ethyl acetate–light petroleum, 1:19) and crystallized from ethyl acetate–*n*-hexane to give the corresponding acetate: mp 72–73°; M^+ 281, $(M+2)^+$ 283 (32% of M^+); $\nu_{max}^{CCl_4}$ 1750, 1590, 1570, 1475, and 1220 cm^{-1}; nmr ($CDCl_3$) δ 1.74 (3 H, CH_3CO–), 1.76 (CH), 2.95 (1 H, m), 4.25 (1 H, m) 6.00 (1 H, s, *H*COAc), 7.30–6.40 (4 H, aromatic). *Anal.* Calcd for $C_{14}H_{16}NO_3Cl$: C, 59.66; H, 5.73; N, 4.97. Found: C, 59.10; H, 5.92; N, 4.83.

Reduction of Alcohol 8. The alcohol **8** (25 mg) in 1 ml of ether was added to a solution of lithium aluminum hydride (30 mg) in ether (3 ml). After stirring for 2 hr, the excess hydride was decomposed with saturated potassium sodium tartrate. Isolation of the product gave 22 mg showing two spots on thin-layer chromatography. Separation by thick-layer chromatography (eluent, ethyl acetate–benzene, 1:4) gave 18 mg of *cis*-2-(3′-chloroanilino)-cyclopentanylcarbinol (**9**). This was identical in every way with a synthetic specimen prepared as described below, as was the derived monoacetate and bis-*p*-nitrobenzoate.

Synthesis of *cis*-2-(3′-Chloroanilino)cyclopentanylcarbinol. A mixture of methyl and ethyl esters of 2-cyclopentanonecarboxylic acid (Aldrich) (800 mg) and 660 mg of *m*-chloroaniline in 20 ml of benzene was refluxed for 20 hr under a Dean–Stark apparatus. The product was chromatographed on silica gel (70 g) to give 650 mg of a mixture of methyl and ethyl esters of 2-(3′-chloroanilino)-cyclopent-1-enecarboxylic acid. This mixture (600 mg) in ethyl acetate (20 ml) was hydrogenated over platinum oxide until an uptake of 120 ml of hydrogen was observed (5.36 mmol). After concentration, the product was added to 60 g of silica gel. Benzene eluted unreacted starting material (130 mg). Ethyl acetate–benzene (1:19) then eluted 340 mg of the dihydro ester mixture. This showed the expected physical properties in the infrared and nmr spectrum. The mixed esters (100 mg) in ether (5 ml) were then added to lithium aluminum hydride (80 mg) in ether (5 ml) and the mixture was stirred for 2 hr. After decomposition (potassium sodium tartrate) the carbinol **9** was isolated: $\nu_{max}^{CHCl_3}$ 3590, 3380, 1590, 1570, 1480 cm^{-1}; nmr δ 1.67 (7 H), 2.23 (1 H, m, C*H*N), 3.3 (2 H, N*H*, O*H*), 3.70 (2 H, d, $J \sim 6$ Hz CH_2O), 6.40–7.30 (4 H, aromatic); mol wt (mass spectrum) 225, 227 (32% of 225). *Anal.* Calcd for $C_{12}H_{16}NOCl$: C, 63.84; H, 7.15; N, 6.2. Found: C, 64.32; H, 7.38; N, 6.34. The acetate (acetic anhydride–pyridine, room temperature, 24) had $\nu_{max}^{CHCl_3}$ 3430, 1735, 1600, 1575, 1500, 1485, and 1220 cm^{-1}; nmr ($CDCl_3$) δ 1.67 (7 H), 2.46 (1 H, m, C*H*N), 3.80 (1 H, NH), 4.07 (2 H, d, $J \sim 7$ Hz), 6.3–7.2 (4 H, aromatic); mol wt (mass spectrum) 267,269. *Anal.* Calcd for $C_{14}H_{18}NO_2Cl$: C, 62.68; H, 6.78; N, 5.23. Found: C, 63.27; H, 6.53; N, 5.13. The bis-*p*-nitrobenzoate had the following characteristics: mp 117–118°; $\nu_{max}^{CCl_4}$ 1725, 1660, 1600, 1590, 1475, 1530, 1270, and 1100 cm^{-1}; nmr δ 1.85 (7 H), 3.0 (1 H, C*H*N), 4.5 (2 H, CH_2O), and 7.0–8.3 (12 H, aromatic). *Anal.* Calcd for $C_{26}H_{22}N_3O_7Cl$: C, 59.58; H, 4.23; N, 8.02. Found: C, 59.45; H, 4.00; N, 7.89.

Thiabenzenes. III. Synthesis and Properties of Thiabenzene 1-Oxides[1a]

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Abstract: The synthesis of a representative series of 1-methyl-3,5-disubstituted thiabenzene 1-oxides (**2**) by the reaction of dimethyloxosulfonium methylide with 1,3-disubstituted 2-propynones (**1**) is described. In several cases, the initially formed allylides (**3**) were isolated and converted to the 1-oxides (**2**) under basic as well as neutral conditions. Alkylation of the 1-oxide **2a** on the *S*-methyl group was effected in stages *via* generation of the anion and treatment with methyl iodide to yield the *S*-ethyl and *S*-isopropyl derivatives **6a** and **6b**. Reduction of **2a** with hydrogen over platinum or zinc in acetic acid lead to reductive cleavage of the S-ring yielding **11** or **12**. Nmr (^1H, ^{13}C) and proton exchange data are described and discussed in relation to the types of bonding possible for thiabenzene 1-oxides. An ylide-like bonding structure is proposed for the thiabenzene 1-oxides.

