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STUDIES ON α,β-UNSATURATED THIONE S-IMIDES AND S-OXIDES: THE SYNTHESIS OF β-AMINOVINYLARYLTHIONE S-IMIDES AND S-OXIDES FROM THE THIONES

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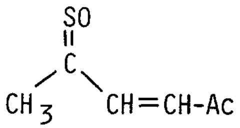
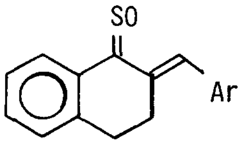
Abstract: β-Aminovinylarylthione S-imides and S-oxides were synthesized from the corresponding thiones. Their chemical properties have been studied.

The synthesis and chemical properties of ylidenesulfimides (thione S-imides, >C=S=N-), a novel type of thiocumulene, have recently been investigated.[1] For example, fluorenethione S-tosylimides react not only as a 4π-system (1,3-dipoles, enophiles) but also as a 2π-system (dienophiles) in cycloaddition reactions.[2] On the other hand, thione S-oxides (sulfines, >C=S=O) are well-known and have been thoroughly investigated.[3] However, non-cyclic α,β-conjugated sulfines as well as α,β-unsaturated thione S-imides are very inaccessible compounds. To our knowledge there have been only few reports concerning these thiocumulenes, viz. the formation of 1 by singlet-oxygen oxidation of 2,5-dimethylthiophene in methanol[4] and the thermal ganeration of 2 from its dimer obtained by mCPBA oxidation of the corresponding thione dimer.[5] Periselectivity[6] and site selectivity in the reaction of these α,β-conjugated thiocumulenes also constitute an attractive subject.

This communication deals with the first synthesis of the monomeric β-aminovinylarylthione S-imides and S-oxides.


$CH_3C(=SO)CH=CH\text{-}Ac$ 1



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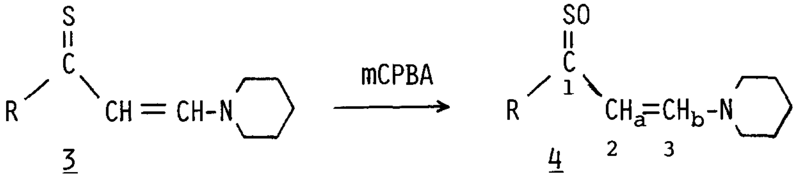
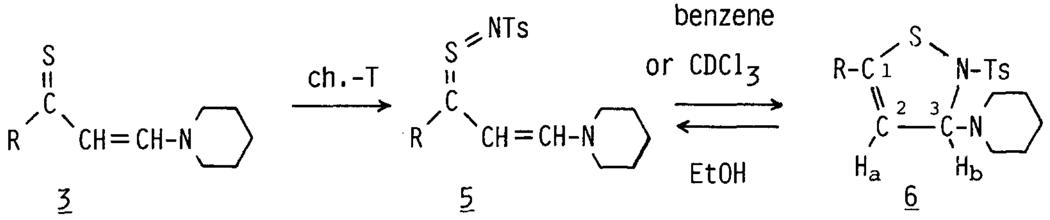
An equivalent amount of mCPBA (85%, 5.70 mmol) in 25 ml of CH_2Cl_2 was dropwise added with stirring to a CH_2Cl_2 solution (50 ml) of the 1-aryl-3-piperidino-2-propene-1-thione 3 (5.70 mmol) in the presence of $NaHCO_3$ (2.0g) at -10~0°C. After completion of the reaction (monitored by TLC, ca. 1h), the reaction mixture was washed with water, dried and the solvent was removed in vacuo. Column chromatography of the residue (alumina, CH_2Cl_2) gave sulfine 4[7] as yellow-orange crystals (Table I). The IR spectra (KBr disk) of compounds 4a-d showed strong absorptions of νCSO at ca. 1050 and 950 cm^{-1}, and the mass spectra displayed molecular ions (M^+) and fragment peaks (M^+-HSO) as base peaks. The ^{13}C-NMR spectra showed C(1)-signals at ca. 181-190 ppm, C(2) at 96 ppm, and C(3) at 148 ppm. C(1) resonated at higher field than that of the corresponding thione 3 ($\Delta \approx 20$ ppm), while chemical shifts for the other carbons (C(2) and C(3)) were almost unchanged from those of 3.[8] The ^1H-NMR spectra of 4 displayed signals centered at δ6.25-6.31 (d, H_a) and δ7.05-7.62 (br. d, H_b) with a large coupling constant (J_{ab}= 13 Hz) which indicated a trans-relationship (E) for H_a and H_b.[9]



R = a: C_6H_5, b: p-BrC_6H_4, c: p-$MeOC_6H_4$, d: 2-Thienyl

Table I. 1-Aryl-3-piperidino-2-propene-1-thione-S-oxides (4)[11]

