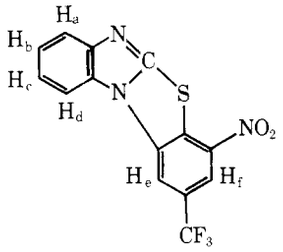
25–30 °C. The crude product, **3**, mp 247–249 °C, was obtained in 94% yield. After recrystallization from isopropyl alcohol **3** melted at 248–250 °C; NMR (Me_2SO-d_6) δ 6.90–7.60 (m, 4), 8.65 (s, 2); mass spectrum *m/e* (rel intensity) 384 (38), 338 (57), 292 (60), 274 (30), 251 (15), 223 (18), 133 (100), 106 (21), 102 (12), and 90 (23).

Anal. Calcd for $C_{14}H_7F_3N_4O_4S$: C, 43.76; H, 1.84; F, 14.83; N, 14.58; S, 8.38. Found: C, 43.85; H, 1.81; F, 14.70; N, 14.54; S, 8.57.

2-(2-Nitro-4-trifluoromethylphenylthio)benzimidazole (4). The procedure was identical with that described for product **3** except that 0.2 mol of 4-chloro-3-nitrobenzotrifluoride was substituted for the 4-chloro-3,5-dinitrobenzotrifluoride and the stirred reaction mixture was heated at 90–100 °C for 24 h. The crude product (**4**), mp 214–215 °C, was obtained in 95% yield. After recrystallization from methyl alcohol **4** melted at 218 °C; NMR (Me_2SO-d_6) δ 7.00–8.10 (m, 6), 8.45 (s, 1, $H_{3'}$); mass spectrum *m/e* (rel intensity) 339 (54.1), 294 (17.3), 293 (100), 292 (22.2), 206 (35.4), 133 (50.7), 122 (17.5), 106 (16.4), 90 (23.0), and 63 (21.0).

Anal. Calcd for $C_{14}H_8F_3N_3O_2S$: C, 49.56; H, 2.38; F, 16.80; N, 12.38; S, 9.45. Found: C, 49.50; H, 2.27; F, 17.06; N, 12.30; S, 9.50.

2-(Trifluoromethyl)-4-nitrobenzimidazo[2,1-*b*]benzothiazole (5). Method I. The charge and procedure were identical with those described for **3** except that after the addition of 4-chloro-3,5-dinitrobenzotrifluoride the stirred reaction mixture was heated at 90–100 °C for 24 h. During this heating period a brownish-yellow gas was liberated. The crude product, mp 26–269 ° C, was obtained in 86% yield. After recrystallization from DMF it melted at 275 °C; NMR (Me_2SO-d_6) below (sample was run on 90 MHz at ambient temperature with time averaging for 340 scans; a computer simulation was obtained of the four-spin system with assignments taken from the experimental spectrum); IR (CsI) 3090 (ArC–H), 1690–1480 (C=N), 1545(NO_2 asymmetric), 1400–1100 (C–F), 1295 (NO_2 symmetric), and 700–600 cm^{-1} (C–S); mass spectrum *m/e* (rel intensity) 337 (100), 318 (3), 291 (78), 279 (5), 271 (2), 247 (7), 227 (5), 222 (3), 178 (2), 168.5 (5), and 69 (7).



δ H_a 2143 Hz (8.7 ppm)	J_{ab} = +7 Hz
δ H_b 2038 Hz (7.5 ppm)	J_{bc} = +7 Hz
δ H_c 2028 Hz (7.4 ppm)	J_{cd} = +7 Hz
δ H_d 2062 Hz (7.8 ppm)	J_{ac} = +1.5 Hz
δ H_e 2168 Hz (8.9 ppm)	J_{bd} = +1.5 Hz
δ H_f 2134 Hz (8.6 ppm)	J_{ad} = 0

Method II. A stirred charge containing 19.2 g (0.05 mol) of **3** in 100 ml of DMf was heated at 90–100 °C for 24 h. During this heating period a brownish-yellow gas was liberated. After cooling to 30 °C, 400 ml of water was added and stirring continued for 1 h. The solid was collected by filtration, washed with water until the washings were neutral to litmus, and dried at 25–30 °C. The crude product, mp 272–274 °C, was obtained in 83% yield. After recrystallization from DMF it melted at 275 °C. A mixture melting point with the product obtained from method I was not depressed and the NMR and IR spectra of the two were superimposable.

Anal. Calcd. for $C_{14}H_6F_3N_3O_2S$: C, 49.86; H, 1.79; F, 16.90; N, 12.46; S, 9.51. Found: C, 49.94; H, 1.80; F, 16.73; N, 12.43; S, 9.46.

Attempted Cyclization of 4. A stirred mixture containing 34 g (0.1 mol) of **4** and 100 ml of dimethylformamide, *o*-dichlorobenzene, or nitrobenzene was heated at reflux temperatures for 24 h. During this heating period no gas was liberated and the solution became black. The first solvent furnished unchanged **4** and the latter two solvents afforded decomposed **4** (tars).

Registry No.—**1**, 60968-20-9; **2**, 60968-21-0; **3**, 60968-22-1; **4**, 60968-23-2; **5**, 60968-24-3; 2-benzothiazolol, 934-34-9; 4-chloro-3,5-dinitrobenzotrifluoride, 393-75-9; 4-chloro-3-nitrobenzotrifluoride, 121-17-5; 2-mercaptobenzimidazole, 583-39-1.

Supplementary Material Available. Mass spectral fragmentation routes for **3** and **5** (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Presented at 172nd National Meeting of the American Chemical Society, Organic Division, San Francisco, Calif., Sept 1976.
(2) J. J. D'Amico, C. C. Tung, and W. E. Dahl, *J. Org. Chem.*, **41**, 3564 (1976).
(3) See paragraph at end of paper regarding supplementary material.
(4) (a) G. F. Buffin and J. D. Kendall, *J. Chem. Soc.*, 361 (1956); (b) J. A. Van Allan, *J. Org. Chem.*, **21**, 24 (1956); (c) J. J. D'Amico, R. H. Campbell, and E. C. Guinn, *ibid.*, **29**, 865 (1964).

Syntheses and Some Properties of 4-Acyl-1-methyl-2-azathiabenzene 1-Oxides

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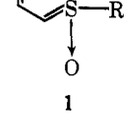
A series of 4-acyl-1-methyl-2-azathiabenzene 1-oxides have been prepared by base-catalyzed cyclization of *N*-(β,β-diacylvinyl)dimethylsulfoximines which, in turn, were obtained by the reactions of 3-ethoxymethylene-2,4-pentanedione, diethyl ethoxymethylenemalonate, ethyl 2-(ethoxymethylene)acetoacetate, and 2-acetyl-3-methoxy-2-cyclohexen-1-one with dimethylsulfoximine. Comparison of the physical and chemical properties of the azathiabenzene 1-oxides with those of the corresponding 4-acyl-1-methylthiabenzene 1-oxides suggests that both the ylidic and betainelike properties of the 2-azathiabenzene 1-oxides are much lower than those of the latter.

