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Formation of Spirocompounds by Rearrangement of N,N-Dimethylhexahydrothienoazocinium or Azoninium Ylides

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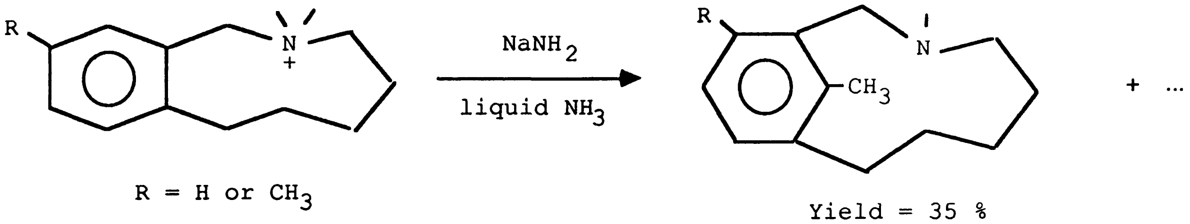
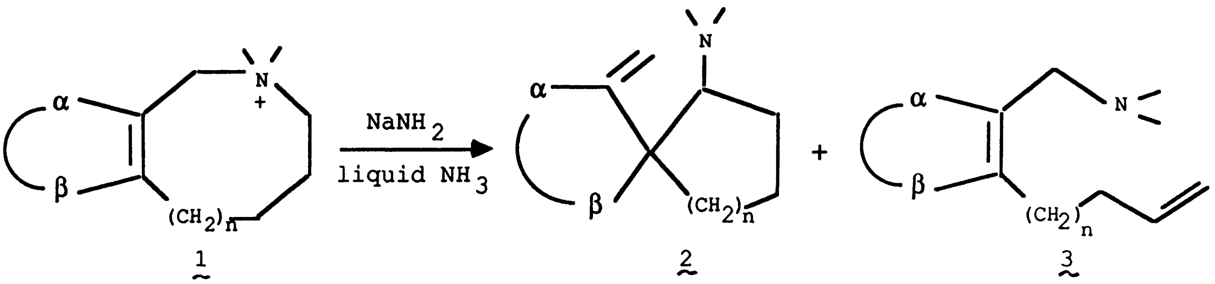
Treatment of N,N-dimethylhexahydrothienoazocinium or azoninium salts by sodium amide in liquid ammonia affords spirocompounds. These products arise from ammonium ylides by [2,3] sigmatropy and are easily hydrolyzed to carbonyl compounds by dilute acids.

Recent papers on rearrangement of sulfonium ylides by presumed spirocyclic intermediates$^{1-3)}$ prompt us to report our results on rearrangement of ammonium ylides where spirocompounds are isolated and characterized. Treatment of N,N-dimethyl-2,3,4,5,6,7-hexahydro-1H-2-benzazoninium iodides by sodium amide in liquid ammonia has been previously investigated$^{4)}$: 2-aza(7)metacyclophanes were the main products.



Scheme 1.

In the present work we found that similar treatment of N,N-dimethylhexahydrothieno-azocinium or azoninium ylides 1 affords spirocompounds 2.



Scheme 2.

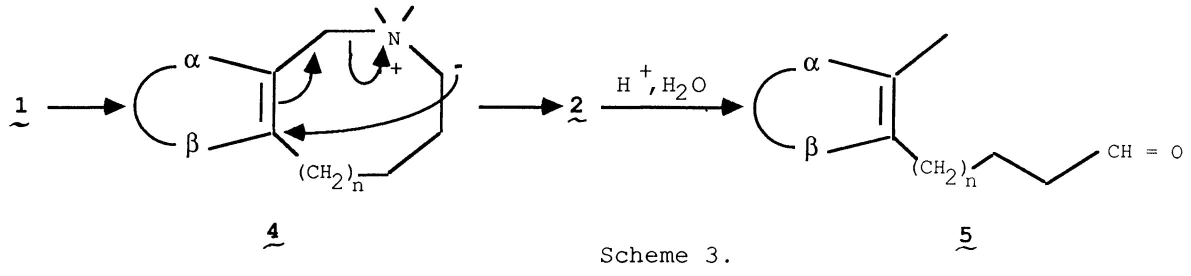
Compounds 1 are obtained from 2-[2(or 3)-thienyl]pyrrolidinium or piperidinium salts$^{5)}$ and are allowed to react with sodium amide (2 equiv.) in liquid ammonia for 20 min; after addition of ammonium chloride and dilution with ether, the ammonia and the solvent are evaporated, and the mixture of amines is distilled.

Table 1. Rearrangement of ammonium salts

	n	α–β	**1** Yield/%	**2** Yield/%	**3** Yield/%
a	1	CH = CH - S	48	100	0
b	2	CH = CH - S	63	70	30
c	1	S - CH = CH	90	85	15
d	2	S - CH = CH	32	0	100

Alkenes **3** are the Hofmann elimination products; the dimethylaminomethyl and the vinyl groups are easily identified by ^{1}H-NMR spectroscopy [for instance 3**d** exhibits singlets at δ ($CDCl_3$) 2.27 [$N(C\underline{H}_3)_2$], 3.54 ($C\underline{H}_2N$) and multiplets at 4.99 (=$C\underline{H}_2$) and 5.81 ($C\underline{H}$=)]. Compounds **2** arise from ammonium ylides **4** by [2,3] sigmatropy (Scheme 3); elemental analyses and mass spectral data of 2**a** (M+, m/z 195), i.e., indicate a molecular formula of $C_{11}H_{17}NS$. The ^{1}H-NMR spectrum of this compound has resonances at δ ($CDCl_3$) 1.70 (m,$CH_2C\underline{H}_2CH_2$), 1.90 and 2.40 (2m, $CHC\underline{H}_2$), 2.10 (m, $C\underline{H}_2CH_2CH_2$), 2.25 [s, $N(C\underline{H}_3)_2$], 2.75 (dd, $C\underline{H}CH_2$, J=9.8 and 7.4 Hz), 4.92 and 5.27 (d and s, =$C\underline{H}_2$), 5.95 (d, S-C$\underline{H}$=, J=5.8 Hz), and 6.45 ppm (dd, S-CH=C$\underline{H}$, J=5.8 and 1.4 Hz). The spiro stucture of 2**a** is also supported by its ^{13}C-NMR spectrum: δ ($CDCl_3$) 21.7(t), 31.6(t), 45.0(q), 48.3(t), 67.9(s), 77.5(d), 109.1(t), 125.0(d), 130.9(d), and 156.8 ppm (s).

Compounds **2** are easily hydrolyzed by dilute acids to the aldehydes **5** via presumed immonium salts. Those carbonyl compounds are identified by mass spectrometry and NMR spectroscopy (features of carbonyl and thienyl structure).



Scheme 3.

References

1) M.Hori, T.Kataoka, H.Shimizu, M.Kataoka, A.Tomoto, and M.Kishida, Tetrahedron Lett., 24, 3733 (1983).

2) M.Hori, T.Kataoka, H.Shimizu, and O.Komatsu, J.Chem.Soc., Chem.Commun., 1985, 883.

3) K.Ohkata, K.Okada, K.Maruyama, and K.Akiba, Tetrahedron Lett., 27, 3257 (1986).

4) D.Barbry, B.Hasiak, and D.Couturier, 7th Symposium on Heterocyclic Chemistry, Marseille, 1981.

5) P.Cotelle, B.Hasiak, D.Barbry, and D.Couturier, in press; compounds **1** give spectroscopic and analytical data in agreement with their stucture.

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