The existence of bonds of the $p\pi$–$d\pi$ type, formed by interaction of d AO's of second-row elements with p AO's of first-row elements, is generally accepted.[2] However, due to the directional character associated with the d AO's having proper symmetry for such interaction, several modes of overlap of d AO's with p AO's have been proposed, and consequently the nature of $p\pi$–$d\pi$ bonds is still a subject of speculation. In addition, the question of the degree to which conjugative effects can be transmitted through such bonds in potentially "aromatic" cyclic conjugated systems is an intriguing one which continues to receive attention.[2-4]

Our interest in this area was stimulated by the discovery that the reaction of dimethyloxosulfonium methylide[5] with disubstituted acetylenic ketones (**1**) affords a route to 1,3,5-trisubstituted thiabenzene 1-oxides (**2**),[6] a novel class of cyclic compounds containing a conjugated six π-electron system. Through-conjugation at sulfur, if it is possible, can occur only *via* $2p\pi$–$3d\pi$ bonds in the thiabenzene 1-oxides (assuming that only 3s and 3p valence orbitals are used in the tetrahedrally oriented σ bonds at sulfur). Thus, from the standpoint of bonding in the C_2–S–C_6 moiety in the thiabenzene 1-oxides, these compounds may be formally compared with the cyclotriphosphazines,[2-4,7] cyclotrithiatriazene trioxides,[8] phosphabenzenes,[9] and related substances. Since most published studies on the properties of thiabenzenes,[10] thianaphthalenes,[11]

(1) (a) Abstracted in part from the Ph.D. Dissertation of Ronald Lee Harris, Washington University, 1970; (b) National Science Foundation Trainee, 1968–1969.

(2) K. A. R. Mitchell, *Chem. Rev.*, **69**, 157 (1969), and references cited therein.

(3) L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, New York, N. Y., 1966, pp 158–176.

(4) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, pp 430–436.

(5) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1353 (1965); **84**, 867 (1962).

(6) A preliminary report describing the preparation and some properties of **2a** has been published: A. G. Hortmann, *ibid.*, **87**, 4972 (1965).

(7) H. R. Allcock and W. J. Birdsall, *ibid.*, **91**, 7541 (1969).

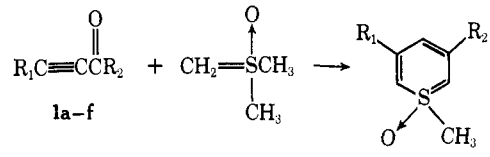
(8) T. J. Maricich, *ibid.*, **90**, 7179 (1968).

(9) G. Märkl, *Angew. Chem.*, **77**, 1109 (1965).

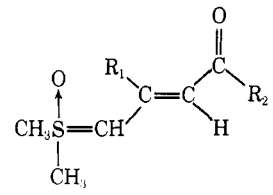
(10) M. Polk, M. Siskin, and C. C. Price, *J. Amer. Chem. Soc.*, **91**, 1206 (1969), and previous papers in this series. See also ref 25 below.

(11) C. C. Price and D. M. Follweiler, *J. Org. Chem.*, **34**, 3202 (1969).

and other potentially aromatic thiacyclic systems[12,13] have involved compounds where the alternate possibility of the use of $2p\pi$–$3p\pi$ bonds exists for through-conjugation at sulfur,[14] it was felt that a study of the chemical and physical properties of a representative series of the 1-oxides (**2**) would lead to a better understanding of the conjugative ability of $p\pi$–$d\pi$ bonds involving sulfur, particularly with regard to the possibility of conduction (or nonconduction) of a ring current in conjugated thiacyclic ring systems containing $(2n + 4)$ π electrons.



1a–f **2a–e**



3a–c

a, $R_1 = R_2 = C_6H_5$
b, $R_1 = CH_3$; $R_2 = C_6H_5$
c, $R_1 = C_6H_5$; $R_2 = C(CH_3)_3$
d, $R_1 = R_2 = C_2H_5$
e, $R_1 = R_2 = CH_3$
f, $R_1 = C_6H_5$; $R_2 = CH_3$

Results

Synthesis of Thiabenzene 1-Oxides. Syntheses of the required acetylenic ketones **1a–f** were accomplished by standard techniques. Addition of the acetylenic ketone **1a** in dimethyl sulfoxide (DMSO) to 1.5 mol equiv of dimethyloxosulfonium methylide[5] in DMSO at 16–18° afforded 1-methyl-3,5-diphenylthiabenzene 1-oxide (**2a**) in 76% yield. When initial attempts were made to prepare the 1-oxides **2b–d** under similar conditions, the yields were erratic; however, they could be optimized (50–75%) if the reaction mixtures were heated for a short period to effect complete cyclization of the intermediate allylides, **3** (see below). The yields of **2e** were consistently low over a wide range of conditions.

Spectral Data. The infrared spectra of 1-oxides **2a–e** each exhibit a characteristic strong band for S→O stretching at 1125–1145 cm^{-1}. In the nmr spectra (see Table I), the 3,5-diphenyl compound, **2a**, exhibits a 2 H doublet at δ 5.83 (J = 1.1 Hz) and a 1 H triplet at δ 6.26 (J = 1.1 Hz) for the S-ring protons and a 3 H singlet at δ 3.50 for the *S*-methyl group; in the 1,3,5-trialkyl compounds the corresponding peaks for the *S*-ring protons are shifted upfield and appear at δ 5.18 (2 H) and 5.32 (1 H) for **2d** and δ 5.30 (2 H) and 5.47 (1 H) for **2e**. In the unsymmetrically substituted 1-oxides **2b** and **2c**, H-2 and H-6 differ in δ value and are strongly coupled to each other with $J_{2,6}$ = 4.3 Hz in **2b** and $J_{2,6}$ = 4.2 Hz in **2c**. This strong coupling interaction between H-2 and H-6 could also be observed in the carbon-13 satellite spectra of the symmetrical 1-oxides **2a** ($J_{2,6}$ = 4.5 Hz), **2d** ($J_{2,6}$ = 4.4 Hz), and **2e** ($J_{2,6}$ = 4.4 Hz).[15] In the ultraviolet spectra (see Table II), the phenyl-substituted compounds **2a–c**, which are yellow in color, each exhibit three high intensity absorption bands at λ_{max} 365–350, 250–240, and 210 nm; the trialkyl compounds **2d** and **2e** (see Experimental Section) have their long wavelength band shifted to 333–335 nm and are colorless.