Thiabenzene 1-oxides (**1**) are of substantial intrinsic interest as heterocycles containing six π electrons in a cyclic conjugated ring system; if the 6π electrons can delocalize in the ring through sulfur, they are expected to be aromatic. Previous syntheses and studies of the properties of such 6π heterocycles,[1-5] however, have demonstrated that they can be best represented as cyclic ylidic structures.

The introduction of a heteroatom into the thiabenzene 1-oxides ring system is expected to alter significantly the electronic structure of **1**. Cram and Williams[6] have recently synthesized 3,5-diphenyl-1-methyl-2-azathiabenzene 1-oxide (**2**) and suggested that it is not aromatic on the basis of NMR



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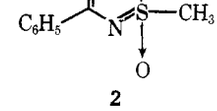
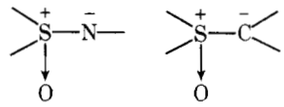


2

spectral data. However, because there is still limited information available concerning the properties of this heterocyclic system, we have now prepared a series of 4-acyl-1-methyl-2-azathiabenzene 1-oxides,[7,8] and compared their physical and chemical properties with those of the corresponding 4-acyl-1-methylthiabenzene 1-oxides.[4]

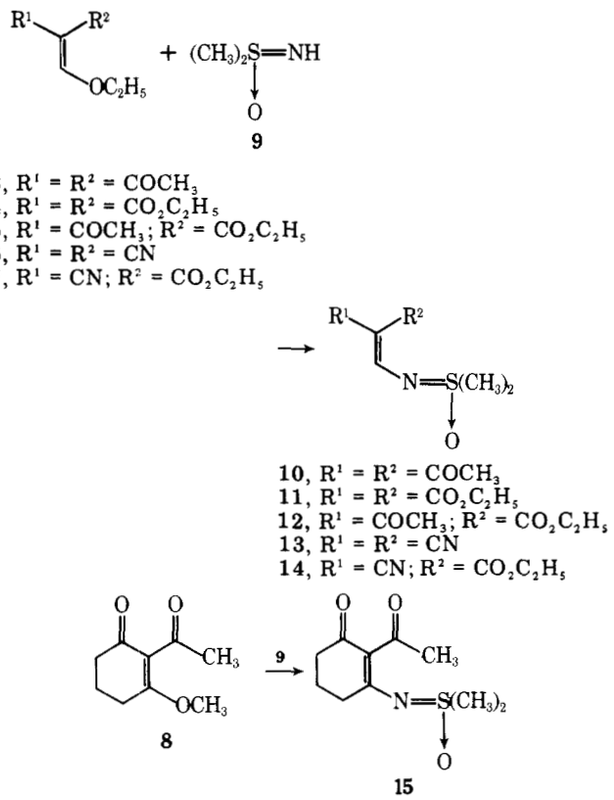
Syntheses. The 4-acyl-1-methyl-2-azathiabenzene 1-oxides were synthesized by application of the route used for the syntheses of 4-acyl-1-methylthiabenzene 1-oxides.[4] When 3-ethoxymethylene-2,4-pentanedione (**3**) was treated with dimethylsulfoximine (**9**) in chloroform at room temperature, there formed in 75% yield *N*-(β,β-diacetylvinyl)dimethylsulfoximine (**10**). Compounds **11–15** were also obtained in good yield from the reactions of diethyl ethoxymethylenemalonate (**4**), ethyl 2-(ethoxymethylene)acetoacetate (**5**),[9] ethoxymethylenemalononitrile (**6**), ethyl ethoxymethylenecyanoacetate (**7**), and 2-acetyl-3-methoxy-2-cyclohexen-1-one (**8**), respectively, with **9**. The structures of these new derivatives of sulfoximines were assigned on the basis of elemental and spectral data (see Experimental Section). The most striking feature of the NMR spectrum of **10** is that the two acetyl methyl groups give lines of equal intensity (δ 2.42 and 2.30) whose coalescence temperature is about 120 °C.[10] Similarly the signals due to the ethoxy methylene groups of **11** have different chemical shifts (δ 4.52 and 4.20), which remained invariant over a substantial temperature range (35–160 °C). These phenomena are in analogy to those observed with dimethyloxosulfonium 3,3-dicarbethoxy- and 1-carbethoxy-3,3-diacetylallylides,[4b] but in contrast to those observed with dimethylsulfonium 1-carbethoxy-4,4-diacetylallylide,[4b] 2,2-diacyl-*N*-(1-pyridinio)vinylaminides,[11] and 3,3-diacyl-(1-pyridinio)prop-2-enides,[11] in which the resonance due to two acetyl or ethoxy methylene groups is averaged owing to rapid rotation of these groups about the partial double bond.[12] The restricted rotation observed with the sulfoximines and oxosulfonium ylides suggests that structures are characterized by the presence of considerable bond localization. It is possible that such bond localization results from strong pπ–dπ bonding (contribution from ylene structures) in bonds i and ii, respectively.



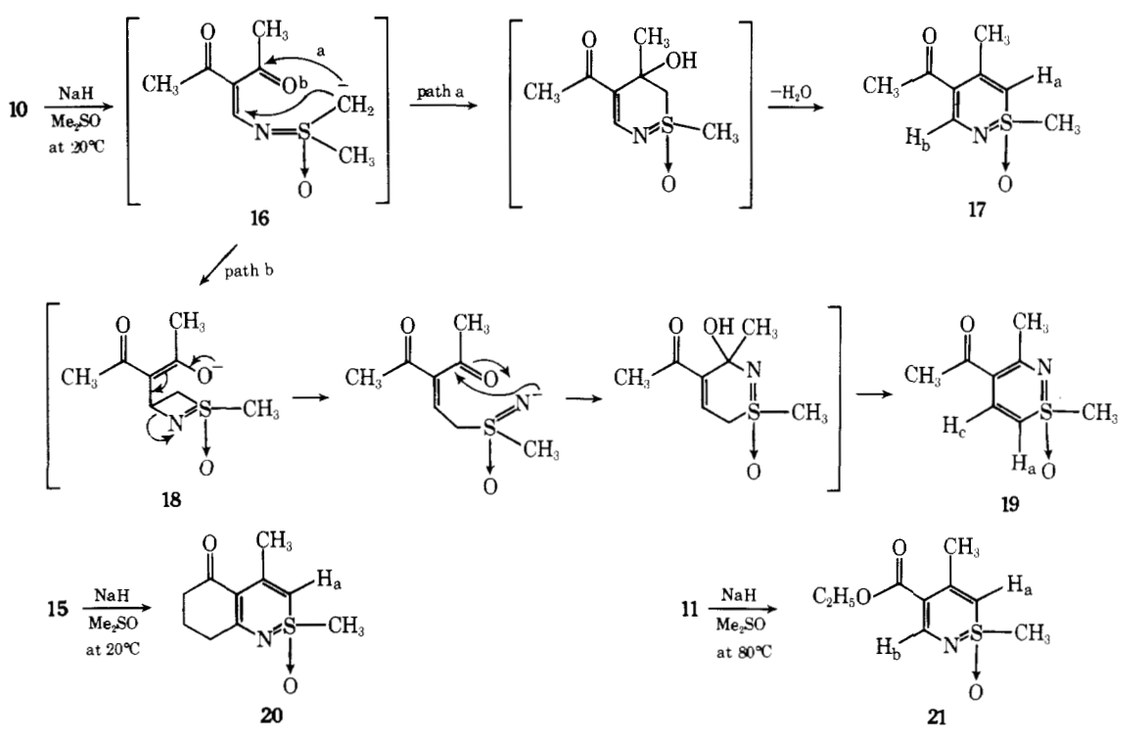
i ii

In the cases of **12** and **14**, the possibility of geometrical isomerism arises. In fact, the NMR spectrum of a freshly prepared deuteriochloroform solution of **12** shows signals for one of the isomers, but, after ca. 10 min, new signals corre-

Scheme I



Scheme II



sponding to the other isomer appear. At equilibrium the mixture consists of two isomers in a ratio of 1:1. Compound **14** was shown to exist as either one of the isomers by its NMR spectrum. In this case no isomerization took place.

