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PERICYCLIC REACTIONS OF PSEUDO-TRIENES. ELECTROCYCLIZATION OF S-BUTADIENYL SULFILIMINES

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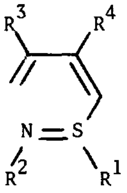
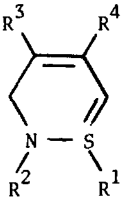
N-Tosyl-S-butadienyl sulfilimines were prepared from butadienyl sulfides and were thermally converted into N-tosyl pyrroles, probably via cyclic azasulfonium ylides

S-Butadienyl sulfilimines (1) may be formally considered to be thia-aza analogues of all-carbon hexatrienes.[2] Like the latter, they contain a system of six electrons in *p*-orbitals, and these are arranged in an apparently adequate configuration/conformation for effective overlap of terminal orbitals, with possible delocalization and eventual formation of new bonds. As a consequence, compounds 1 may be expected to undergo a thermal electrocyclization reaction[3] to the corresponding heterocyclohexadienes, namely, the azasulfonium ylides 2.



1



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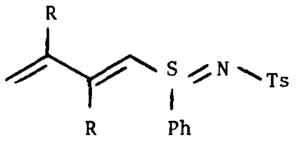
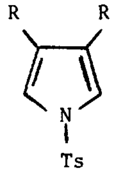


3 a, R=H
b, R=Me



4 a, R=H
b, R=Me

Sulfilimines 1a (R^1=Ph, R^2=Ts, R^3=R^4=H), mp 119-120 °C, and 1b (R^1=Ph, R^2=Ts, R^3=R^4=Me), mp 132-133 °C, were prepared by reaction of the corresponding *Z*-sulfides with Chloramine-T[4] in methanol-dichloromethane.[5] The sulfides were obtained by reduction of the *Z*-sulfoxides,[6] using phosphorus pentasulfide[7] for the unsubstituted butadienyl compound and triphenylphosphine[8] for the dimethyl compound.[9]

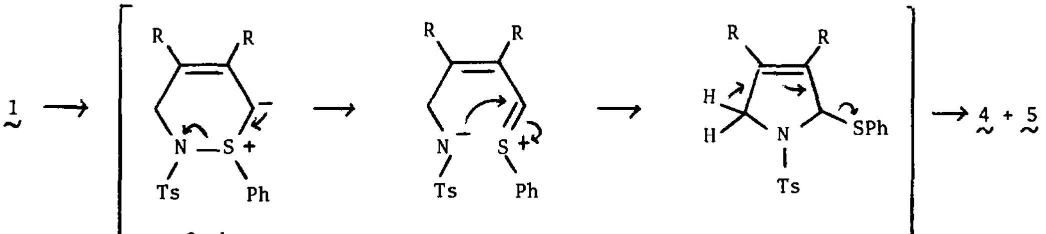
The related *E*-sulfilimines (3) were prepared for comparative purposes. Compound 3a, mp 125-126 °C, was obtained by photochemical isomerization of 1a with a 100 W lamp and iodine, followed by chromatographic separation of the equilibrium mixture (*E*/*Z* $\sim$ 5). Compound 3b, mp 123-124 °C, was obtained through thermal cis-trans isomerization of the *Z*-sulfide, followed by reaction with Chloramine-T.

When 1a or 1b are heated in deuteriobromoform at 130 °C, the ^{1}H NMR spectrum after 0.5 h is practically that of a 1:1 mixture of the corresponding N-tosyl pyrrole (4) and benzene thiol (5). Under the same conditions, the trans isomer 3a is unaffected, while 3b shows ca 30% conversion into the above mixture, probably through concurrent geometrical isomerization (see below).

The transformation 1 → 4 + 5 could be carried out preparatively in various solvents but was best performed in phenylisocyanate, which trapped 5 as its N-phenylthiourethane PhNHCOSPh

(**6**). Chromatographic separation provided **4a**[10] and **4b** in over 80% yield, relative to unrecovered **1** (recovery of **1** was of 5 to 15%).

The transformation of sulfilimines **1**, where the nitrogen is bound to two sulfur atoms, into **4**, where it is bound to two carbons and one sulfur atom, indicates that a prior rearrangement into **2** has occured This is then probably followed by a Stevens-type rearrangement involving migration of nitrogen from sulfur to carbon,[11] with subsequent elimination of benzene thiol (Scheme)



2a,b

Scheme

At temperatures lower than 130 °C, the cyclization reaction becomes slow relative to a concurrent geometrical isomerization, particularly for **1b** After two hours at 80 °C in $CDBr_3$, **1b** is converted into a 1 1 mixture with **3b**, with no apparent formation of **4b** After 18 h at the same temperature, the mixture consists of **4b**, **3b**, and **1b** in an approximate ratio of 4 7 1, respectively. After 0 5 h at 110 °C the ratio of **4b** to **3b** is 1 4, and that of **4a** to **3a** is 1. At 130 °C **3b** is, however, converted in 2 h into the same mixture of **4** and **5** which is obtained from **1b** in 0.5 h, probably through shift of the cis-trans equilibrium by rapid cyclization of the cis-isomer

References and Notes

1. This work was carried out during a sabbatical leave at the Organisch-chemisches Institut der Technische Universität München, Garching
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10 M.A.R. Khayat, F S. Al-Isa, Tetrahedron Lett , 1970, 1351 (the authors mistakingly report the aromatic methyl signal at τ 8 39, δ 1 61)
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