We are indebted to Professor Olofson for a generous gift of this material.

(9) For a discussion of these factors see R. Breslow, *J. Am. Chem. Soc.*, **80**, 3719 (1958), and ref. 7.

(10) This work was begun at the Department of Chemistry, Yale University.

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## Evidence for a Thiete (Thiacyclobutene)[1,2]

Sir:

We have obtained evidence for the existence of the first aliphatic thiete, 7-thiabicyclo[4.2.0]-1(8)-octene (1). Paquette has reported the synthesis of the first fused aromatic derivatives of thiete.[3] A pentane solution of 1 is obtained by treatment at 0° of the quaternary salt


1
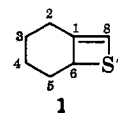
2 in dimethylformamide with potassium *t*-butoxide followed by extraction with pentane. N-Methylpyrrolidine is isolated as the picrate, m.p. 221° (lit.[4] m.p. 221°). The yield was 50–60%.

The clear, colorless pentane solution of 1 was oxidized with monoperphthalic acid at −10° to give an oil (possibly the sulfoxide[5]) which was oxidized further at 70° with 30% hydrogen peroxide in acetic acid to 7-thiabicyclo[4.2.0]-1(8)-octene 7,7-dioxide (3), in 20% yield (based on 2), m.p. 88–89° (lit.[3,6] m.p. 88–89°, 89.5–90.5°). The infrared spectrum of sulfone 3 is identical with that of an authentic sample, and a mixture melting point with an authentic sample showed no depression.

2   3
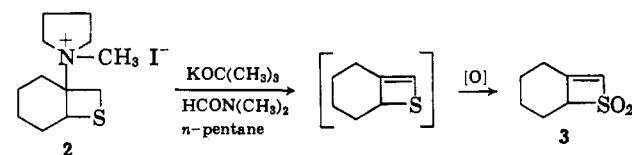
Quaternary salt 2 is prepared from 1-(1-pyrrolidinyl)-7-thiabicyclo[4.2.0]octane 7,7-dioxide[6] which is first reduced to the sulfide which is alkylated with methyl iodide to give the salt, m.p. 133–135°. *Anal.* Calcd. for $C_{12}H_{22}INS$: C, 42.47; H, 6.53; N, 4.13; S, 9.45. Found: C, 42.61; H, 6.49; N, 3.93; S, 9.47. The proton n.m.r. spectrum (in D_2O at 60 Mc.) showed absorptions at *ca.* δ 2.2 (relative area 13, probably the 9 protons of the cyclohexane ring and the 4 β-protons of the pyrrolidine ring), 3.2 (relative area 4, probably the 3 protons of the methyl group and one of the protons of the thietane ring), and 3.8 (relative area 5, probably the 4 α-protons of the pyrrolidine ring and 1 of the protons of the thietane ring). An aid in the assignment of the chemical shift of the methyl protons and the α- and β-protons of the pyrrolidine ring was the proton n.m.r. spectrum of N,N-dimethylpyrrolidinium iodide.

4
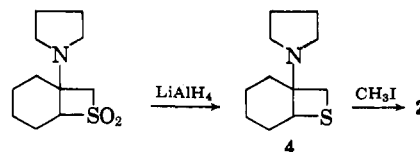
(1) This work was supported by Grant GP-726 of the National Science Foundation.

(2) Reported in part at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

(3) L. A. Paquette, *J. Org. Chem.*, **30**, 629 (1965).

(4) K. Löffler and C. Freytag, *Ber.*, **42**, 3427 (1909).

(5) The oil showed absorption at 1067 cm.⁻¹ in the infrared, typical of a sulfoxide. Trimethylene sulfide when treated with monoperphthalic acid under the same conditions gave a 93% yield of trimethylene sulfoxide.

(6) D. C. Dittmer and F. A. Davis, *J. Org. Chem.*, **29**, 3131 (1964).

If the pentane solution of **1** is allowed to stand at room temperature for 24 hr., a white, apparently polymeric material is obtained. This polymer has not been characterized although it contains sulfur and no nitrogen and has an infrared absorption at 1600 cm.$^{-1}$ which may indicate the presence of a double bond.

Oxidation as before of half of a pentane solution of **1** gives a 21% yield of the sulfone **3**. Before oxidation, the pentane solution was washed with dilute hydrochloric acid.[7] The other half of the solution is allowed to stand at room temperature for 24 hr., the polymer is removed by filtration, and the solution is oxidized with monoperphthalic acid at $-10°$ and then at 70° with 30% hydrogen peroxide in acetic acid. No thiete sulfone, **3**, is obtained from this latter solution. This result eliminates the possibility that the thiete sulfone was derived from **2** or from **4** by oxidation of the sulfur and elimination of the amine fragment during or subsequent to the oxidation since **2** and **4** are stable at room temperature. The polymer apparently is derived from the substance (presumably **1**) in the pentane solution which yields sulfone **3** on oxidation since there is no longer any oxidizable product if polymerization is allowed to proceed prior to oxidation.