The next step was the cyclization of these sulfoximines **10–15**. Treatment of **10** with sodium hydride in dimethyl sulfoxide for 3 h at room temperature gave two isomeric products **17** and **19** in 30 and 18% yields, respectively, whose structures were assigned on the basis of the elemental analyses and spectroscopic data (vide infra). This transformation can be formulated as shown in Scheme II. The initially formed ylidic anion **16** undergoes an intramolecular cyclization followed by dehydration to give **17** (path a). If the ylidic anion **16** competitively undergoes an intramolecular Michael addition reaction (path b), a four-membered ring intermediate **18** would be formed. This step may be followed by a C–N bond cleavage, cyclization, and dehydration to lead to **19.**

Similar treatment of **15** gave a bicyclic compound **20** in 73% yield. Compound **11** was less reactive and did not cyclize at room temperature, but gave **21** in 60% yield when the reaction mixture was heated at 80 °C for 5 min.

The cyclization of **12** was found to be markedly affected by the reaction temperature. Thus, after 3 h at room temperature **12** gave a mixture of three products, **22** (35%), **23** (13%), and **24** (7%), whereas in 5 min at 80 °C it gave a mixture of four products, **25** (41%), **22** (8%), **23** (13%), and **24** (1%). The structures of **22** and **25** were readily assigned by spectral comparison with those of **17** and **21,** respectively. The structure of **23** was confirmed by alkaline hydrolysis of **22** into **23.** Compound **24** was shown to be dimeric by mass spectrometry (M^+, *m/e* 430) and examination of the IR, UV, and NMR spectra enabled us to assign structure **24.** The IR spectrum shows two carbonyl absorption at 1710 and 1700 cm^{-1} and its UV spectrum closely resembles that of **22.** The NMR spectrum (90 MHz) reveals H_a and H_b at δ 6.33 and 8.39 (singlets), H_c and H_d at δ 3.67 as a doublet (2 H, J = 6 Hz), H_e at δ 5.14 as a broad signal, and H_f and H_g at δ 3.60 as an AB quartet with a further small splitting (J = 18 Hz). Irradiation of H_e resulted in collapse of the doublet at δ 3.67 (H_c and H_d) into a singlet. The remaining signals indicate the presence of two ethoxyl groups, one *S*-methyl group, and two *C*-methyl groups.

The main reaction course of the cyclization of **12** at room temperature involves the cyclization at the acetyl carbonyl groups, while the reaction at higher temperature resulted in formation of a product derived from the cyclization at the ester carbonyl group. Since the acetyl carbonyl group is more reactive than the ester carbonyl group as shown by the cycli-