Table I. Chemical Shifts of S-Ring Protons and *S*-Methyl Group Protons in Thiabenzene 1-Oxides[a]

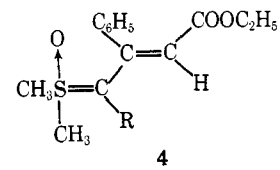
Compd	H-2, H-6	H-4	S-CH_3
2a	5.83[b]	6.26[c]	3.50
2b	5.28 and 5.47[d]	5.67[c]	3.33
2c	5.23 and 5.79[d]	5.91[c]	3.44
2d	5.18[e]	5.32[e]	3.32
2e	5.30[e]	5.47[e]	3.45
6a	5.57[b]	6.25[c]	
6b	5.53[b]	6.23[c]	

[a] Peaks given as δ (ppm) from TMS; spectra were run in $CDCl_3$. [b] Doublet. [c] Triplet. [d] Centers of AB portion of an ABX pattern. [e] Singlet (broad).

Isolation and Properties of Allylide Intermediates. When the preparations of **2a–c** were attempted at lower temperatures using THF–DMSO mixtures as solvent and care was taken to avoid heating the product above room temperature during work-up and crystallization, only the allylides **3a–c** were obtained; the allylides **3b** and **3c** could be converted to the 1-oxides **2b** and **2c** by simply heating in refluxing chloroform for 24–36 hr or in refluxing NaOEt–EtOH for 4 hr.

The allylides **3a–c** probably arise *via* Michael addition of dimethyloxosulfonium methylide to acetylenic ketones **1a–c** followed by protonation of intermediate allenolate anions. Similar addition reactions of this ylide have been reported for ethyl phenylpropiolate[16,17] (as well as a number of phenyl-substituted analogs)[17] to yield 2-phenyl-3-ethoxycarbonylallylide **4a** which has spectral features similar to those of **3a–c**.

We have also noted, in consonance with Ide and Kishida's observations on **4a**,[17] that when **3c** is treated with D_2O–THF, rapid and nearly complete exchange of the proton at C-1 (δ 7.13) and of the six *S*-methyl protons (δ 2.98) occurs, whereas exchange of the 3-proton (δ 5.38) proceeds only very slowly. This result suggests that there is a mobile equilibrium in solution between **3c** and a related species which has anionic character at the *S*-methyl groups and is presumably involved in the observed intramolecular cyclization to yield **2c**.



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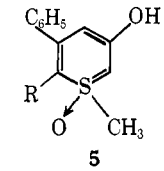


5

a, R = H
b, R = COC_6H_5

(12) K. Zahradnik, *Advan. Heterocycl. Chem.*, **5**, 1 (1965).
(13) T. E. Young and R. Lazarus, *J. Org. Chem.*, **33**, 3770 (1968).
(14) W. G. Salmond, *Quart. Rev., Chem. Soc.*, **22**, 253 (1968).

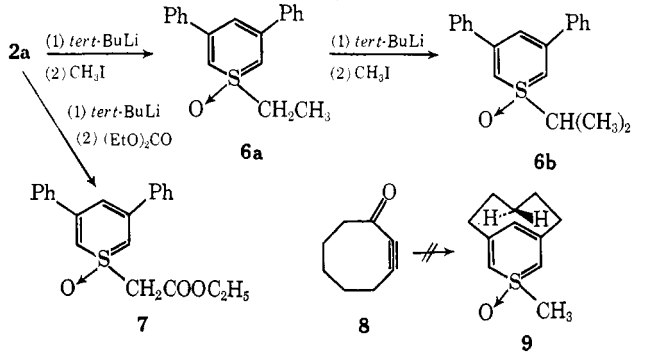
(15) The ^{13}C satellites in the proton nmr spectra were observed using a Varian A-60A instrument; signal-to-noise ratios were improved using a Varian Associates C-1024 time averaging computer. For **2a**, $J_{^{13}C-H_2}$ = 181.5 Hz and $J_{^{13}C-H_4}$ = 166.5 Hz; for **2e**, $J_{^{13}C-H_2}$ = 177 Hz, $J_{^{13}C-H_4}$ = 167 Hz. Estimated accuracies are ±0.1 Hz for J_{H_2,H_6} and about ±2 Hz for $J_{^{13}C-H}$ values.
(16) C. Kaiser, B. Trost, J. Beeson, and J. Weinstock, *J. Org. Chem.*, **30**, 3972 (1965).
(17) J. Ide and Y. Kishida, *Tetrahedron Lett.*, 1787 (1966); *Chem. Pharm. Bull.*, **16**, 793 (1968).

