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REACTIONS OF 1-METHYLTHIABENZENE 1-OXIDES AND 1-METHYL-2-AZA-THIABENZENE 1-OXIDES WITH ACETYLENEDICARBOXYLATE

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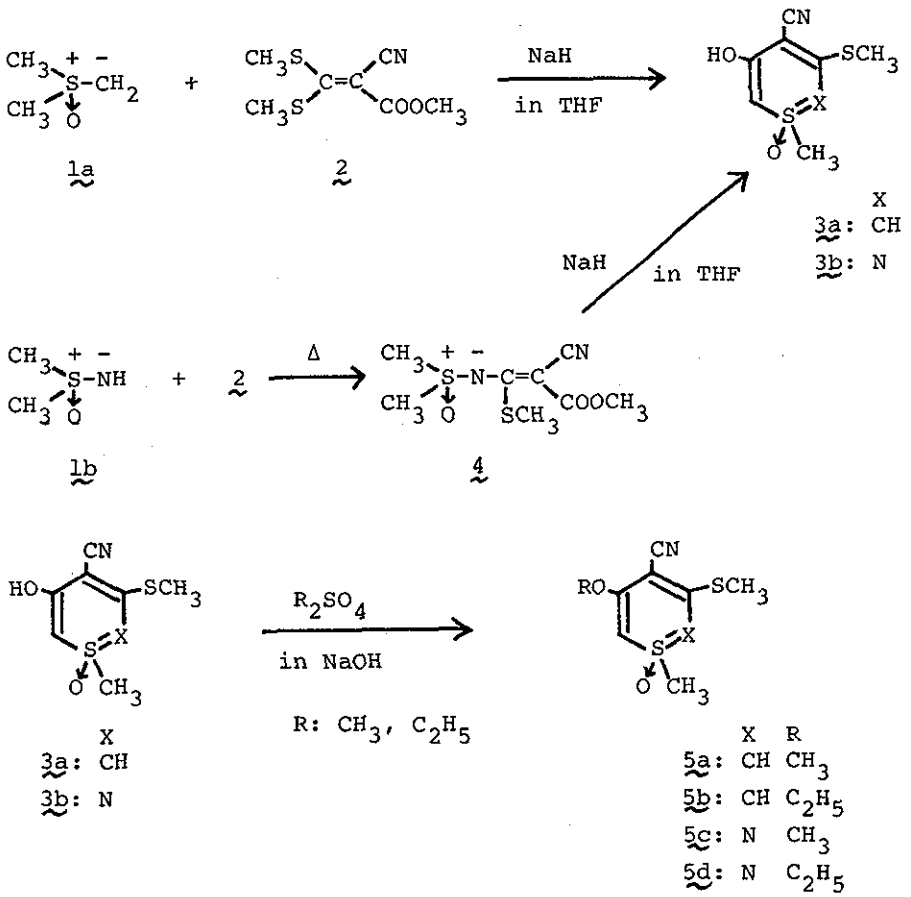
1-Methylthiabenzene 1-oxide (3a) and 1-methyl-2-azathiabenzene 1-oxide (3b) were synthesized by the reaction of dimethyloxosulfonium methylide and dimethylsulfoximine with ketenethioacetal (2) in the presence of base catalyst. 1-Methylthiabenzene 1-oxides (5a, 5b) and 1-methyl-2-azathiabenzene 1-oxides (5c, 5d) were treated with acetylenedicarboxylate (6) for comparison of chemical reactivities. Biscycloheptatriene derivative (7), 1,3-addition product, was obtained from the former and phthalate derivatives (10a, 10b), 1,4-addition products, from the later as major products.

1-Methylthiabenzene 1-oxide derivatives and 1-methylazathiabenzene 1-oxide derivatives, whose synthetic methods were reported by the several groups[1a-l] since 1965, were suggested

cyclic ylidic structures on the basis of spectral data [infrared absorption (IR), ^{1}H and ^{13}C nuclear magnetic resonance (NMR)[1e,1h,1k]] and chemical reactions (deuterium exchange, bromination, nitration etc.). From the above reports, 1-methyl-azathiabenzene 1-oxide derivatives are expected the alteration of electronic and chemical behavior to 1-methylthiabenzene 1-oxide derivatives.