	Yield,%	Mp,°C	IR,cm^{-1} νCSO	^1H-NMR,ppm -CH_a=CH_b-N	^{13}C-NMR,ppm C(1)	C(2)	C(3)
4a	61	107-109	1050 950	6.31(d,J=13Hz,Ha) 7.05(br.d,13Hz,Hb)	190.3	96.0	148.0
4b	62	115-117	1050 960	6.27(d,J=13Hz,Ha) 7.10(br.Hb)	188.9	96.0	147.9
4c	62	86-89	1025 955	6.31(d,J=13Hz,Ha) 7.05(br.d,13Hz,Hb)	190.3	96.1	148.0
4d	57	84-86	1020 950	6.25(d,J=13Hz,Ha) 7.62(br.d,13Hz,Hb)	181.9	95.9	148.2



R = a: C_6H_5, b: p-BrC_6H_4, c: p-$MeOC_6H_4$, d: 2-Thienyl

Treatment of thiones 3 (10 mmol) with chloramine-T (hydrate, 11 mmol) in ethanol (35-40 ml) at -10 ~ 0°C for 1h afforded thione S-imides 5 as yellow crystals in fairly good yields (Table II). The IR spectra (KBr) showed strong absorptions of νCSN at ca. 950, 940 cm^{-1} and of νSO_2 at ca. 1250, 1120, and 1090 cm^{-1}. When 5a was recrystallized from benzene-pentane, thiazoline 6a was obtained in 80% yield, mp 85-86°C (dec). The compound (6a) did not display the characteristic νCSN peak in the IR spectrum (KBr) and showed a small coupling constant (J= 3.0Hz) between H_a (δ5.84) and H_b (δ5.38) as compared with that of 3 (trans, J= 12Hz) in the ^{1}H-NMR. These findings agree with the assigned structure 6a. Surprisingly, 5a had identical mass spectral fragmentation pattern and ^{1}H- and ^{13}C-NMR spectra with those of 6a. The ^{1}H- and ^{13}C-NMR spectra for 5b-d also indicated that the compounds were in the cyclized form 6b-d in $CDCl_3$ solution.[10] Addition of ethanol to a saturated solution of 6a in $CHCl_3$ on cooling (-70°C) gave back 5a.

These findings can be reasonably explained by assuming that in a polar solvent such as EtOH or in the solid state, the polar structure 5 exists predominantly, while in a solvent such as benzene or $CDCl_3$, 5 easily undergoes a reversible intramolecular 1,5-dipolar cyclization to give 6.

References and Notes

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3) a) B. Zwanenburg, Recl. Trav. Chim. Pays-Bas, 101, 1 (1982); b) E. Block, "New Sulfine Chemistry", 9th International Symposium on Organic Sulfur Chemistry, Pergamon Press, 15 (1981).

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Table II. 1-Aryl-3-piperidino-2-propene-1-thione-S-tosylimides (5)[11]

	Yield,%	Mp,°C	IR,cm^{-1} νCSN	^{1}H-NMR,ppm =CHa—CHb-N	^{13}C-NMR,ppm C(1)	C(2)	C(3)
5a	74	96-98	960 940	5.84(d,J=3.0Hz,Ha) 5.38(d,J=3.0Hz,Hb)	132.2	110.5	94.1
5b	76	100-101	950 940	5.82(d,J=3.0Hz,Ha) 5.36(d,J=3.0Hz,Hb)	130.6	111.3	93.9
5c	69	85-86	950 940	5.84(d,J=2.8Hz,Ha) 5.24(d,J=2.8Hz,Hb)	131.5	108.7	94.1
5d	70	96-97	950 940	5.91(d,J=3.0Hz,Ha) 5.28(d,J=3.0Hz,Hb)	130.9	110.3	95.4

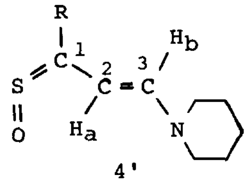
5) T. Karakasa and S. Motoki, Tetrahedron Lett., 3961 (1979); T. Karakasa, H. Ohmura, and S. Motoki, Chem. Lett., 825 (1980).

6) By "periselectivity" we mean the possible preference of a conjugated sulfine such as 1 or 2 or thione S-imide for reaction in a 2π, 4π or 6π mode over competitive modes.

7) Oxidation of β-aminovinylarylthione by $KMnO_4$, H_2O_2, I_2, HgO, or $Hg(OAc)_2$ gives no sulfine but its degradation products. H. Quiniu, Phosphorus and Sulfur, 10, 1 (1981); C. R. Acad. Sc., 274, (C), 1641 (1972).

8) E. Kleinpeter and M. Plust, J. Prakt. Chem., 322, 575 (1980).

9) Furthermore, there are four isomers possible by virtue of the CSO moiety being bent and the possibility of restricted rotation around the C(1)-C(2) bond in the light of the case of 3.[a)] The Z,E,s-E isomer 4' is the most likely of the four, based on ASIS measurement[b)] for the aryl-ortho protons and comparison of the chemical shifts for H_a and H_b with those of 3. a) J. B. Rasmussen, R. Shabana, and S.-O. Lawesson, Tetrahedron, 37, 197 (1981); b) A. Tangerman and B. Zwanenburg, Tetrahedron Lett., 79 (1973).



4'

10) Once thione S-imides 5b-d were dissolved, it appeared difficult to isolate them again either 5b-d or 6b-d because of their instability in solution.

11) All new compounds gave satisfactory elemental analyses.

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