Treatment of the pentane solution of **1** with 2,4-dinitrophenylhydrazine reagent yields a 2,4-dinitrophenylhydrazone, m.p. 219–220°, whose melting point and infrared and ultraviolet spectra are identical with those of the 2,4-dinitrophenylhydrazone of 1-cyclohexene aldehyde.[8]
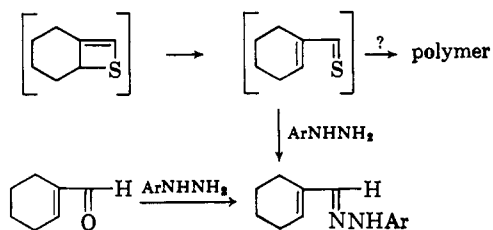
Attempts to isolate **1** by carrying out the elimination reaction with potassium *t*-butoxide in dimethyl sulfoxide at 0.5 mm. give a small amount of polymer and 60–65% of N-methylpyrrolidine which is identified as its picrate and by its infrared spectrum. The colorless material collected in the traps gives a 2,4-dinitrophenylhydrazone and semicarbazone (m.p. 210–213°, lit.[9] m.p. 212–213°) identical with the same derivatives from 1-cyclohexene aldehyde. Hydrogen sulfide is evolved during formation of the semicarbazone and 2,4-dinitrophenylhydrazone. The colorless material in the traps polymerizes when it is warmed to room temperature; under these conditions cyclohexene aldehyde is stable. It is possible that the colorless material in the traps was, in part, the thiete **1** since thiocarbonyl compounds are usually colored. The intermediacy of an aromatic thiete derivative previously was suggested to account for the formation of a thioaldehyde derivative in the reduction of a naphthothiete sulfone by lithium aluminum hydride.[10]

(7) Compound **4** is removed from the pentane solution by the acid wash. The salt **2** is insoluble in pentane, but any trapped mechanically would be removed in the aqueous acid washings.
(8) I. Heilbron, E. R. H. Jones, R. W. Richardson, and F. Sondheimer, *J. Chem. Soc.*, 737 (1949).
(9) W. Borsche and R. Schmidt, *Ber.*, **43**, 3400 (1910).
(10) D. C. Dittmer and N. Takashina, *Tetrahedron Letters*, 3809 (1964).

Work is in progress on the isolation of **1** and its anion, the latter which might have considerable relative stability.[11]

(11) D. C. Dittmer and M. E. Christy, *J. Am. Chem. Soc.*, **84**, 399 (1962).

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Cyclosenegenin, a Derivative of Senegenin in *Polygala senega*

Sir:

Recent work on the sapogenins of *Polygala senega* has resulted in the assignment of structures to senegenin ($C_{30}H_{45}ClO_6$, I) and senegenic acid ($C_{29}H_{44}O_6$, II).[1,2] Since senegenin contains chlorine and senegenic acid has one less carbon than I, it was suspected that both compounds are artifacts produced during the vigorous hydrolysis of senegin by hydrochloric acid.[1,2] We wish to report the isolation and structure of a new sapogenin obtained by the mild hydrolysis of senegin.

The hydrolysis of senegin[3] in aqueous sulfuric acid followed by acetylation and silica gel chromatography furnished two crystalline acids as the acetates. One of these was identified as senegenic acid diacetate (IIb). The other compound[4] (IIIb), $C_{36}H_{52}O_{10}$, m.p. 329–332° (with effervescence), $[\alpha]^{22}D$ +21.3° (c 0.94, EtOH), upon alkaline hydrolysis, gave the acetyl-free compound (IIIa), $C_{30}H_{46}O_7$, m.p. 246–253° (with effervescence), $[\alpha]^{22}D$ +5.7° (c 0.71, EtOH). Acetylation of IIIa regenerated IIIb. Compound IIIb shows no hydroxyl absorption in the infrared and gives an amorphous methyl ester whose p.m.r. spectrum shows the presence of three acetyl groups (τ 8.07, 7.95, and 7.93), two methyl ester moieties (τ 6.33 and 6.40), and five C-methyl groups (τ 9.13, 9.11, 9.00, 8.88, and 8.69). Therefore, the oxygen functions of IIIa are accounted for as two carboxyl and three hydroxyl groups. Moreover, there is an unsharp AB system (τ 6.10 and 5.65 ($J = 12$ c.p.s.)), suggesting an acetoxy methylene group connected with an asymmetric center.[5]

Treatment of IIIa with dilute sulfuric acid at reflux for 18 hr. afforded a diene (IV) which proved to be identical with that obtained by dehydrochlorination of I with quinoline.[1] Clearly, this new sapogenin may be assigned structure IIIa and is therefore the "hydroxysenegenin" proposed by Dugan, de Mayo, and Starratt as the precursor which leads to senegenic acid (IIa) by a reverse Prins reaction.[1]

The solvolysis of the chlorine in I led to interesting results. Treatment of I with 2 N NaOH solution followed by careful acidification and repeated crystalliza-

(1) J. J. Dugan, P. de Mayo, and A. N. Starratt, *Can. J. Chem.*, **42**, 491 (1964); *Tetrahedron Letters*, 2567 (1964); *Proc. Chem. Soc.*, 264 (1964).
(2) S. W. Pelletier, N. Adityachaudhury, M. Tomasz, J. J. Reynolds, and R. Mechoulam, *Tetrahedron Letters*, 3065 (1964).
(3) W. A. Jacobs and O. Isler, *J. Biol. Chem.*, **119**, 155 (1937).
(4) Satisfactory analyses were obtained for all compounds cited in this paper. P.m.r. spectra were taken in CDCl₃ unless specified.
(5) L. M. Jackmann, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1959, p. 102.