SYNTHESIS AND YLIDIC PROPERTIES OF 1-ARYLTHIABENZENE 1-OXIDES

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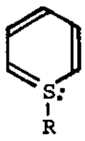
Abstract— 1-Arylthiabenzene 1-oxides were prepared by condensation reactions between arylmethyloxosulfonium methylides and 1,3-diphenyl-2-propyn-1-one (or 2-acetylcyclohexanone). An ylide-like bonding structure is proposed for the 1-arylthiabenzene 1-oxides.

Thiabenzenes (1) and thiabenzene 1-oxides (2) are of interest as heterocycles containing six π electrons in a cyclic conjugated ring system.[1] Mislow et al. reported that the configuration of the sulfur atom in thiabenzenes (1) is pyramidal and an optically active thiabenzene (4) was obtained by deprotonation of the sulfonium salt precursor (3) with brucine.[2]



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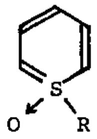

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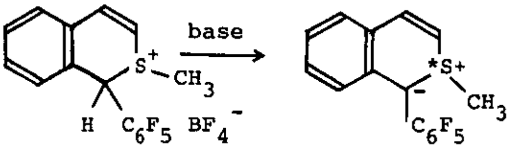

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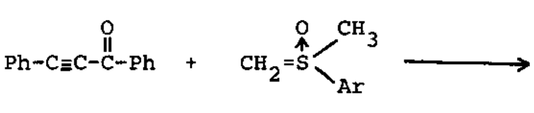
Thiabenzenes, except for suitably substituted thiabenzenes which can stabilize a negative charge on carbon, are inherently unstable compounds under ordinary conditions.[1] On the other hand, thiabenzene 1-oxides (2)[3-7] are thermally stable compared with thiabenzenes. These 1-methylthiabenzene 1-oxides (R= CH_3, 2)[3-7] were prepared by reactions of dimethyloxosulfonium methylide with 1,3-disubstituted 2-propynones,[3] β-diketones,[4] ethyl phenylpropiolate,[5] enol ether of dibenzoylmethane[6] and 3-ethoxymethylene-2,4-pentanedione.[7] To date there are a few reports concerning synthesis of 1-arylthiabenzene 1-oxides, because the corresponding arylmethyloxosulfonium methylides could not be easily prepared.

Recently we developed the simple synthetic method of aryldimethyloxosulfonium salts by oxidation of the corresponding sulfonium salts with aqueous solution of sodium m-chloroperbenzoate.[8] In the course of our studies on the reactivity of arylmethyloxosulfonium methylides (6) we attempted the synthesis of 1-arylthiabenzene 1-oxides.



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6a; Ar= C_6H_5
6b; Ar= C_6H_4-CH_3-p
6c; Ar= C_6H_4-Cl-p

7a; Ar= C_6H_5
7b; Ar= C_6H_4-CH_3-p
7c; Ar= C_6H_4-Cl-p

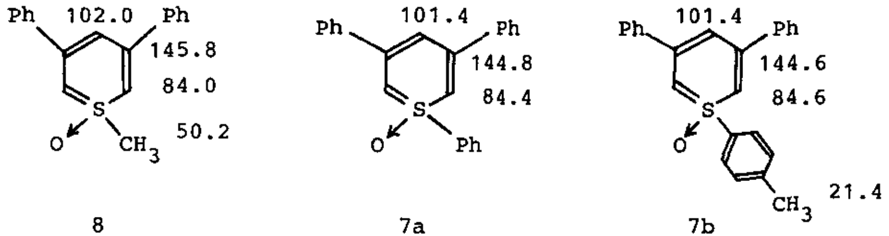
In a typical preparation a solution of 1,3-diphenyl-2-propyn-1-one (5) (2 mmol) in 5 ml of dry dimethyl sulfoxide was added rapidly with stirring under nitrogen to a solution of phenylmethyloxosulfonium methylide (6a)[9] (3 mmol) in 10 ml of dimethyl sulfoxide at room temperature. After 2h of stirring at room temperature the resulting red-orange solution was poured into water. Ether extraction afforded 67% of 1-phenyl-3,5-diphenylthiabenzene 1-oxide (7a) as yellow needles, mp 143-144.5 °C. Its infrared spectrum contains no carbonyl band, the principal absorption being at 1140 cm^{-1} (S=O). Its ^1H-nmr spectrum (in $CDCl_3$) shows signals at δ 5.69 (2H, doublet, J= 1.2 Hz), 6.41 (1H, triplet, J= 1.2 Hz), and 7.30-8.05 ppm (15H, multiplet).

