

Further evidence for the abstraction mechanism was obtained by adding a few per cent oxygen to the reaction vessels. In these experiments, which were done at high pressure, the ethane, chloroethane, and 1,2-dichloroethane reaction products were virtually completely eliminated. This is true for both diazomethane and ketene as the methylene sources. It is well known that the reaction of  $O_2$  with singlet methylene is slow<sup>4,6</sup> while  $O_2$  is a good scavenger for alkyl-type radicals. Consequently these oxygen results support strongly the abstraction mechanism.

In conclusion we can set a limit from our data of less than 5% C-H or C-Cl insertion for the gas phase reaction of methylene with methyl chloride. The principal reaction is Cl abstraction; however, some H abstraction occurs concurrently. Further work is continuing with other alkyl halides with the objectives of determining the factors which govern insertion vs. abstraction reactions of  $CH_2$  as well as studying the unimolecular decomposition reactions of the vibrationally excited alkyl halides.

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## Heterocyclic Diquaternary Salts

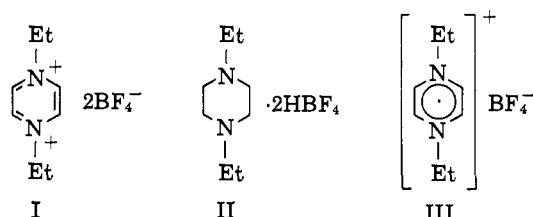
Sir:

All previous attempts to prepare diquaternary salts of pyrazines, pyrimidines, and pyridazines have apparently met with failure.<sup>1</sup> We now wish to report that both pyrazines and pyrimidines can be converted to diquaternary salts by the action of triethyloxonium fluoroborate<sup>2</sup> in refluxing dichloroethane.

The following bases have been dialkylated by this procedure (yield in parenthesis): pyrazine (97%), 2,5-dimethylpyrazine (95%), 2,6-dimethylpyrazine (46%), 2,3,5,6-tetramethylpyrazine (6%), pyrimidine (86%), and 4,6-dimethylpyrimidine (97%). The structures assigned to the alkylation products follow from elemental analyses and n.m.r. spectra,<sup>3</sup> the latter indicating the presence in every case of two equivalent ethyl groups located on nitrogen. In addition, 1,4-diethylpyrazinium difluoroborate (I) has been catalytically reduced to 1,4-diethylpiperazinium dihydrofluoroborate (II), identical in all respects with a sample prepared from authentic 1,4-diethylpiperazine and fluoroboric acid.

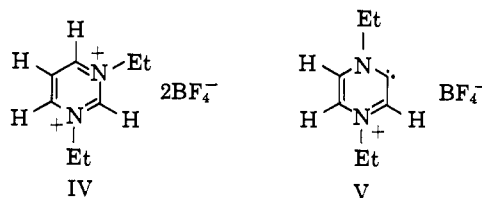
The presence of two positive charges in a conjugated ring might lead to unusual reactivity, processes resulting in net loss of a positive charge being strongly favored. In point of fact, pyrazinium and pyrimidinium di-

quaternary salts are extremely reactive substances. Alcoholic solutions of the pyrazinium salts give rise to strong e.p.r. signals. For example, a  $10^{-3}$  M solution of I in ethanol shows a complex spectrum (greater than 200 lines), analysis<sup>4</sup> of which fully supports the conclusion that the paramagnetic species present is the radical cation III. Identical e.p.r. spectra were obtained from solutions of I in methyl, ethyl, and isopropyl alcohols and, moreover, these solutions when prepared *in vacuo* showed little spectral change after 3 months. The radical cation is thus readily formed from the dication and is stable in the absence of air.



It was also possible to observe formation of III by n.m.r. techniques. When a trifluoroacetic acid solution of I in an open tube was briefly contacted with granulated zinc, the radical cation formed<sup>5</sup> caused such line broadening that virtually no n.m.r. spectrum could be observed. However, as the concentration of III decreased with time,<sup>6</sup> broad peaks began to appear and to sharpen, until after 30 min. the original spectrum had reappeared with only slightly diminished intensity.