Scheme 1

In this paper we wish to describe the difference of chemical reactivities of 1-methylthiabenzene 1-oxides and 1-methylazathiabenzene 1-oxides with dimethyl acetylenedicarboxylate.

Previously, we reported[1j] a new synthetic route to 1-methyl-2-azathiabenzene 1-oxides (3b, 5c) and 1-methyl-4-azathiabenzene 1-oxides by the reaction of dimethylsulfoximine (1b) and dimethyloxosulfonium methylide (1a) with methyl 3,3-bis(methylthio)-2-cyanoacrylate (2) and dimethyl cyanamidedithiocarboxylate, respectively. In the similar manner as described above, 1-methyl-3-methylthio-4-cyano-5-hydroxythiabenzene 1-oxide (3a) was prepared from 1a and 2 in 42% yield (Scheme 1). The structure of 3a was determined on the basis of the elemental analysis and IR, ultraviolet absorption (UV), and NMR spectra. The reactions of 3a with dimethyl sulfate and diethyl sulfate gave 1-methyl-3-methylthio-4-cyano-5-methoxythiabenzene 1-oxide (5a) as colorless needles, mp 216-217° [mass spectrum (MS) m/e 229 (M^+), IR (KBr) 2190 cm^{-1} (CN), UV λ_{max}^{EtOH} nm (log ε) 224 (4.16), 247 (4.53), 271 (4.01), and 318 (3.91), NMR (δ in DMSO-d_6) 2.41 (3H, s, SCH_3), 3.61 (3H, s, $SOCH_3$), 3.72 (3H, s, OCH_3), 5.82 (1H, d, J=4 Hz, C_6-H), and 5.98 (1H, d, J=4 Hz, C_2-H)] and 1-methyl-3-methylthio-4-cyano-5-ethoxythiabenzene 1-oxide (5b) as colorless needles, mp 214-215° in 78% and 42% yield, respectively. Similarly, the treatment of 1-methyl-3-methylthio-4-cyano-5-hydroxy-2-azathiabenzene 1-oxide (3b) with diethyl sulfate afforded 1-methyl-3-methylthio-4-cyano-5-ethoxy-2-azathiabenzene 1-oxide (5d) as colorless needles, mp 192-194°, which was also assigned on the

basis of the elemental analysis and IR, UV, and NMR spectra.

The ^{13}C-NMR spectral data of 5b and 5d are shown in Figure 1. The ^{13}C-NMR spectrum of 5b shows the ylidic anionic shielding of C-2, C-6, and C-4 which resonate at 75.6 ppm, 82.0 ppm, and 73.0 ppm in comparison with C-3 (149.3 ppm) and C-5 (162.8 ppm). In the ^{13}C-NMR spectrum of 5d, similar high shielding of C-4 (76.7 ppm) and C-6 (77.1 ppm) are observed.

The reactions of 1-methylthiabenzene 1-oxides (5a, 5b) and 1-methyl-2-azathiabenzene 1-oxides (5c, 5d) with dimethyl acetylenedicarboxylate (6) were outlined in Scheme 2. A solution of 5a and 6 in toluene was refluxed for 2 hr under an atmosphere of nitrogen to give 1,1'-dicyano-2,2'-dimethylthio-4,4',5,5'-tetramethoxycarbonyl-7,7'-dimethoxy-7,7'-bis(1,3,5-cycloheptatriene) (7) as yellow prisms in 12.5% yield, mp 219-220°. The structural assignment of 7 is based on following evidence. Its elemental analysis and MS comfirmed the molecular formula