Table 1. Yields, Mps and Chemical Shifts of Thiabenzene 1-Oxides 7

Compd	Yield(%)	mp(°C)	Chemical shifts[a)]		
			Aromatic-H	2,6-H	4-H
7a	67	143-144.5	7.30-8.05(m)	5.69(d)	6.41(t)
7b	60	158-160	7.24-7.89(m)[b)]	5.67(d)	6.40(t)
7c	63	183-185	7.23-8.00(m)	5.67(d)	6.41(t)

a) Peaks given as δ (ppm) from TMS; spectra were run in $CDCl_3$.
b) The ^1H-nmr spectrum of 7b shows a singlet at δ 2.43 ppm (CH_3 group).

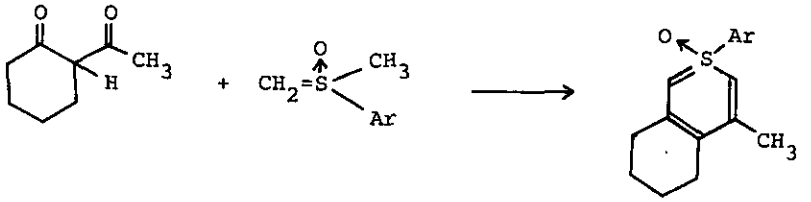
As shown in Table 1, the H-4 protons, although in the olefinic proton region, have chemical shift values which are sufficiently far upfield to suggest that no appreciable ring current effects are operative in the 1-oxides. The chemical shifts of H-2 and H-6 protons in 7a-c are also well outside of the aromatic region of ^{1}H-nmr spectrum and the more pronounced shielding of H-2 and H-6 compared with H-4 indicates more carbanionic character at C-2 and C-6 than C-4.



8 7a 7b

Figure 1. Selected carbon-13 chemical shifts in thiabenzene 1-oxides. Values were obtained for 8, 7a and 7b in $CDCl_3$ solution (δ ppm from TMS).[10]

The ^{13}C-nmr spectra (Figure 1) of 7a,b closely resemble that of 8 and the δ values also appear to indicate very high shielding of C-2 and C-6 and moderately high shielding of C-4 when they are compared with normal δ values for olefinic and benzenoid carbon atoms.[3] These results suggested that an ylide-like bonding structure is also proposed for 1-aryl-3,5-diphenylthiabenzene 1-oxides (7a-c). Similarly, reaction of the β-diketone 9 with the ylide 6a and followed by purification on silica gel preparative TLC, afforded a yellow oil (46%) to which we assigned structure (10a) based on spectral data; ir (neat) 1150 cm^{-1} (S=O); ^{1}H-nmr ($CDCl_3$) signals at δ 1.50-2.80 (8H, m, four CH_2-groups), 2.10 (3H, s, CH_3 group), 4.94 (1H, d, J= 4.8 Hz), 5.24 (1H, d, J= 4.8 Hz) and 7.35-7.95 (5H, m, phenyl group). The results are summarized in Table 2.



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6a; Ar= C_6H_5
6b; Ar= C_6H_4-CH_3-p
6c; Ar= C_6H_4-Cl-p

10a; Ar= C_6H_5
10b; Ar= C_6H_4-CH_3-p
10c; Ar= C_6H_4-Cl-p

Table 2. Yields and Selected Chemical Shifts of Thiabenezene 1-Oxides 10

Compd	Yield(%)	^{1}H-chemical shifts a)		^{13}C-chemical shifts a)	
		2,6-H b)	CH_3	2,6-C	CH_3
10a	46	4.94(d) 5.24(d)	2.10(s)	81.5 87.3	21.7
10b	49	4.96(d) 5.26(d)	2.11(s)	81.7 87.4	21.3
10c	58	4.96(d) 5.26(d)	2.13(s)	81.5 87.1	21.7

a) Peaks given as δ (ppm) from TMS; spectra were run in $CDCl_3$.
b) Coupling constant; J= 4.8 Hz.

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8. H. Takeuchi, M. Mori, H. Matsuyama, H. Minato, and M. Kobayashi; see abstracts of the 36th Annual Meeting of Chemical Society of Japan, Tokyo, 1977, II, p. 1066; $C_6H_5(CH_3)_2\overset{+}{S}(\rightarrow O)\ ClO_4^-$ (mp 107-109.5 °C), $p\text{-}CH_3\text{-}C_6H_4(CH_3)_2\overset{+}{S}(\rightarrow O)\ ClO_4^-$ (mp 172.5-174 °C), $p\text{-}Cl\text{-}C_6H_4(CH_3)_2\overset{+}{S}(\rightarrow O)\ ClO_4^-$ (mp 166.5-167 °C).
9. 6a was generated by deprotonation of phenyldimethyloxosulfonium perchlorate with NaH in dry dimethyl sulfoxide.
10. Values for 8 were calculated from ref. 3 and ^{13}C-nmr data (CS_2; 192.8 ppm from TMS).

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