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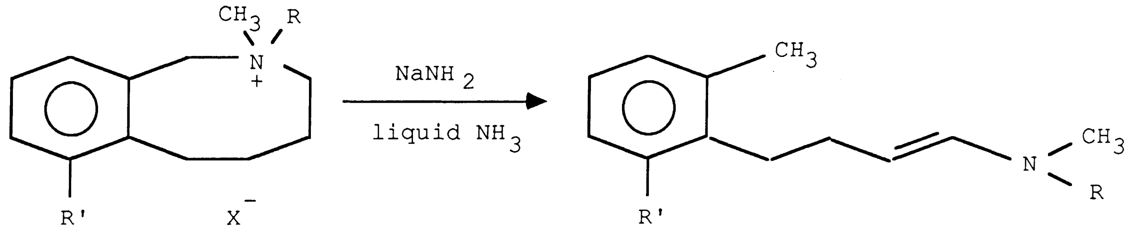
Thermal Rearrangement of Dimethylaminomethylenethiaspirononenes and thiaspirodecenes

Philippe COTELLE, Didier BARBRY,* Bruno HASIAK, and Daniel COUTURIER
Laboratoire de Synthèse Organique,
Université des Sciences et Techniques de Lille Flandres-Artois,
59655 Villeneuve d'Ascq Cedex, France

Enamines are the thermal rearrangement products of (5R*,6R*)-6-dimethylamino-4-methylene-1-thiaspiro(4,5)-2-decene and (4,4)-2-nonene, and (5R*,6S*)-6-dimethylamino-1-methylene-2-thiaspiro(4,4)-3-nonene. The mechanism of formation of these compounds is discussed.

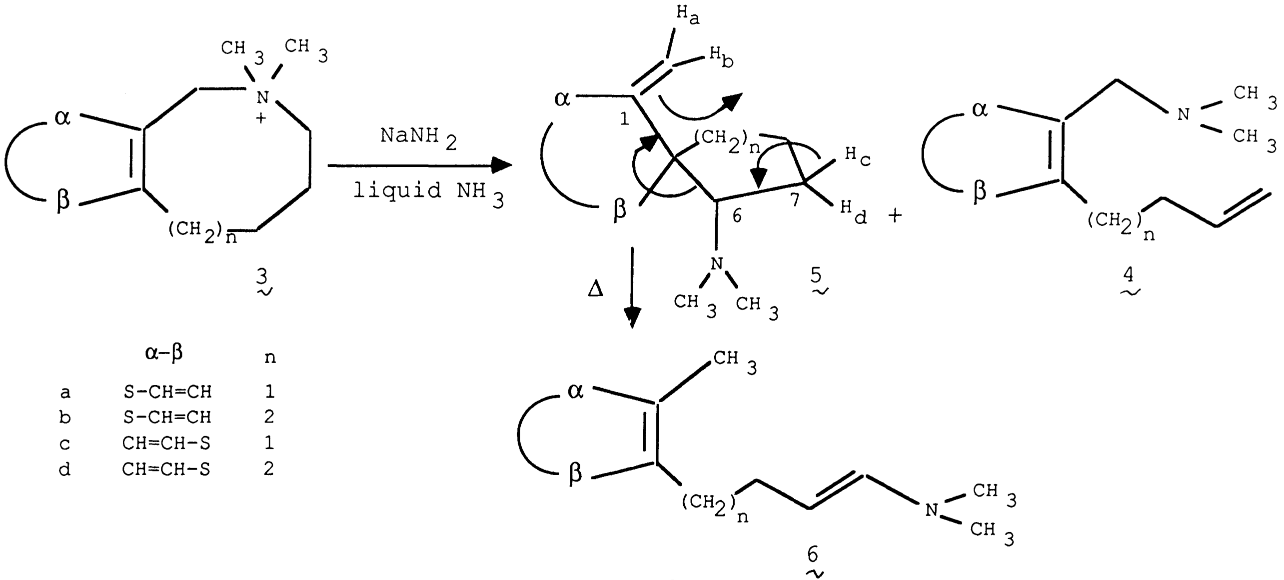
Spirocyclic compounds have been involved as intermediates in the rearrangement of sulfonium ylides.[1-3] We recently report the unexpected synthesis of enamines 2 obtained by treatment of 2,2-dialkyl-1,2,3,4,5,6-hexahydro-2-benzazocinium halides 1 with sodium amide in liquid ammonia [4] (Scheme 1). In the same conditions, the N,N-dimethylhexahydrothieno(3,2-c) or (2,3-c) azocinium and azoninium salts 3 afford Hofmann elimination products 4, and spirocompounds 5 (Scheme 2).[5]



1

Scheme 1.

2



3 5 4 6

	α-β	n
a	S-CH=CH	1
b	S-CH=CH	2
c	CH=CH-S	1
d	CH=CH-S	2

Scheme 2.

We here report the thermal rearrangement of spirocompounds **5** to enamines **6**. These compounds **6** have the E-configuration as expected by the value of the coupling constant between the olefinic hydrogens. Intramolecular mechanism easily explains the formation of **6** (Scheme 2). This process has been previously described in thermal rearrangement.$^{6)}$ The absolute configurations of compounds **5** are established by NOE's : irradiation of the hydrogens of the dimethylamino group of **5a** induces an enhancement of S-CH=C$\underline{H}$- (20%). By irradiation of Hb of **5d**, the H-6 part of the ^{1}H spectrum exhibits an enhancement of 15%. So the configuration is (5R*,6R*) for **5c** and **5d** and (5R*,6S*) for **5a**. Such diastereoselectivity in ylide rearrangement was previously noted $^{7)}$ but the reaction here is stereospecific. Proximity of H-7c and methylene group are required for this rearrangement : the dimethylamino group and H-7c should be transoid and this leads to the E-configuration for **6**.

Table 1. Thermal rearrangement of spirocompounds **5**

	n	α–β	Temperature °C	Time min	**6** (yield/ %)
a	1	S-CH=CH	80	30	5
			150	5	60
c	1	CH=CH-S	80	30	0
			180	5	12
d	2	CH=CH-S	80	30	0
			200	5	20

Compounds **6** arise from thermal degradation of **5** in a sealed tube and the crude products are flash chromatographed on a short column (diameter 30 mm ; length 45 mm) with 230-400 mesh silica gel to give pure samples of **6**. The 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra of **6a** support the enamine structure δ(CDCl$_3$):2.20(q,CH$_2$C$\underline{H}_2$CH=,^{3}J=6.8 Hz), 2.36(s,N(C$\underline{H}_3$)$_2$), 2.52(s,C$\underline{H}_3$), 2.53(t, C$\underline{H}_2$CH$_2$CH=), 4.23 (quint.-like, C$\underline{H}$=CH-N, ^{3}J= 6.8 and 13.7 Hz), 5.91(d,CH=C$\underline{H}$-N), 6.79(d, C$\underline{H}$=CH-S, ^{3}J=5.3 Hz),7.00(d, CH=C$\underline{H}$-S); 12.9(q,C$\underline{H}_3$),30.6(t,$\underline{C}$H$_2$CH$_2$CH=),36.3(t,CH$_2\underline{C}$H$_2$CH=),41.0(q,N($\underline{C}$H$_3$)$_2$),99.2(d,$\underline{C}$H=CH-N),120.5 (d,CH=$\underline{C}$H-S),128.9(d,$\underline{C}$H=CH-S),133.0(s,S$\underline{C}$(CH$_3$)=),136.5(s,SC=$\underline{C}$(CH$_2$)),140.4(d,CH=$\underline{C}$H-N).

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