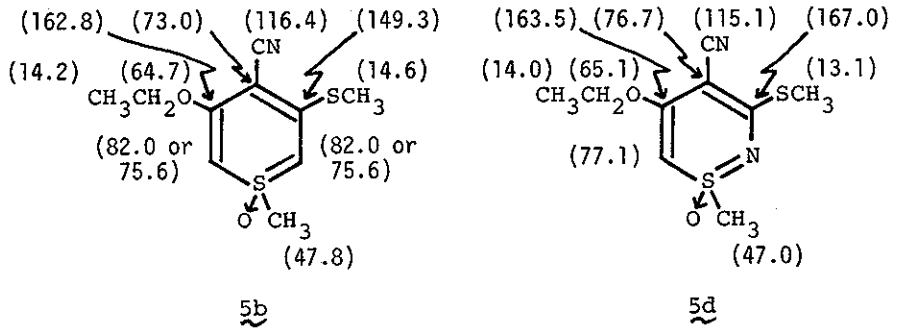
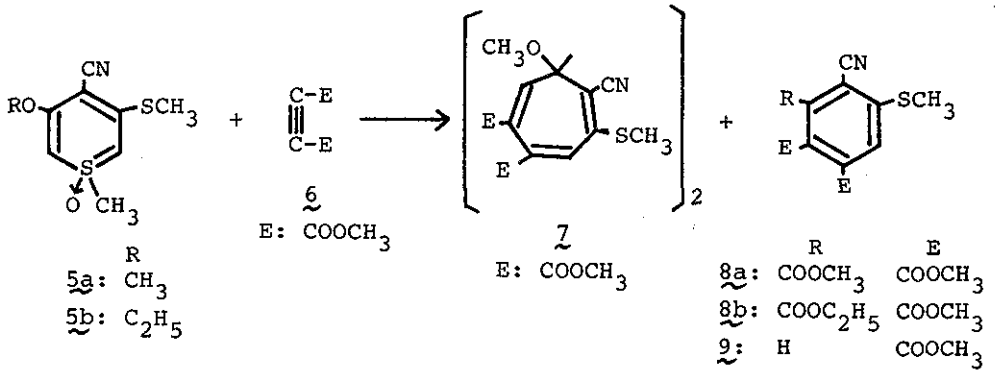


Figure 1 ^{13}C-NMR Chemical Shifts in DMSO-d_6 (ppm from Tetramethylsilane)

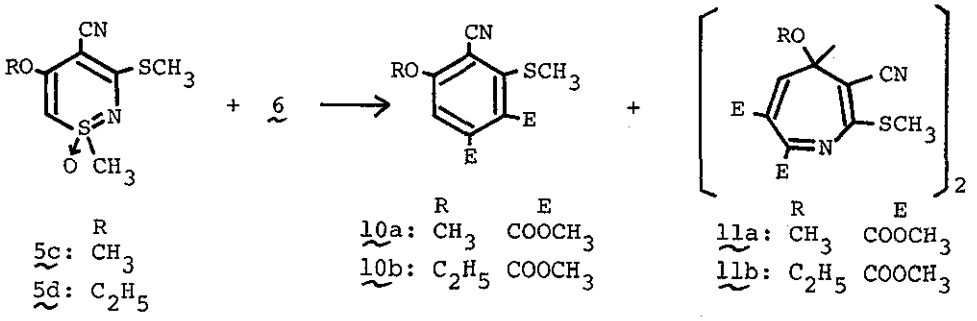


R
5a: CH_3
5b: C_2H_5

6
E: $COOCH_3$

7
E: $COOCH_3$

	R	E
8a:	$COOCH_3$	$COOCH_3$
8b:	$COOC_2H_5$	$COOCH_3$
9:	H	$COOCH_3$



R
5c: CH_3
5d: C_2H_5

	R	E
10a:	CH_3	$COOCH_3$
10b:	C_2H_5	$COOCH_3$

	R	E
11a:	CH_3	$COOCH_3$
11b:	C_2H_5	$COOCH_3$

Scheme 2

$C_{28}H_{28}O_{10}N_2S_2$ (M^+ m/e 616). The IR (KBr) spectrum showed two carbonyl bands at 1710 cm^{-1} and 1730 cm^{-1} and cyano band at 2200 cm^{-1}. The NMR ($CDCl_3$) spectrum revealed the absence of the signal attributable to $SOCH_3$, and showed signals at 2.57 ppm (3Hx2, s, SCH_3), 3.76 ppm (3Hx2, s, OCH_3), 3.85 ppm (3Hx2, s, OCH_3), 3.88 ppm (3Hx2, s, OCH_3), 4.52 ppm (1Hx2, s, ring proton) and 5.90 ppm (1Hx2, s, ring proton). The UV spectrum [λ_{max}^{EtOH} nm (log ε)] revealed maximum at 286 (4.32) which is similar absorption pattern to that of cycloheptatriene derivatives[2].

