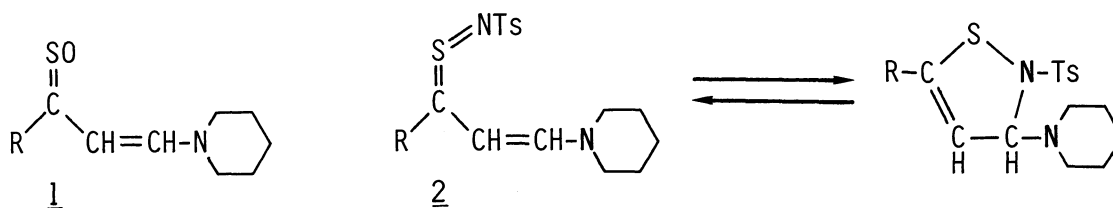


Synthesis of α -Arylmethylenethiocamphor S-Oxides and S-Imides

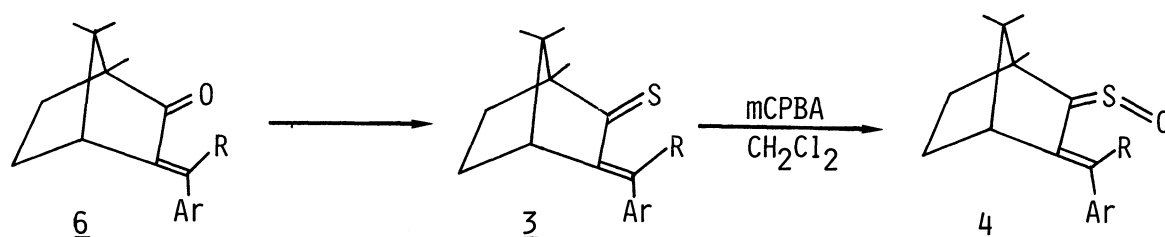
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α -Arylmethylenethiocamphor S-oxides and S-imides were synthesized from the corresponding thioketones. Most of them were found to be stable α,β -unsaturated thione S-oxides and S-imides.

α,β -Unsaturated sulfines and thione S-imides contain thiocumulene groups conjugated with carbon-carbon double bonds and are expected to undergo a variety of reactions. However there have been only few reports concerning these conjugated thiocumulenes.¹⁾ Previously, we reported the synthesis of sulfines 1 and thione S-imides 2 derived from the corresponding enaminothioketones.²⁾ It is considered that the stability of these thiocumulenes would be attributed to the electron donating effect of the nitrogen atom at the β -position to the thiocumulene moiety. On the other hand, α -arylmethylenethiocamphor 3 is one of the few examples of monomeric stable α,β -unsaturated thioketones having cisoid conformation, the stability of which seems to come from the steric protection of three methyl groups.³⁾ Therefore, we considered that the corresponding α -arylmethylenethiocamphor S-oxides 4 and S-imides 5 could also be obtained as stable compounds.



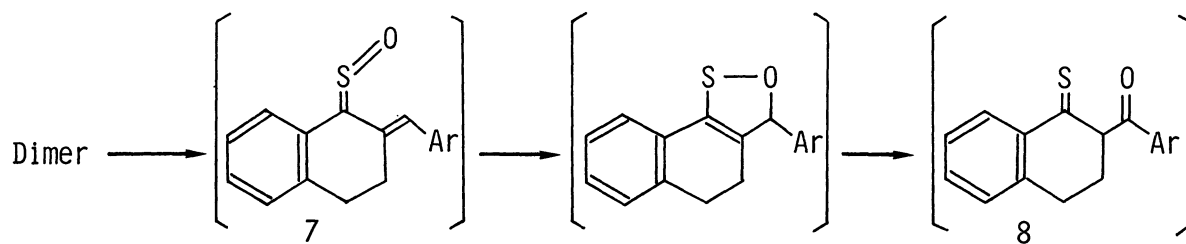
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Table 1. α -Arylmethylenethiocamphor S-oxides (4)

	R	Ar	Yield/%	Mp/ $^{\circ}\text{C}$	IR ν/cm^{-1}	^{13}C -NMR δ/ppm
					νCSO	C(2)
a	H	C_6H_5	97	100-101	1038	195.34
b	H	$p\text{-ClC}_6\text{H}_4$	92	132-134	1038	195.05
c	H	$p\text{-CH}_3\text{OC}_6\text{H}_4$	93	132-134	1038	195.64
d	H	$p\text{-(CH}_3)_2\text{NC}_6\text{H}_4$	92	201-203	1026	195.56
e	C_6H_5	C_6H_5	31	227-229	1046	200.79