All the pyrazinium diquaternary salts prepared thus far have yielded strong e.p.r. signals upon solution in alcohols. It seems reasonable to conclude that such facile electron abstraction is due in part to the reduction of an unfavorable charge interaction in the parent dication. One might therefore expect pyrimidinium diquaternary salts to undergo even more facile electron abstraction. We have, however, been unable to show radical cation formation from 1,3-diethylpyrimidinium difluoroborate (IV) by either of the techniques used for the analogous pyrazinium compounds. It is, of course, possible that a short-lived radical was formed in these experiments but was undetected by the techniques employed. We are currently investigating this possibility.



The facility with which the pyrazinium diquaternary salts formed radical cations suggested that they might readily lose a proton to form cation ylides, for example V. Unfortunately, attempts to exchange deuterium into the ring hydrogens of I under a variety of conditions led to decomposition without observable exchange. When, however, the analogous pyrimidinium salt IV

(1) The literature abounds with examples of alkylations in which use of a large excess of alkyl halide leads only to monoalkylation. See also: Y. T. Pratt in "Heterocyclic Compounds," Vol. 6, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1957, p. 400; C. T. Bahner and L. L. Norton, *J. Am. Chem. Soc.*, **72**, 2881 (1950); A. E. Blood and C. R. Noller, *J. Org. Chem.*, **22**, 844 (1957).

(2) H. Meerwein, E. Battenberg, H. Gold, E. Pfeil, and G. Willfang, *J. prakt. Chem.*, **154**, 83 (1939).

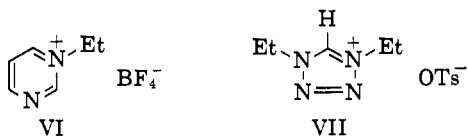
(3) Observed in trifluoroacetic acid.

(4) This analysis was carried out by Professor Charles Johnson of Yale University and will be reported elsewhere.

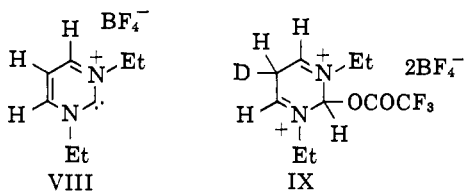
(5) That III was formed under these conditions was demonstrated by conducting the zinc reduction in a sealed evacuated tube and examining the resulting solution in the e.p.r. spectrometer. The spectrum observed was identical with that of the diquaternary salt in alcohol.

(6) Presumably due to reaction with atmospheric oxygen.

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<sup>7,8</sup> under our conditions and found it to be 6 hr. We made this measurement in order to relate our results to those of Olofson,<sup>7</sup> who reported that even in 2 N DCl VII undergoes rapid exchange involving base-catalyzed ylide formation.



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<sup>9</sup> 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.



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.

T. J. Curphey

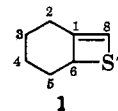
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## Evidence for a Thiete (Thiacyclobutene)<sup>1,2</sup>

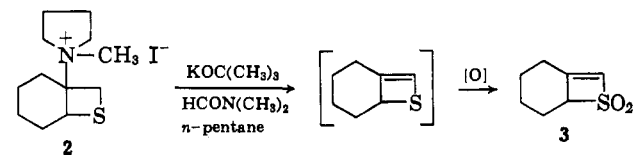
Sir:

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.<sup>3</sup> A pentane solution of **1** is obtained by treatment at 0° of the quaternary salt

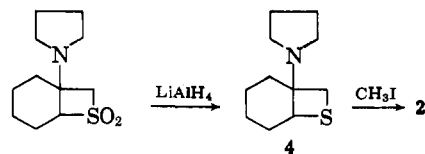


**2** in dimethylformamide with potassium *t*-butoxide followed by extraction with pentane. *N*-Methylpyrrolidine is isolated as the picrate, m.p. 221° (lit.<sup>4</sup> m.p. 221°). The yield was 50–60%.

The clear, colorless pentane solution of **1** was oxidized with monopero-phthalic acid at –10° to give an oil (possibly the sulfoxide<sup>5</sup>) 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.<sup>3,6</sup> 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.



Quaternary salt **2** is prepared from 1-(1-pyrrolidinyl)-7-thiabicyclo[4.2.0]octane 7,7-dioxide<sup>6</sup> 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<sub>12</sub>H<sub>22</sub>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<sub>2</sub>O 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.



(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.<sup>-1</sup> in the infrared, typical of a sulfoxide. Trimethylene sulfide when treated with monopero-phthalic acid under the same conditions gave a 93% yield of trimethylene sulfone.

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