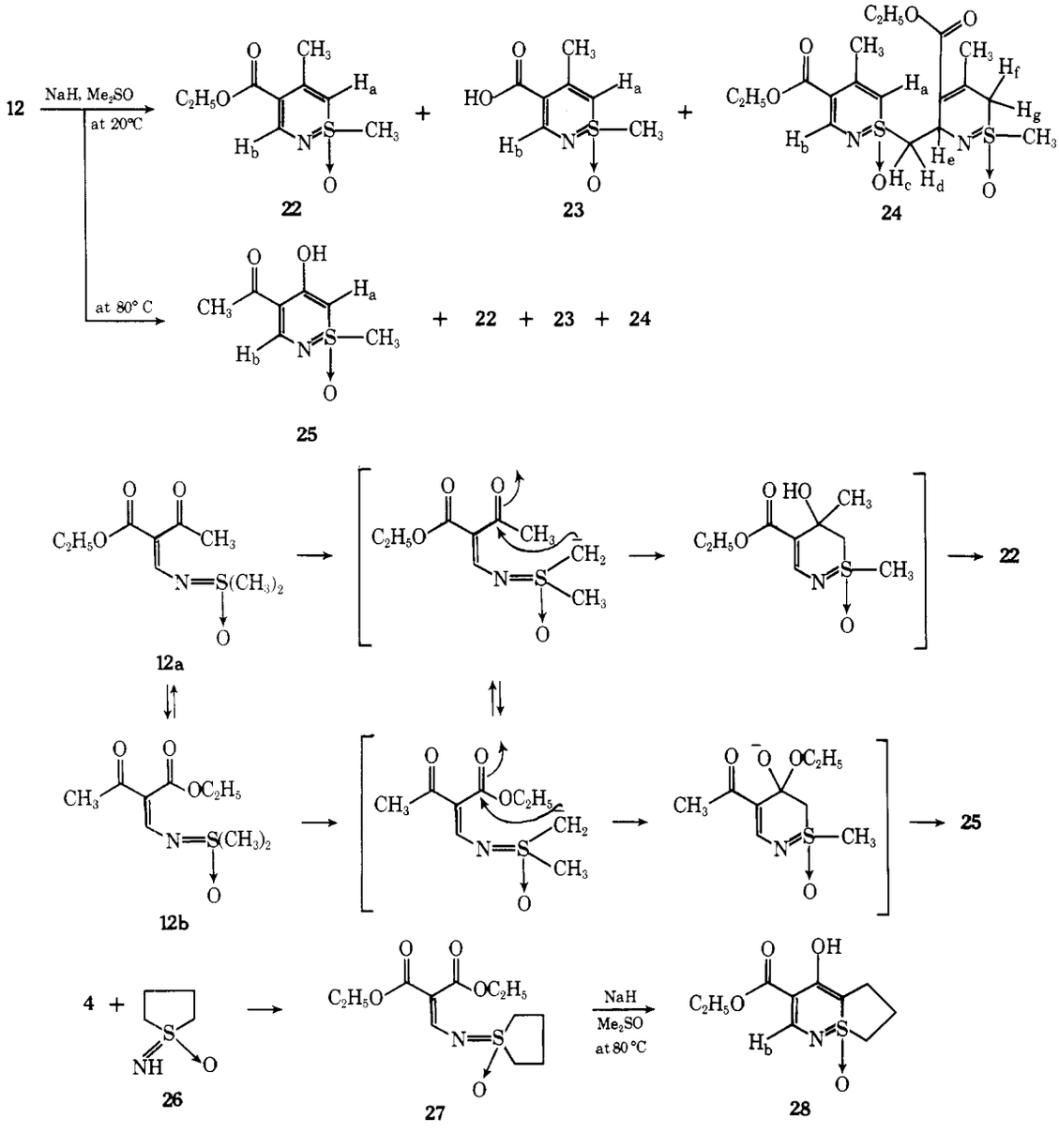


Table I. NMR Data (60 MHz, in $CDCl_3$) of 2-Azathiabenzene 1-Oxides

Registry no.	Compd	$H_a(H_a')$	H_b	H_c	SCH_3	CCH_3	Other protons
49836-29-5	17	5.81 (m)	8.26 (bs)		3.34 (s)	2.48 (d) J = 1 Hz	2.36 ($COCH_3$)
60803-98-7	19	5.93 (d) J = 10 Hz		7.78 (d) J = 10 Hz	3.35 (s)	2.58 (s)	2.35 ($COCH_3$)
49836-31-9	20	5.74 (bs)			3.23 (s)	2.46 (d) J = 1 Hz	1.65–2.85 (m) [$-(CH_2)_3-$]
60803-99-8	22	5.80 (m)	8.43 (bs)		3.34 (s)	2.46 (d) J = 1 Hz	4.24 (q), 1.33 (t) (OCH_2CH_3)
49836-26-2	29	5.45–5.72 (m)	7.76		3.44 (s)	2.51 (bs)	2.31 ($COCH_3$)
49836-27-3	30	5.42–5.78 (m)	8.00		3.46 (s)	2.53 (bs)	4.20 (q), 1.32 (t) (OCH_2CH_3)
49836-34-2	31	5.50 (s) 5.36 (s)			3.37 (s)	2.53 (bs)	1.70–2.80 (m) [$-(CH_2)_3-$]

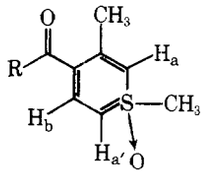
zation reaction of **10** but not **11** at room temperature and because **12** exists as an equilibrium mixture of two geometrical isomers in solution at room temperature, it is not unexpected that the products **22** and **23** were predominantly formed at room temperature. At higher temperature, however, it is reasonably assumed that the cyclization at the ester carbonyl group may compete with the cyclization at the acetyl carbonyl group to lead to formation of **25**. One possible rationalization for the formation of **24** may involve a Michael addition of a carbanion derived from either **12** or **22** to **12** followed by cyclization.

As a further extension of this method, we applied it to the synthesis of a 2-azathiabenzene 1-oxide containing a sulfur atom at a bridgehead position. Thus, sulfoximine **27** obtained from **4** and tetramethylenesulfoximine **26** was treated with sodium hydride in dimethyl sulfoxide to give **28**, whose structure was readily assigned by a comparison of the spectral data with those of **21**.

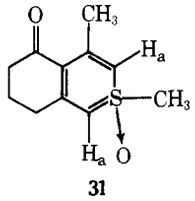
Lastly, cyano-substituted sulfoximines **13** and **14** did not give cyclized products under the reaction conditions we used and the starting material was recovered.

Physical Properties of 2-Azathiabenzene 1-Oxides. Comparison of the NMR spectra of 2-azathiabenzene 1-oxides **17**, **19**, **20**, and **22** with those of **29–31** (Table I) indicates that the signals due to S–CH_3, C–CH_3, and $COCH_3$ or $CO_2C_2H_5$ appear essentially at the same positions. However, the ring proton signals (H_a and H_b) of the 2-azathiabenzene 1-oxides are slightly shifted to lower field than those of the corresponding thiabenzene 1-oxides. The shift of H_a may be associated with less carbanionic character at this position and the shift of H_b may be attributed mainly to an electronegative effect of the nitrogen atom.

The IR carbonyl absorption bands of **17**, **19**, **20**, and **22** appear at 1658, 1655, 1645, and 1692 cm^{-1}, respectively, which are higher than those of the corresponding thiabenzene 1-oxides **29** (1641 cm^{-1}), **30** (1632 cm^{-1}), and **31** (1686 cm^{-1}),



29, R = CH_3
30, R = OC_2H_5



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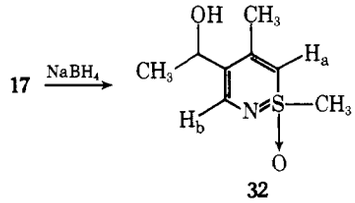
suggesting that the betainelike character (a polarization of the carbonyl group) of 2-azathiabenzene 1-oxides is considerably lower than that of the thiabenzene 1-oxides.

The electronic spectra of the 2-azathiabenzene 1-oxides **17**, **19**, and **20** have a major absorption band at 270–275 nm, which is slightly hypsochromic compared to the corresponding absorption band of thiabenzene 1-oxides **29** and **31** (297–299 nm).[4] Of particular interest is that the position of the absorption maximum was affected neither by the solvent used nor by addition of ethanolic 6 N hydrochloric acid. This is in contrast to the cases of thiabenzene 1-oxides **29** and **31**, in which protonation takes place at the carbonyl oxygen atom under acidic conditions and a new absorption band appeared at 320–330 nm. This difference appears to reflect the decreased basicity of the 2-azathiabenzene 1-oxides.

Chemical Properties of 2-Azathiabenzene 1-Oxides. Deuterium Exchange. In a deuteriochloroformic solution containing deuterium oxide at 35 °C, no significant exchange of any protons of 2-azathiabenzene 1-oxides **17** or **22** occurred. However, when **17** or **22** was dissolved in deuteriochloroform containing acetic acid-d_4, a slow decrease in the intensity of the H_a signal was observed, and ca. 50% of H_a was exchanged after 1 week at 35 °C. In the presence of trifluoroacetic acid-d, **17** or **22** had exchanged at H_a by the time the NMR spectrum could be measured. In comparison, thiabenzene 1-oxides **29** and **30** exchanged at H_a and H_a' completely after 8 h at 35 °C under the neutral conditions[4] and underwent complete exchange rapidly in the presence of acetic acid-d_4.

The less facile exchange of the ring protons in 2-azathiabenzene 1-oxides than in thiabenzene 1-oxides is attributed to the lower carbanionic character of the former, in agreement with the NMR findings.

Reduction with Sodium Borohydride. Sodium borohydride reduction of **17** in ethanol produced a colorless oil **32**



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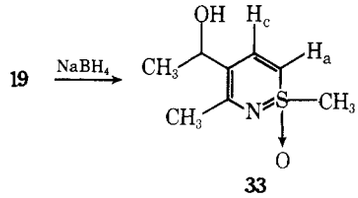

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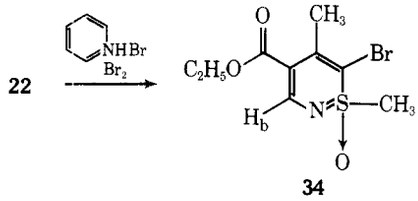
displaying the correct molecular ion peak at m/e 187 in its mass spectrum and IR absorption at 3280 cm^{-1} due to a hydroxyl group. The NMR spectrum shows a doublet (J = 7 Hz) at δ 1.43 attributable to CH_3CHOH, a broad quartet at δ 4.72 (CH_3CHOH), and a broad singlet at δ 2.53 (OH). In addition, an S-methyl singlet is displayed at δ 3.27, and a ring methyl signal (δ 2.25, d, J = 1 Hz), H_a (δ 5.78), and H_b (δ 7.43) are also seen.