Table II. Effect of Acid on the Uv Spectra of Thiabenzene 1-Oxides

Compd	Solvent	λ, nm	ε	Acidic medium	λ, nm	ε
2a	MeOH	240	26,200	HCl–MeOH	313[a]	
		364	10,000			
2b	EtOH	210	19,900	4:1 12 *N*	208	
		248	15,200	HCl–EtOH	227	
		351	7,100		330 (br)	
2c	EtOH	212	17,500	1:4 12 *N*	225	10,300
		222	11,200	HCl–EtOH	320 (br)	8,800
		248	13,400			
		351	7,700			
2d	EtOH	214	19,900	1:4 12 *N*	227	
		237	4,400 (sh)	HCl–EtOH	330 (br)	
		248	3,100 (sh)			
		335	7,700			

Attempts to extend our synthesis of thiabenzene 1-oxides to the preparation of the 3-hydroxy-5-phenyl analog **5a** *via* cyclization of the known allylide **4a**[16,17] have been unsuccessful. It is noteworthy, however, that Ide and Kishida have been able to effect such a cyclization of the corresponding 1-benzoyl derivative **4b** to yield **5b**.[18,19] Two other syntheses of thiabenzene 1-oxides have been described recently,[20,21] and formation of the 4-aza analog of **2a** as a by-product in the reaction of benzonitrile with dimethyloxosulfonium methylide has also been reported.[22]

Alkylation of Thiabenzene 1-Oxides at the S-Methyl Group. As generally expected for *S*-methyl compounds bearing a formal positive charge on sulfur,[5] the 1-oxide **2a** was found to undergo nearly complete base-catalyzed (NaOD) exchange of its *S*-methyl protons for deuterium in refluxing CH_3OD–D_2O. The intermediate anion could also be generated in solution by treatment of **2a** with 1 mol equiv of *tert*-butyllithium in THF; quenching the solution with methyl iodide gave the *S*-ethyl compound **6a** which could be further methylated in the same manner to yield the *S*-isopropyl analog **6b**. Similarly, addition of diethyl carbonate to a solution of the anion of **2a** in THF gave a 1:1 mixture of **2a** and **7**; formation of the first 0.5 mol equiv of **7** presumably provides a proton source which quenches the remaining 0.5 mol equiv of unreacted anion of **2a**.



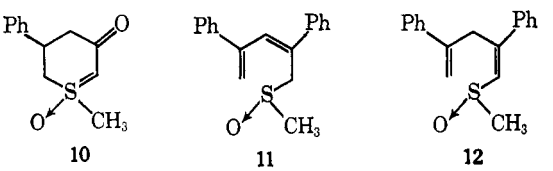
6a 6b 7 8 9

The reactions of the anion of **2a** represent a potentially simple route to a variety of 1-substituted thiabenzene analogs which would be unobtainable *via* the transformation **1** → **2** due to the inaccessibility of the sulfoxonium salts needed for preparation of the requisite ylides.

Other Possible Routes to 1-Oxides. Attempts to extend the reaction of dimethyloxosulfonium methylide with acetylenic carbonyl compounds met with failure when dimethyl acetylenedicarboxylate (*cf.* ref 17), propynal, and phenylpropynal were used as substrates. An attempt to form **2a** by treating dibenzoylmethane with the ylide was also unsuccessful (*cf.* ref 21).

The reported ease of removal of hydrogen bromide from 3-bromo-2-cycloocten-1-one with sodium carbonate in methanol to give the cyclic acetylenic ketone **8**[23] suggested the possibility of using this bromo ketone in an elimination–condensation sequence with 2 mol equiv of dimethyloxosulfonium methylide to prepare **9**. Examination of Dreiding models of **9** indicate that a transannular interaction between the proton at the C-4 position of the *S*-ring with the pair of methylene protons shown on the cyclooctyl ring of **9** would restrict movement of the 4-proton through the ring; thus, the preparation of two geometrical isomers of **9** having the five-carbon bridge situated syn or anti to the *S*-methyl group might be possible. When condensations of the ylide with the β-bromo ketone precursor of **8** (obtained by Jones oxidation of the corresponding alcohol) were tried, the crude products obtained were devoid of *S*-methyl groups in their nmr spectra (δ 3.0–4.0 region) and the results were not sufficiently encouraging for further study.

Another route to thiabenzene 1-oxides which was explored involved attempted transformations of the cyclic ketooxosulfonium ylide **10**.[24] Treatment of **10** with phenylmagnesium bromide, $LiAlH_4$, and aluminum isopropoxide in separate attempts to prepare 3-hydroxy derivatives of **10** which were to be subjected to dehydration followed by dehydrogenation conditions led to oily products which also lacked *S*-methyl protons in



10 11 12

(18) Y. Kishida and J. Ide, *Chem. Pharm. Bull.*, **15**, 360 (1967).
(19) C. Tamura, S. Sato, and Y. Kishida, *Tetrahedron Lett.*, 2739 (1968).
(20) T. M. Harris, C. M. Harris, and J. C. Cleary, *ibid.*, 1427 (1968).
(21) B. Holt, J. Howard, and P. A. Lowe, *ibid.*, 4937 (1969).
(22) H. König, H. Metzger, and K. Seelert, *Chem. Ber.*, **98**, 3724 (1965).
(23) P. E. Eaton and C. E. Stubbs, *J. Amer. Chem. Soc.*, **89**, 5722 (1967).
(24) E. J. Corey and M. Chaykovsky, *Tetrahedron Lett.*, 169 (1963). We thank Dr. Chaykovsky for supplying us with details for the preparation of **10**.

their nmr spectra; further experimentation along these lines was discontinued.

Reduction of Thiabenzene 1-Oxides. Initial attempts to reduce the 1-oxides were directed toward the preparation of 1-methyl-3,5-diphenylthiabenzene[25] *via* direct deoxygenation of **2a**. Lithium aluminum hydride is reported to reduce sulfoxides to sulfides,[26] but when **2a** was treated with an excess of $LiAlH_4$ in diethyl ether, no reaction occurred. Refluxing a mixture of **2a** and $LiAlH_4$ in dioxane gave a mixture of uncharacterizable products.

Castrillón and Szmant[27] have reported that sulfoxides can be deoxygenated to sulfides with triphenylphosphine in carbon tetrachloride; however, **2a** was unaffected when subjected to the conditions described.