An equivalent amount of mCPBA (80%, 4 mmol) in 20 ml of dichloromethane was dropwise added at 0°C with stirring to a dichloromethane solution (20 ml) of the thione 3 (4 mmol) prepared from the ketone 6. After completion of the reaction, the reaction mixture was washed with aq. Na_2CO_3 , dried and the solvent was removed in vacuo. Column chromatography of the residue (silica gel, dichloromethane) gave the S-oxides 4 as yellow to orange crystals (Table 1). The IR spectra of compounds 4 showed strong absorption of νCSO at ca. 1038 cm^{-1} and the mass spectra displayed molecular ions (M^+). The ^{13}C -NMR spectra showed the C(2) signal at ca. 195 ppm. C(2) resonated at higher field than that of the corresponding thione 3 ($\Delta\delta=55\text{ ppm}$), while chemical shifts for the other carbons were almost unchanged from those of 3. The ^1H -NMR spectra of 4a-d showed the signal of an olefinic proton at ca. $\delta=8.7$. This olefinic proton resonated at lower field than that of the corresponding thione 3 ($\Delta\delta=1.2$) or ketone 6 ($\Delta\delta=1.5$) (Table 2), then, the obtained sulfoxides 4a-d seem to have E-configuration.⁴⁾ The configuration of 4e could not be determined because of the absence of the olefinic proton. The sulfoxides 4 were very stable and did not change even by heating in xylene. The result is in contrast to the fact that the sulfoxide 7 generated by the thermolysis of the corresponding dimer easily gives the β -

thioxoketone 8 via the 1,2-oxathiolene intermediate⁵⁾ (The product 8 was identified by conversion to the disulfide).



An equivalent amount of chloramine T (hydrate, 4 mmol) in methanol (20 ml) was added to a solution of the thione 3d,e (4 mmol) in dichloromethane at -10°C . After the completion of the reaction, the reaction mixture was separated by column chromatography (florisil gel, dichloromethane) to give the thione S-imide 5d,e in fairly good yield (Table 3). The IR spectra showed absorptions of ν_{CSN} at 940 cm^{-1} and of ν_{SO_2} at 1180 and 1350 cm^{-1} and the mass spectra displayed molecular ions (M^+). Satisfactory results were also obtained in the elemental analysis.

Table 2. $^1\text{H-NMR}$ Spectra of the olefinic protons in sulfine 4 and the related compounds

	Ketone <u>6</u>	Thione <u>3</u>	Sulfine <u>4</u>
a	a)	a)	8.70
b	7.15	7.48	8.63
c	7.15	7.54	8.72
d	7.15	7.59	8.69

a) The signals of these proton were masked by those of aromatic protons.

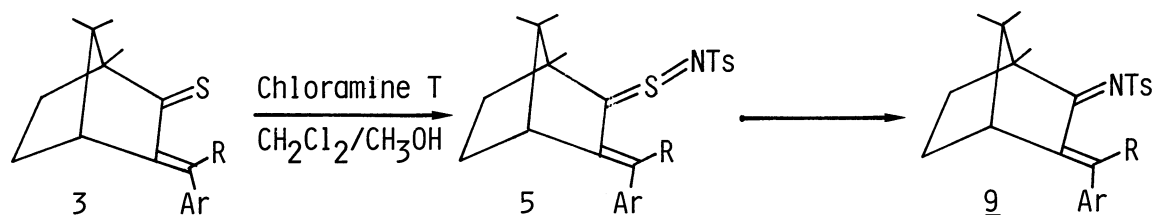


Table 3. α -Arylmethylenethiocamphor S-imides (5)

	R	Ar	Yield/%	Mp/ $^{\circ}\text{C}$	IR ν/cm^{-1}		
					ν_{CSN}	ν_{SO_2}	
d	H	$p\text{-(CH}_3)_2\text{NC}_6\text{H}_4$	82	48-51	946	1164	1354
e	C_6H_5	C_6H_5	79	133-135(dec.)	954	1160	1346

However, the ^1H -NMR and ^{13}C -NMR spectra were complex and could not be assigned except in the case of ^1H -NMR spectra of 5e. In the ^1H -NMR spectra of 5e, two sets of signals of four kinds of methyl protons in tosyl group and bornane skeleton were observed. This suggests that the thione S-imides 5d,e are a mixture of E and Z isomers with respect to the geometry of the sulfur atom. Attempts to separate the isomers were unsuccessful. The thione S-imides 5d,e were moderately stable at room temperature and did not change even on standing for long time, but they decomposed to give the imine 9d,e nearly quantitatively upon heating in xylene. When the thione 3a-c was allowed to react with chloramine T at -78°C in the same manner, the color of the solution turned from deep blue to red or reddish brown. However, when the solution was brought to room temperature, red color faded and TLC indicated the formation of many kinds of products including the imine 9a-c.

References

- 1) C. N. Skold and R. H. Schlessinger, *Tetrahedron Lett.*, 1970, 791; H. H. Wasserman and W. Strehlow, *ibid.*, 1970, 795; W. J. M. van Tilborg, *Recl. Trav. Chim. Pays-Bas*, 95, 140 (1976); K. Goldnick, *ibid.*, 103, 4921 (1984); T. Karakasa and S. Motoki, *Chem. Lett.*, 1979, 3961; M. F. Neumann, *Tetrahedron Lett.*, 1979, 2397.
- 2) T. Saito, N. Shibahara, and S. Motoki, *Tetrahedron Lett.*, 24, 4435 (1983).
- 3) D. C. Sen, *J. Indian Chem. Soc.*, 13, 523 (1936).
- 4) B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, 101, 1 (1982).
- 5) T. Karakasa, H. Ohmura, and S. Motoki, *Chem. Lett.*, 1980, 825.

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