On the other hand, a mixture of 5a and 6 was heated in an oil bath at 130° in the absence of solvent for 4 hr to give 7 in 3.7% yield, dimethyl 3-methoxycarbonyl-4-cyano-5-methylthiophthalate (8a) in 1.4% yield, and dimethyl 4-cyano-5-methylthiophthalate (9) in 6.9% yield after the separation on column chromatography. The structures of 8a and 9 were comfirmed on the basis of the elemental analyses and IR, UV, and MS spectra. It is supposed that compound 7 is converted to 8a and 9 by atmospheric oxidation. Practically, when the similar reaction was carried out under an atmosphere of nitrogen, the yields of 8a and 9 decreased and that of 7 increased to 7.4% yield. The reaction of 5b with 6 at 130° produced only dimethyl 3-ethoxycarbonyl-4-cyano-5-methylthiophthalate (8b) in yield of 3.7%.

The reaction of 1-methyl-3-methylthio-4-cyano-5-methoxy-2-azathiabenzene 1-oxide (5c) with 6 in the absence of solvent gave dimethyl 3-methylthio-4-cyano-5-methoxyphthalate (10a) in 57.8% yield as colorless needles, mp 108-109° [MS m/e 295 (M^+), IR (KBr) 1730 cm^{-1} (CO) and 2200 cm^{-1} (CN), UV λ_{max}^{EtOH} nm (log ε) 221 (4.42), 255 (4.08), and 329 (3.78), NMR (δ in $CDCl_3$) 2.52 (3H, s, SCH_3), 3.90 (3H, s, OCH_3), 3.98 (3H, s, OCH_3), and 7.52 (1H, s, aromatic proton)] and 2,2'-dimethylthio-3,3'-dicyano-4,4'-dimethoxy-6,6',7,7'-tetramethoxycarbonyl-4,4'-bis(4H-azepine) (11a) in 2.9% yield as pale yellow prisms, mp 234-236° [MS m/e 618 (M^+), IR (KBr) 1713 cm^{-1} (CO), 1740 cm^{-1} (CO), and 2200 cm^{-1} (CN), UV λ_{max}^{EtOH} nm (log ε) 263 (4.41) and 310 (4.21, shoulder), NMR (δ in $CDCl_3$) 2.48 (3Hx2, s, SCH_3), 3.79 (3Hx2, s, OCH_3),

3.83 (3Hx2, s, OCH_3), 4.00 (3Hx2, s, OCH_3), and 4.16 (1Hx2, s, ring proton)]. In the similar manner, dimethyl 3-methylthio-4-cyano-5-ethoxyphthalate (**10b**) and 2,2'-dimethylthio-3,3'-dicyano-4,4'-diethoxy-6,6',7,7'-tetramethoxycarbonyl-4,4'-bis(4H-azepine) (**11b**) were prepared by the reaction of 1-methyl-3-methylthio-4-cyano-5-ethoxy-2-azathiabenzene 1-oxide (**5d**) with **6** in 63% yield and in a trace, respectively. A solution of **5c** and **6** in toluene was refluxed on an oil bath to give **10a** in 23.8% yield, and the starting material (**5c**) was recovered in 20% yield. We tried the reactions of **5c** with N-phenylmaleimide or methyl propiolate in place of **6** in the similar conditions, but the starting materials were recovered in quantitative.

From the above facts, the main reaction course of 1-methylthiabenzene 1-oxide with acetylenedicarboxylate involved 1,3-addition of acetylenes. On the other hand, 1,4-addition occurred by the reaction of acetylenedicarboxylate and 1-methyl-2-azathiabenzene 1-oxide. The above results suggested that the bond localization of $>\underset{O}{\overset{+}{S}}-\overset{-}{N}$ is stronger than that of $>\underset{O}{\overset{+}{S}}-\overset{-}{C}$ and 1-methyl-2-azathiabenzene 1-oxide ring react with acetylenedicarboxylate as cyclic diene system.

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