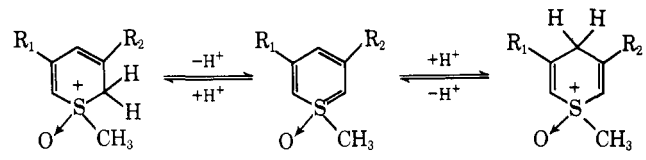
When **2a** was hydrogenated over palladium, and the reaction was halted after uptake of 1 mol equiv of hydrogen, a sulfoxide (ir ν_{max} 1030 cm^{-1}) having the formula $C_{18}H_{18}OS$ could be obtained in 40% yield. The same substance could be obtained in nearly quantitative yield on treatment of **2a** with zinc in acetic acid. The nmr spectrum of the product exhibits peaks at δ 2.37 ($S-CH_3$), 5.51 (t, 1, J = 1.1 Hz), 5.72 (s [br], 1), 6.82 (s [br], 1), 7.0–7.7 (m, 10), and an AB pattern with doublets (J = 13 Hz) centered at 3.73 and 4.21 ppm. The ultraviolet spectrum shows strong absorption at λ_{max} 252 nm (ϵ 29,700). The data suggest two possible structures, **11** or **12**, in which the geometry of substitution at the double bonds cannot be defined. The AB pattern could be due to coupling interactions of the geminal methylene protons of either **11** or **12**; the magnetic nonequivalence of these protons might result from restricted rotation and/or the proximate presence of an asymmetric center at sulfur. Structure **12** is presently favored on the basis of the uv spectrum (λ_{max} for a 1,3-diphenylbutadiene would normally occur at longer wavelength [>280 mμ])[28] and the low-field singlet at δ 6.82 in the nmr spectrum which seems best interpreted as the olefinic proton α to S→O in **12**.[26] However, the similarity of the δ values for the geminal protons in the reduction product with those of compounds related to **11**,[29] and the lack of adequate examples to help in predicting either expected λ_{max} values for nonplanar conformations of **11** or expected δ values for the geminal protons in **12**, leave the structure of the reduction product open to question.

Proton Exchange Studies. Replacement of the S-ring protons of **2a–e** by deuterium occurred when the 1-oxides were dissolved in 1:1 chloroform-*d*–acetic acid-d_4 mixtures. The exchange was sufficiently slow on the nmr time scale so that small residual peaks for H-2, H-4, and H-6 could still be observed at δ values similar to those observed for these protons when **2a–e** were dissolved in chloroform-*d* alone; the protons exchanged to the solvent medium appeared at δ 10.5–11.0 ppm. No significant exchange of *S*-methyl protons or of protons on phenyl, methyl, and ethyl substituents in **2a–e** was detectable in acidic media.

Exchange in the case of **2a** apparently occurred at a considerably faster rate in the presence of stronger acids as evidenced by an experiment in which a solution of **2a** in chloroform-*d*, when treated with 0.5 mol equiv of trifluoroacetic acid-*d*, gave rise to a broad absorption band due to *ca.* three protons at δ 5.3–6.9 which included a one-proton peak ($w_{1/2} \sim 8$ Hz) at δ 6.35. The result also suggests that H-2 and H-6 exchange at a faster rate than H-4, a conclusion which is confirmed by experiment in which **2a** in deuteriochloroform was treated with a limited amount (9 mol equiv) of acetic acid-d_4; a spectrum recorded after 1 min revealed that *ca.* 80% of H-2, -6 and *ca.* 35% of H-4 had exchanged for deuterium; a final distribution of *ca.* 85% deuterium at the C-2, C-4, and C-6 positions was eventually reached.

The facile exchange of S-ring protons in acetic acid-d_4 suggested the experiment of observing the exchange of S-ring protium of **2a** for deuterium in deuterium oxide–dimethyl-d_6 sulfoxide. The data obtained (see Experimental Section) clearly indicate that a very slow exchange of the S-ring protons of **2a** also occurs in this medium.[30]

The exchange experiments suggest that **2a–e** are in equilibrium with the corresponding 2*H*- and 4*H*-thiinium 1-oxides. In the weakly acidic media described,



the equilibria lie strongly in favor of the 1-oxides. In more strongly acidic media, ultraviolet spectra of **2a–d** show pronounced changes from the spectra run in neutral media (Table II), suggesting that the equilibria can be readily shifted in favor of the thiinium 1-oxides.

Discussion

Characterization of Bonding in Thiabenzene 1-Oxides. Some pertinent conclusions related to the question of bonding in thiabenzene 1-oxides may be inferred from the nmr and exchange data presented above.

The H-4 protons, although occurring 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 the H-2, -6 protons in **2a–e** and **6a–b** (Table I) are also well outside of the aromatic region of the nmr spectrum and are *markedly* upfield from the range for olefinic protons on sp^2 carbons α to sulfur as defined by known olefinic sulfur compounds (Table III). The nmr data, when considered with the proton exchange data, suggest that the C-2, -4, and -6 positions of the S-ring bear relatively high electron densities and are carbanionic in character. Consequently, the thiabenzene 1-oxides may be viewed as cyclic sulfoxonium ylides[31] in which the carbons at the termini of a pentadienyl carbanion system form weak $2p\pi$–$3d\pi$ bonds with the σ-bonded sulfur atom which in turn bears an essentially isolated positive charge of nearly two units. The more pronounced shielding of H-2 and H-6 compared with H-4 which is evidenced in the proton nmr spectra may

(25) A. G. Hortmann and R. L. Harris, *J. Amer. Chem. Soc.*, **92**, 1803 (1970).
(26) G. A. Russell, E. Sabourin, and G. Mikol, *J. Org. Chem.*, **31**, 2854 (1966); see also footnote *c* in Table II.
(27) J. P. A. Castrillón and H. H. Szmant, *ibid.*, **30**, 1338 (1965).
(28) *Cf.* H. O. House and A. G. Hortmann, *ibid.*, **26**, 2190 (1961).
(29) I. Iwai and J. Ide, *Chem. Pharm. Bull.*, **13**, 663 (1965).
(30) Exchange of the S-ring protons of **5b** and its methyl ether have been observed by Ide and Kishida.[18]
(31) See relevant discussions concerning cyclic phosphonium and sulfonium ylides in A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966, pp 84–87, 354–356.