Similarly, **19** was reduced to alcohol **33** in 66% yield.

By contrast, thiabenzene 1-oxide **29** was found to be inert to $NaBH_4$ reduction.

Bromination. When **22** was treated with pyridine bromide perbromide in acetic acid at room temperature, monobromo derivative **34** was obtained in 58% yield. Under similar conditions, **17** gave a less stable compound which we consider to be most likely **35** on the basis of the NMR data.



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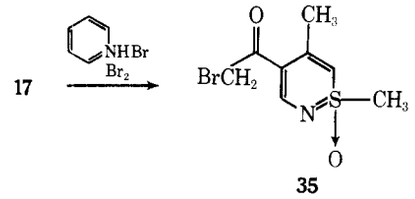

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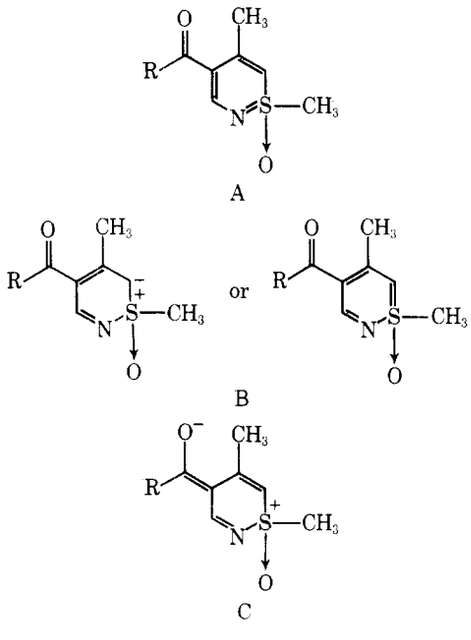
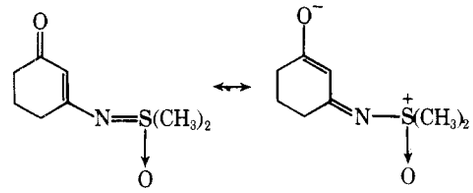
Structure of 2-Azathiabenzene 1-Oxides. As noted previously,[4] thiabenzene 1-oxides **29–31** are best regarded as the stabilized cyclic ylides, in which both the carbanionic and betainelike properties are lowered compared with the corresponding acyclic oxosulfonium ylides. These properties can be understood by consideration of the charge delocalization in the ring (but no conjugation through sulfur) and the contribution of $p\pi$–$d\pi$ bonding in the C_2–S–C_6 bond.[13]

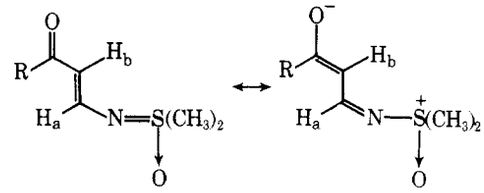
Comparison of the physical and chemical properties of 2-azathiabenzene 1-oxides with thiabenzene 1-oxides demonstrated that both the carbanionic (contribution from structure B) and betainelike properties (contribution from structure C) in the former are much lower than those of the latter. It is possible that the contribution from canonical form A in which the carbonyl group and double bonds exist in a localized state is considerably greater in 2-azathiabenzene 1-oxides. In this arrangement an appreciable negative charge will reside on the nitrogen atom presumably owing to the strong $p\pi$–$d\pi$ bonding between the sulfur and nitrogen.[14]



In this connection, it should be noted that a similar difference in the extent of delocalization of the negative charge is also seen in acyclic systems. UV and NMR spectral investigations of the electronic structures of sulfoximine **36** and oxosulfonium ylide **39** have revealed that the negative charge of the latter is well delocalized over the enone system while in the former the polarization is relatively small.[15] Comparison of the wavelengths of the carbonyl absorption of the sulfoximines with those of the corresponding oxosulfonium ylides in the infrared spectra provides further support for their

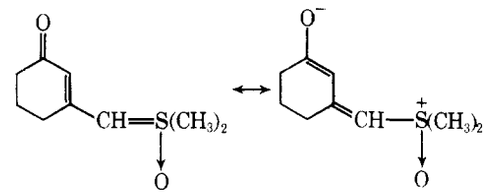


36 (1624 cm^{-1})[15]

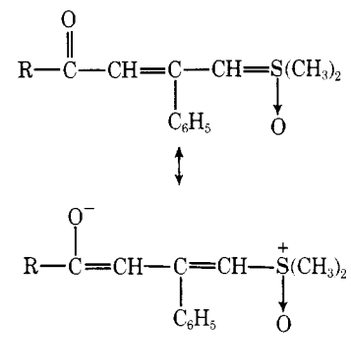


37, R = CH_3 (1658 cm^{-1})[16]
38, R = OC_2H_5 (1685 cm^{-1})[16]

electronic structures; the carbonyl bands of **36–38** are shifted to higher frequency when compared with those of **39–41.**



39 (1589 cm^{-1})[15]



40, R = t-C_4H_9 (1597 cm^{-1})[1]
41, R = OC_2H_5 (1670 cm^{-1})[2]

These results can also be rationalized if we assume that $p\pi$–$d\pi$ bonding in i is stronger than in ii.

Further studies on the electronic structures of both thiabenzene 1-oxides and 2-azathiabenzene 1-oxides using x-ray analysis are in progress.

Experimental Section

Melting points are uncorrected. NMR spectra were determined with Hitachi R-20A (60 MHz) and R-22 (90 MHz) spectrometers using tetramethylsilane as an internal standard. IR spectra were recorded

with a Hitachi EPI-G3 spectrophotometer and UV spectra with a Hitachi 124 spectrophotometer. Mass spectra were obtained with a Hitachi RMU-6D with a direct inlet system operating at 70 eV.

***N*-(2,2-Diacetylvinyl)dimethylsulfoximine (10).** To a solution of 3.12 g (0.02 mol) of **3** in 10 ml of $CHCl_3$ was added 1.86 g (0.02 mol) of dimethylsulfoximine (**9**). The reaction was slightly exothermic. After 30 min, the reaction mixture was scratched. A precipitated white solid was collected and recrystallized from AcOEt to yield 3.58 g (75%) of **10**: mp 165 °C; IR ($CHCl_3$) 1650, 1530 cm^{-1}; UV max (EtOH) 297 nm (log ϵ 4.32), 258 (3.89); NMR ($CDCl_3$) δ 8.10 (s, 1, olefinic proton), 3.27 [s, 6, $S(CH_3)_2$], 2.42 (s, 3, $COCH_3$), 2.30 (s, 3, $COCH_3$); mass spectrum *m/e* 203 ($M^{\cdot+}$).

Anal. Calcd for $C_8H_{13}NO_3S$: C, 47.29; H, 6.45; N, 6.89. Found: C, 47.15; H, 6.48; N, 6.83.