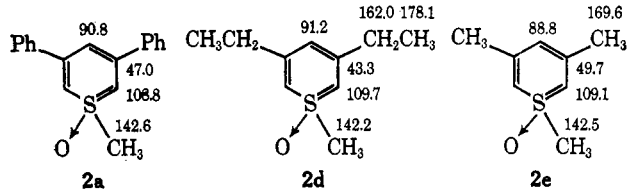


Figure 1. Selected carbon-13 chemical shifts in thiabenzene 1-oxides.[33] Values were obtained for **2a**, **2d**, and **2e** in $CHCl_3$ solution and are given in parts per million from CS_2 based on $\delta_{CS_2} = \delta_{CHCl_3} + 115.2$ ppm.

be taken to indicate more carbanionic character at C-2 and C-6 than at C-4,[32] a suggestion which seems to be a reasonable consequence of electrostatic attraction of negative charge to the termini of the pentadienyl carbanion system by the positively charged sulfur.

Table III. Chemical Shifts of Protons Adjacent to Sulfur in Known Compounds

Compd	$\delta_{H\alpha}$	Solvent
$H_2C{=}CHSCH_3$	6.43[a]	$CDCl_3$
$H_2C{=}CHSO_2CH_3$	6.70[a]	$CDCl_3$
PhCD=CHSCH$_3$ (trans)	6.68[b]	Neat
PhCH=CHSOCH$_3$ (trans)	7.20 or 6.91[c]	
$[PhCD{=}CHS(CH_3)_2]^+BF_4^-$ (trans)	6.95[b]	CH_2Cl_2
Thiophene	7.30[a]	$CDCl_3$

[a] N. S. Bhacca, L. J. Johnson, and J. N. Holland, "High Resolution NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962, Spectra No. 35, 36, and 52. [b] M. Caserio, R. E. Pratt, and R. J. Holland, *J. Amer. Chem. Soc.*, **88**, 5747 (1966). [c] See ref 26; note that the assignments for δ_A (7.20) and δ_B (6.91) in this compound may be reversed; *cf.* footnote *b*.

The presence of a pentadienyl carbanion system in the 1-oxides appears to be further corroborated by the ^{13}C nmr spectra of **2a**, **2d**, and **2e**[33] in which a pronounced alternation in chemical shift values (Figure 1) for the S-ring carbons is noted; 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 (~45–70 ppm) and benzenoid (~65 ppm) carbon atoms. A similar alternating effect in the proton chemical shift values for pentadienyl anions has already been noted by Bates, *et al.*[34]

Although the data presented thus far provide strong presumptive evidence for ylide-like bonding character in thiabenzene 1-oxides, there are, however, not sufficient data to discount the possibility of some through-conjugation at sulfur and the existence of at least small ring-current effects similar to those generally considered characteristic of aromatic systems.

An approach to the problem of detection of ring currents in potentially aromatic compounds has been described by Goldstein and Reddy,[35] who have suggested that a correlation between ^{13}C–H coupling constants and proton chemical shifts can be used to estimate the diamagnetic anisotropy effect in a molecule. It is stated[35] that a correlation between ^{13}C–H coupling constants and proton chemical shifts will show deviations from linearity when an anisotropic effect is present in the molecule because proton chemical shifts are sensitive to such effects while ^{13}C–H coupling constants appear to be insensitive to these same effects.

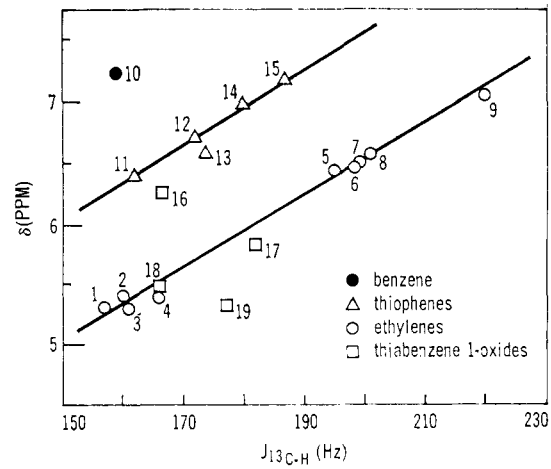
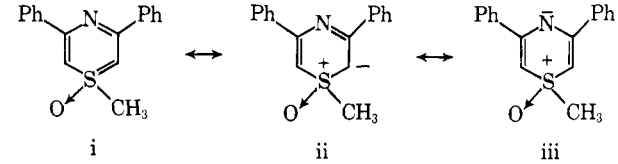


Figure 2. Plot of proton chemical shifts (δ) *vs.* $J_{^{13}C-H}$ values for some ethylenic compounds, thiophenes, and thiabenzene 1-oxides. All data, except those for the 1-oxides, were taken from ref 35. The compounds whose chemical shifts are plotted are as follows: (1) ethylene; (2) vinyl chloride (cis); (3) vinyl chloride (trans); (4) vinylidene chloride; (5) vinyl chloride (α); (6) *cis*-dichloroethylene; (7) *trans*-dichloroethylene; (8) trichloroethylene; (9) vinylidene carbonate; (10) benzene; (11) 2,5-dimethylthiophene; (12) 2,5-dibromothiophene; (13) 2,5-dichlorothiophene; (14) thiophene (β-H); (15) thiophene (α-H); (16) 1-methyl-3,5-diphenylthiabenzene 1-oxide (**2a**, H-4); (17) 1-methyl-3,5-diphenylthiabenzene 1-oxide (**2a**, H-2,6); (18) 1,3,5-trimethylthiabenzene 1-oxide (**2e**, H-4); and (19) 1,3,5-trimethylthiabenzene 1-oxide (**2e**, H-2,6).

In Figure 2 are plotted some of the data of Goldstein and Reddy.[35] In addition, ^{13}C–H coupling constants[15] *vs.* chemical shifts of the S-ring protons in **2a** and **2e** are also plotted in order to estimate the extent of diamagnetic anisotropy present in the thiabenzene 1-oxides. Goldstein and Reddy have argued that the vertical distance between lines 1 and 2 in Figure 2 is due to the presence of a diamagnetic anisotropic effect of the ring current type in thiophene; a much larger diamagnetic anisotropic effect is clearly present in benzene (point 10). The plotting of the ^{13}C–H coupling constant *vs.* the chemical shifts of ring protons of the thiabenzene 1-oxides indicates (with the exception of point 16) that there is little, if any, diamagnetic anisotropy of the ring current type (as determined by this correlation method) in thiabenzene 1-oxides and thus adds further support to the assumption that these compounds possess little (if any) aromatic character. The deviation of point 16 from line 1 may be due to local anisotropic effects associated with the phenyl groups flanking H-4 in **2a** since a similar effect is not observed for H-4 of **2e**.

It also seems likely that ring-current effects are negligible in the 4-aza analog i of **2a**[22] and that the deshielding observed for H-2,6 of i (δ 6.30) when compared with **2a** (δ 5.83) arises from relatively greater importance of the contributing structure iii resulting from the



(32) Although the differential rates of proton exchange at C-2, -6 *vs.* C-4 in **2a** might also be cited in this connection, their origin as a consequence of steric effects cannot be excluded.

(33) E. Wenkert, D. Cochran, R. L. Harris, and A. G. Hortmann, *Chem. Commun.*, in press.

(34) R. B. Bates, W. H. Deines, D. A. McCombs, and D. E. Potter, *J. Amer. Chem. Soc.*, **91**, 4608 (1969), and references cited.

(35) J. H. Goldstein and G. S. Reddy, *J. Chem. Phys.*, **36**, 2644 (1962).

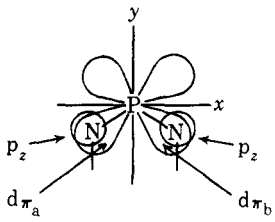


Figure 3. Dewar model for overlap in phosphonitrilic halides. The illustration shows only the upper lobes of the nitrogen $2p_z$ and the phosphorus $d\pi_a$ and $d\pi_b$ orbitals.

greater electronegativity of the nitrogen atom situated at the 4 position.

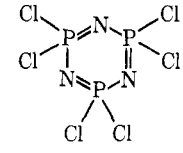
Another interesting feature which emerged from the nmr spectra of the thiabenzene 1-oxides was the large spin coupling interaction which occurs between H-2 and H-6 across the sulfur atom. The magnitude of the coupling observed is larger than the coupling through sulfur noted in the nmr spectra of 2-thiaphenanthrenium ion ($J_{1,3}$ = 3.4 Hz) and 3-thiaphenanthrenium ion ($J_{2,4}$ = 3.0 Hz).[36] It is also larger than that observed for a variety of 3-substituted thiophenes,[37] and for 4-methylthiazolium ion.[38] Small long-range H–H spin coupling interactions through sulfur have also been observed in methyl sulfide derivatives[39] but are absent in oxygen analogs. Thus the occurrence of long-range coupling appears to be dependent on the presence of a sulfur atom in the systems cited, and it seems reasonable to assume that an H–H distance factor is not solely responsible for the magnitude of the coupling. These results imply that d orbitals are involved in the long-range coupling process. However, whether the coupling observed in the thiabenzene 1-oxides is an instance of maximal coupling through C–S bonds with d orbital character or somehow involves transmission through the vacant d orbitals on sulfur cannot be determined, nor does it seem possible to associate this interesting phenomenon with through-conjugation in those systems where it might seem possible to utilize 3p or 3d orbitals of sulfur in delocalization.

The ultraviolet absorption spectra (Table II) of the thiabenzene 1-oxides do not resemble the uv spectra of benzene, thiophene, or other heteroaromatic systems and also support the conclusion that the 1-oxides are not aromatic. The lack of suitable compounds for comparison makes further interpretation of the uv data for **2a–e** difficult.

Several bonding schemes have been proposed for cyclic systems incorporating second-row elements which must utilize d orbitals for bonding ($p\pi$–$d\pi$ bonds). The answer to the question of whether ylide-type bonding or aromatic bonding predominates in a particular system is believed to depend on which d orbitals are used for π bonding as well as their spatial relationships with interacting p orbitals. In order to conjugate with the $2p_z$ orbitals of an adjacent atom, the d orbital must have proper symmetry with respect to the molecular plane for π bonding, and thus must have a node in the plane of reference and lobes of opposite sign above and below the molecular plane. This symmetry restriction rules out interaction of the in-plane d_{xy} and $d_{x^2-y^2}$ orbitals, as well as the d_{z^2} orbital, with, *e.g.*, carbon $2p_z$ orbitals, but might permit $p\pi$–$d\pi$ bonding involving either the d_{xz} or the d_{yz} orbitals, or hybrids of these.