***N*-(2,2-Dicarbethoxyvinyl)dimethylsulfoximine (11).** A mixture of 1.86 g (0.02 mol) of **9** and 4.3 g (0.02 mol) of **4** was heated at 130–140 °C while slowly distilling ethanol out of the reaction mixture. Heating was continued until no more ethanol distilled (ca. 30 min). The resulting oil was passed through a short column of alumina with *n*-hexane–AcOEt as solvent to give 3.7 g (70%) of **11** as a yellow solid: mp 67–69 °C (from ether); IR ($CHCl_3$) 1725, 1700, 1595 cm^{-1}; UV max (EtOH) 281 nm (log ϵ 4.48), 218 (3.81); NMR ($CDCl_3$) δ 7.98 (s, 1, olefinic proton), 4.26 (q, 2, J = 7 Hz, OCH_2CH_3), 4.20 (q, 2, J = 7 Hz, OCH_2CH_3), 3.21 [s, 6, $S(CH_3)_2$], 1.33 (t, 3, J = 7 Hz, OCH_2CH_3), 1.29 (t, 3, J = 7 Hz, OCH_2CH_3); mass spectrum *m/e* 263 ($M^{\cdot+}$).

Anal. Calcd for $C_{10}H_{17}NO_5S$: C, 45.61; H, 6.51; N, 5.32. Found: C, 45.67; H, 6.50; N, 5.56.

***N*-(2-Acetyl-2-carbethoxyvinyl)dimethylsulfoximine (12).** A mixture of 1.86 g (0.02 mol) of **9** and 3.72 g (0.02 mol) of **5** was heated at 90 °C for 3 h. After cooling, the reaction mixture solidified. Recrystallization of the solid from *n*-hexane–AcOEt gave 3.76 g (81%) of **12**: mp 97–97.5 °C; IR (KCl) 1720, 1620, 1580 cm^{-1}; UV max (EtOH) 293 nm (log ϵ 4.23), 230 (3.78); the NMR spectrum taken immediately after dissolving **12** in $CDCl_3$ showed the following signals, δ 8.06 (s, 1, olefinic proton), 4.28 (q, 2, J = 7 Hz, OCH_2CH_3), 3.27 [s, 6, $S(CH_3)_2$], 2.28 (s, 3, $COCH_3$), 1.34 (t, 3, J = 7 Hz, OCH_2CH_3). After 10 min, new signals appeared at δ 4.20 (q, J = 7 Hz, OCH_2CH_3), 2.39 (s, $COCH_3$), and 1.30 (t, J = 7 Hz, OCH_2CH_3); mass spectrum *m/e* 233 ($M^{\cdot+}$).

Anal. Calcd for $C_9H_{15}NO_4S$: C, 46.33; H, 6.48; N, 6.01. Found: C, 46.17; H, 6.57; N, 6.20.

***N*-(2,2-Dicyanovinyl)dimethylsulfoximine (13).** A solution of 0.93 g (0.01 mol) of **9** and 1.22 g (0.01 mol) of **6** in 20 ml of $CHCl_3$ was heated at 70 °C for 10 min and then cooled. The precipitated solid was collected and recrystallized from methanol to yield 1.5 g (89%) of **13**: mp 187 °C; IR (KCl) 2200, 1550 cm^{-1}; UV max (EtOH) 283 nm (log ϵ 4.42); NMR (Me_2SO-d_6) δ 8.19 (s, 1, vinyl proton), 3.55 [s, 6, $S(CH_3)_2$]; mass spectrum *m/e* 169 ($M^{\cdot+}$).

Anal. Calcd for $C_6H_7N_3OS$: C, 42.59; H, 4.17; N, 24.84. Found: C, 42.75; H, 4.13; N, 24.91.

***N*-(2-Cyano-2-carbethoxyvinyl)dimethylsulfoximine (14).** Using a similar procedure to that described for **13**, **14** was obtained from 0.93 g (0.01 mol) of **9** and 2.02 g (0.01 mol) of **7** in 87% yield: mp 188 °C (from ethanol); IR (KCl) 2200, 1680, 1570 cm^{-1}; UV max (EtOH) 286 nm (log ϵ 4.42); NMR (Me_2SO-d_6) δ 8.34 (s, 1, vinyl proton), 4.11 (q, 2, J = 7 Hz, OCH_2CH_3), 3.50 [s, 6, $S(CH_3)_2$], 1.20 (t, 3, J = 7 Hz, OCH_2CH_3); mass spectrum *m/e* 216 ($M^{\cdot+}$).

Anal. Calcd for $C_8H_{12}N_2O_3S$: C, 44.44; H, 5.60; N, 12.96. Found: C, 44.70; H, 5.50; N, 12.80.

***N*-(2-Acetyl-3-oxo-1-cyclohexenyl)dimethylsulfoximine (15).** Using a procedure similar to that previously described for **11**, compound **15** was obtained from 1.86 g (0.02 mol) of **9** and 3.4 g (0.02 mol) of **8** in 85% yield (3.9 g): mp 126–126.5 °C (from AcOEt); IR ($CHCl_3$) 1692, 1630, 1564 cm^{-1}; UV max (EtOH) 296 nm (log ϵ 4.34); NMR ($CDCl_3$) δ 3.13 [s, 6, $S(CH_3)_2$], 2.8–1.7 [m, 6, $(CH_2)_3$], 2.22 (s, 3, $COCH_3$); mass spectrum *m/e* 229 ($M^{\cdot+}$).

Anal. Calcd for $C_{10}H_{15}NO_3S$: C, 52.39; H, 6.60; N, 6.11. Found: C, 52.21; H, 6.57; N, 5.90.

Cyclization of 10. A. A solution of 1.02 g (5 mmol) of **10** in 10 ml of dry Me_2SO was added to a stirred suspension of NaH (0.26 g, ca. 1.1 equiv, as a 50% oil dispersion, washed with dry petroleum ether before use) in 10 ml of Me_2SO at room temperature under nitrogen. After stirring for 3 h at room temperature, the reaction mixture was poured into water and extracted thoroughly with $CHCl_3$. The extract was washed with a saturated NaCl solution and dried ($MgSO_4$). Evaporation of the solvent in vacuo gave a brown oil, which was chromatographed on a short column of silica gel with ether as solvent to yield 0.28 g (30%) of **17** as a solid: mp 94–95 °C (from ether–*n*-hexane); IR ($CHCl_3$) 1658, 1569 cm^{-1}; UV max (EtOH) 300 nm (log ϵ 3.94), 272 (4.17); mass spectrum *m/e* 185 ($M^{\cdot+}$).

Anal. Calcd for $C_8H_{11}NO_2S$: C, 51.88; H, 5.99; N, 7.56. Found: C, 52.16; H, 6.05; N, 7.66.

The aqueous layer from the $CHCl_3$ extraction was slightly acidified with 10% HCl solution and extracted with $CHCl_3$. The extract was washed with water, dried ($MgSO_4$), and concentrated to give a brown oil which was chromatographed on silica gel with *n*-hexane–AcOEt as solvent to yield 0.17 g (18%) of **19** as a solid: mp 150 °C (from acetone); IR ($CHCl_3$) 1655, 1550 cm^{-1}; UV max (EtOH) 305 (log ϵ 3.96), 270 nm (4.19); mass spectrum *m/e* 185 ($M^{\cdot+}$).

Anal. Calcd for $C_8H_{11}NO_2S$: C, 51.88; H, 5.99; N, 7.56. Found: C, 52.00; H, 5.99; N, 7.61.

B. When the same reaction mixture of **10** and NaH in Me_2SO was heated at 80 °C for 5 min under nitrogen, followed by the same workup as described above, **17** and **19** were obtained in 22 and 26% yields, respectively.

Cyclization of 15. In the same way as described above, a stirred suspension of 1.15 g (5 mmol) of **15** and NaH (0.26 g as a 50% oil dispersion) in 10 ml of Me_2SO was heated at 80 °C for 3 min under nitrogen. After workup, the crude product was passed through a short column of silica gel with ether as solvent to give 0.77 g (73%) of **20** which was recrystallized from ether: mp 97–97.5 °C; IR ($CHCl_3$) 1645, 1551 cm^{-1}; UV max (EtOH) 297 sh nm (log ϵ 3.92), 275 (4.26); mass spectrum *m/e* 211 ($M^{\cdot+}$).

Anal. Calcd for $C_{10}H_{13}NO_2S$: C, 56.86; H, 6.20; N, 6.63. Found: C, 56.58; H, 6.21; N, 6.48.

Cyclization of 11. A solution of 1.32 g (5 mmol) of **11** in 10 ml of dry Me_2SO was added to a stirred suspension of NaH (0.26 g as a 50% oil dispersion) in 10 ml of Me_2SO under nitrogen and the reaction mixture was heated at 80 °C for 5 min. After cooling, the reaction mixture was poured into ice–water and a solution was acidified with 10% HCl solution and extracted with $CHCl_3$. The extract was washed with a saturated NaCl solution, dried ($MgSO_4$), and concentrated in vacuo to give 0.65 g (60%) of **21** as a yellowish solid, which was recrystallized from ether: mp 94–95 °C; IR ($CHCl_3$) 3685, 1670, 1605 cm^{-1}; UV max (EtOH) 295 nm (log ϵ 3.36), 250 (3.70), 230 (4.08); NMR ($CDCl_3$) δ 11.94 (s, 1, OH), 8.37 (s, 1, H_b), 5.39 (s, 1, H_a), 4.32 (q, 2, J = 7 Hz, OCH_2CH_3), 3.33 (s, 3, SCH_3), 1.36 (t, 3, J = 7 Hz, OCH_2CH_3); mass spectrum *m/e* 217 ($M^{\cdot+}$). This compound gave a brown color with a ferric chloride solution.

Anal. Calcd for $C_8H_{11}NO_4S$: C, 44.23; H, 5.10; N, 6.45. Found: C, 44.07; H, 5.10; N, 6.45.

Cyclization of 12. A. A solution of 1.17 g (5 mmol) of **12** in 10 ml of dry Me_2SO was added to a stirred suspension of NaH (0.26 g as a 50% oil dispersion) in 10 ml of Me_2SO at room temperature under nitrogen. After 3 h, the reaction mixture was poured into ice–water and extracted with $CHCl_3$. The extract was washed with a saturated NaCl solution, dried ($MgSO_4$), and concentrated to give an oily mixture of two products, which was separated by column chromatography on alumina. Elution with *n*-hexane–AcOEt (1:1) yielded 0.38 (35%) of **22**, which was recrystallized from ether–*n*-hexane: mp 70 °C; IR ($CHCl_3$) 1692, 1570 cm^{-1}; UV max (EtOH) 295 nm (log ϵ 3.46), 245 (4.08); mass spectrum *m/e* 215 ($M^{\cdot+}$).

Anal. Calcd for $C_9H_{13}NO_3S$: C, 50.21; H, 6.08; N, 6.51. Found: C, 50.47; H, 6.16; N, 6.43.

Further elution with the same solvent gave 0.16 g (7%) of **24**, which was recrystallized from benzene–*n*-hexane: mp 153–155 °C; IR ($CHCl_3$) 1710, 1700, 1570 cm^{-1}; UV max (EtOH) 295 nm (log ϵ 3.17), 247 (3.89); NMR ($CDCl_3$, 90 MHz) δ 8.39 (bs, 1, H_b), 6.33 (m, 1, H_a), 5.26–5.04 (m, 1, H_e), 4.30 (q, 2, J = 7 Hz, OCH_2CH_3), 4.22 (q, 2, J = 7 Hz, OCH_2CH_3), 3.67 (d, 2, J = 6 Hz, H_c and H_d), 3.60 (q, 2, J = 18 Hz, H_f and H_g), 3.12 (s, 3, SCH_3), 2.46 (s, 3, ring CH_3), 2.09 (d, 3, J = 1 Hz, vinyl CH_3), 1.38 (t, 3, J = 7 Hz, OCH_2CH_3), 1.24 (t, 3, J = 7 Hz, OCH_2CH_3); mass spectrum *m/e* 430 ($M^{\cdot+}$).

Anal. Calcd for $C_{18}H_{26}N_2O_6S_2$: C, 50.23; H, 6.09; N, 6.51. Found: C, 50.44; H, 6.12; N, 6.52.

The aqueous layer of the $CHCl_3$ extraction was acidified with a 10% HCl solution and extracted with $CHCl_3$. The extract was washed with a saturated NaCl solution, dried ($MgSO_4$), and concentrated to give a crude solid, which was recrystallized from acetone to yield 0.12 g (13%) of **23**; mp 197–199 °C; IR (KCl) 1685, 1570 cm^{-1}; UV max (EtOH) 295 nm (log ϵ 3.39), 244 (3.99); NMR (Me_2SO-d_6) δ 8.28 (bs, 1, H_b), 6.31 (m, 1, H_a), 3.49 (s, 3, SCH_3), 2.39 (s, 3, ring CH_3); mass spectrum *m/e* 187 ($M^{\cdot+}$).

Anal. Calcd for $C_7H_9NO_3S$: C, 44.92; H, 4.82; N, 7.48. Found: C, 44.87; H, 4.85; N, 7.56.

B. A stirred suspension of 1.16 g of **12** and NaH (0.26 g as a 50% oil dispersion) in Me_2SO was heated at 80 °C for 5 min under nitrogen. After workup as described above, the basic extract was chromatographed on alumina with *n*-hexane–AcOEt as solvent to give **22** and **24** in 8 and 1% yields, respectively. Chromatography of the acidic

extract on silica gel with AcOEt gave 0.12 g (13%) of **23** and 0.44 g (47%) of **25.** Recrystallization of the latter from MeOH gave white crystals: mp 181 °C; IR (KCl) 3400, 1630, 1575 cm^{-1}; UV max (EtOH) 294 nm (log ϵ 3.84), 268 (3.99), 244 (4.13); NMR (Me_2SO-d_6) δ 13.76 (bs, 1, OH), 8.52 (s, 1, H_b), 5.75 (bs, 1, H_a), 3.48 (s, 3, SCH_3), 2.40 (s, 3, $COCH_3$); mass spectrum *m/e* 187 ($M^{\cdot+}$). This compound gave a brown color with a ferric chloride solution.

Anal. Calcd for $C_7H_9NO_3S$: C, 44.92; H, 4.82; N, 7.48. Found: C, 44.94; H, 4.93; N, 7.47.

Hydrolysis of 22. A solution of 0.86 g of **22** and 0.24 g of NaOH in 15 ml of ethanol was refluxed for 5 h. After cooling, the solution was concentrated in vacuo, acidified with 10% HCl, and extracted with methylene chloride. The extract was washed, dried ($MgSO_4$), and concentrated to give 0.43 g (58%) of **23,** mp 197–199 °C (from acetone).

***N*-(2,2-Dicarbethoxyvinyl)tetramethylenesulfoximine (27).** Using a similar procedure to that described for the preparation of **11,** compound **27** was obtained from 1.04 g (0.01 mol) of tetramethylenesulfoximine (**26**) and 2.15 g (0.01 mol) of **4** in 79% yield (2.15 g) as a colorless oil: IR ($CHCl_3$) 1695, 1590 cm^{-1}; UV max (EtOH) 283 nm (log ϵ 4.14), 233 (3.65); NMR ($CDCl_3$) δ 8.00 (s, 1, olefinic proton), 4.28 (q, 2, J = 7 Hz, OCH_2CH_3), 4.22 (q, 2, J = 7 Hz, OCH_2CH_3), 3.50–3.15 [m, 4, $S(CH_3)_2$], 2.48–2.05 [m, 4, $(CH_2)_2$], 1.84 (t, 3, J = 7 Hz, OCH_2CH_3), 1.29 (t, 3, J = 7 Hz, OCH_2CH_3). This compound was used without further purification.

Cyclization of 27. Using the same procedure described for **21,** compound **28** was obtained from 0.45 g (1.3 mmol) of **27** and NaH (0.65 g as a 50% oil dispersion) in 10 ml of Me_2SO in 53% yield (0.16 g): mp 87–89 °C (from ether); IR ($CHCl_3$) 3685, 1665, 1620 cm^{-1}; UV max (EtOH) 286 nm (log ϵ 3.58), 263 (3.74), 236 (4.26); NMR ($CDCl_3$) δ 11.72 (s, 1, OH), 8.35 (s, 1, H_b), 4.38 (q, 2, J = 7 Hz, OCH_2CH_3), 3.90–2.95 [m, 4, $(CH_2)_2$], 2.35–2.08 (m, 2, CH_2), 1.42 (t, 3, J = 7 Hz, OCH_2CH_3); mass spectrum *m/e* 243 ($M^{\cdot+}$). This compound gave a brown color with a ferric chloride solution.

Anal. Calcd for $C_{10}H_{13}NO_4S$: C, 49.38; H, 5.39; N, 5.76. Found: C, 49.37; H, 5.38; N, 5.80.

Deuterium Exchange Experiments. A. Under Neutral Conditions. To a solution of 0.1 mmol of a sample of **27** in 0.4 ml of $CDCl_3$ was added 1 drop of D_2O and the mixture was shaken well and kept at 35 °C.

B. With Acid Catalysis. To a solution of 0.1 mmol of a sample in 0.4 ml of $CDCl_3$ was added 1 drop of acetic acid-d_4 or trifluoroacetic acid-*d*.

The exchange was followed by NMR spectroscopy.

$NaBH_4$ Reduction of 17. To a solution of 185 mg of **17** in 10 ml of ethanol was added 40 mg of $NaBH_4$ and the mixture was stirred at room temperature for 8 h. The mixture was diluted with water, extracted with $CHCl_3$, washed, and dried ($MgSO_4$). Evaporation of the solvent gave 143 mg (77%) of **32** as a colorless oil: IR ($CHCl_3$) 3280, 1585 cm^{-1}; UV max (EtOH) 317 nm (log ϵ 3.25), 220 nm sh (3.16); NMR ($CDCl_3$) δ 7.43 (m, 1, H_a), 5.78 (m, 1, H_b), 4.72 (bq, 1, J = 7 Hz, CH_3CHOH), 3.27 (s, 3, SCH_3), 2.53 (bs, 1, OH), 2.25 (d, 1, J = 1 Hz, ring CH_3), 1.43 (d, 1, J = 7 Hz, CH_3CHOH); mass spectrum *m/e* 187 ($M^{\cdot+}$).

$NaBH_4$ Reduction of 19. Using a similar procedure to that described above for **32, 33** was obtained by reduction of 185 mg of **19** with 40 mg of $NaBH_4$ in 66% yield (123 mg): a colorless oil; IR ($CHCl_3$) 3600, 1600, 1575 cm^{-1}; UV max (EtOH) 321 nm (log ϵ 3.12), 220 (3.23); NMR ($CDCl_3$) δ 7.42 (d, 1, J = 1 Hz, H_a), 5.90 (d, 1, J = 10 Hz, H_c), 4.92 (q, 1, J = 7 Hz, CH_3CHOH), 3.31 (s, 3, SCH_3), 2.25 (s, 3, ring CH_3), 1.60 (s, 1, OH), 1.35 (d, 3, J = 7 Hz, CH_3CHOH); mass spectrum *m/e* 187 ($M^{\cdot+}$).

Bromination of 22. A solution of 0.22 g (1 mmol) of **22** and 0.29 g (1.5 mmol) of pyridine bromide perbromide in 20 ml of acetic acid was stirred at room temperature. After 1 h, the reaction mixture was diluted with water and extracted with $CHCl_3$. The extract was washed with a saturated $NaHCO_3$ solution and a saturated NaCl solution, dried ($MgSO_4$), and concentrated to give a red-brown oil which was submitted to preparative TLC using $CHCl_3$ as solvent to afford 0.17 g (58%) of **34** as a brown solid: mp 64 °C (from *n*-hexane); IR ($CHCl_3$) 1700, 1560 cm^{-1}; NMR ($CDCl_3$) δ 8.17 (s, 1, H_b), 4.22 (q, 2, J = 7 Hz, CH_3CH_2), 3.49 (s, 3, SCH_3), 2.57 (s, 3, ring CH_3), 1.28 (t, 3, J = 7 Hz, CH_3CH_2).

Anal. Calcd for $C_9H_{12}BrNO_3S$: C, 36.74; H, 4.11; N, 4.76. Found: C, 36.83; H, 4.42; N, 4.91.

Bromination of 17. Under similar conditions used for bromination of **22** (except for 15 h at room temperature), 185 mg of **17** gave 160 mg of a crude oily material which liberated bromine during purification procedure: NMR ($CDCl_3$) δ 8.32 (bs, 1, H_b), 5.95 (m, 1, H_a), 4.22 (AB q, 2, J = 11 Hz, $BrCH_2$), 3.38 (s, 3, SCH_3), 2.45 (d, 3, J = 1 Hz, ring CH_3).

Registry No.—**3,** 33884-41-2; **4,** 87-13-8; **5,** 3788-94-1; **6,** 123-06-8; **7,** 94-05-3; **8,** 21014-78-8; **9,** 1520-31-6; **10,** 60804-00-4; **11,** 60804-01-5; **12,** 60804-02-6; **13,** 60804-03-7; **14,** 60804-04-8; **15,** 60804-05-9; **21,** 60804-06-0; **23,** 60804-07-1; **24,** 60804-08-2; **25,** 60804-09-3; **26,** 50578-18-2; **27,** 60804-10-6; **28,** 60804-11-7; **32,** 60804-12-8; **33,** 60804-13-9; **34,** 60804-14-0; **35,** 60804-15-1; pyridine bromide perbromide, 39416-48-3.

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