A theoretical bonding scheme for polymeric phosphonitrilic halides, *e.g.*, **13**, has been proposed by Craig.[40] It was concluded that **13**, which has all P–N bonds of equal length, is a new type of aromatic system arising from overlap of phosphorus d_{xz} orbitals with $2p_z$ orbitals of nitrogen. This scheme predicts considerable stabilization by π-electron delocalization in the ring, but there is a node in each of the two bonding molecular orbitals: in one, at phosphorus, and in the other, at nitrogen.[3]

Another suggestion for aromaticity using only one d orbital was proposed for cyclic phosphonium and sulfonium ylides by Price[41] and invokes overlap of the d_{yz} orbital with the $2p_z$ orbitals of adjacent carbon atoms.[42] A significant feature of this proposal is that it predicts *continuous* delocalization about the ring, and therefore one might expect to observe consequent deshielding of S-ring protons due to the presence of an induced ring current when such compounds are immersed in a magnetic field.

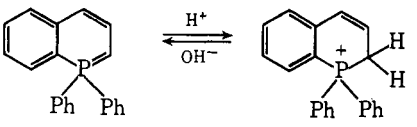


13

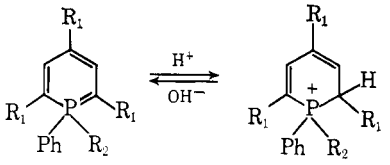
Dewar, *et al.*,[4,43] have argued that Craig's proposal for aromaticity in **13** was due to the neglect of the contribution of the d_{yz} orbitals to the electronic structure of **13**, and that when it is included with the contribution of the d_{xz} orbital, **13** is not aromatic. More explicity, Dewar, *et al.*, proposed that a linear combination of the d_{xz} and d_{yz} orbitals of phosphorus would give a new set of two hybrid orbitals, $d\pi_a$ and $d\pi_b$, which are orthogonal to one another and oriented in the directions of the nitrogen $2p_z$ orbitals. Each of these orthogonal $d\pi$ orbitals would overlap with a p_z orbital on just *one* of the two adjacent nitrogens (Figure 3) giving a series of three P–N–P "islands." It was concluded that, as a result of this orthogonality, cyclic conjugated molecules containing phosphorus or sulfur should exhibit *no* significant through-conjugation at the heteroatom, even though d orbitals are involved in bonding to the heteroatom, and thus this scheme would not permit a ring current in **13**.

The effects of $p\pi$–$d\pi$ bonding in several phosphabenzenes (**14**, **16a–d**) have been reported by Märkl.[44] The phosphabenzenes can be considered as phosphorus analogs of the thiabenzene 1-oxides, and must also be described by a bonding scheme involving $p\pi$–$d\pi$ bonding.

(36) T. Young and C. Ohnmacht, *J. Org. Chem.*, 32, 1558 (1967).
(37) R. White, "Physical Methods in Heterocyclic Chemistry," A. Katritsky, Ed., Academic Press, New York, N. Y., 1963, p 117.
(38) P. Haake and W. Miller, *J. Amer. Chem. Soc.*, 85, 4044 (1963).
(39) See footnote *b* in Table III.
(40) J. Craig, *J. Chem. Soc.*, 997 (1959).
(41) C. C. Price, Abstracts, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, p 6N; cited in ref 31, p 87.
(42) This scheme follows an earlier model proposed for thiophene: H. C. Longuet-Higgins, *Trans. Faraday Soc.*, 45, 173 (1949).
(43) M. J. S. Dewar, E. A. C. Lucken, and M. A. Whitehead, *J. Chem. Soc.*, 2423 (1960).
(44) G. Märkl, *Angew. Chem.*, 75, 168, 669, 1121 (1963); G. Märkl and A. Merz, *Tetrahedron Lett.*, 3611 (1968); 1231 (1969).



14 15



16a–d 17a–d

a, R_1 = H; R_2 = Ph
b, R_1 = Ph; R_2 = CH_3
c, R_1 = Ph; R_2 = C_2H_5
d, R_1 = Ph; R_2 = Ph

Compound **14** was generated by treatment of an aqueous solution of **15** with base; the phosphonium salt **15** can be regenerated in acid. The phosphanaphthalene **14** can be alkylated at C-4 with methyl iodide, and is rapidly oxidized in air. The phosphabenzene **16a** was similarly prepared by treatment of **17a** with base (dilute NaOH); **16a** also readily protonates, and is also oxidized readily in air. The ultraviolet spectrum of **16a**, λ_{max} 409 nm, is similar to that of the cyanine dye **18** (λ_{max} 432 nm) and implied that a similarity in electronic

$$(Ph)_3\overset{+}{P}CH{=}CHCH{=}CHCH{=}P(Ph)_3$$
18

structure existed between **16a** and **18**. On the basis of these data, Märkl suggested that bonding in **14** and **16a** probably does not involve conjugation through phosphorus, and might best be represented by the Dewar model for C–P–C bonding.

The phosphabenzenes **16b–d** show absorption peaks for H-3 and H-5 in their nmr spectra at δ 7.42, 7.62, and 7.7, respectively, but unfortunately no nmr data are available for **16a** in which chemical shifts for H-2, -4, and -6 might be observed. The phosphanaphthalene **14**, however, exhibits an upfield resonance peak at δ 5.54 (d, 1, J = 9 Hz)[9] which may be due to the 2-proton; the remaining sixteen protons show absorption from δ 6.5 to 7.7 ppm. Additional nmr data for monocyclic phosphabenzenes unsubstituted at C-2, -4 and -6 would be desirable.

A comparison of the thiabenzene 1-oxides with the phosphabenzene derivatives reveals that the 1-oxides are far more stable toward oxygen. In addition, we have found that the 1-oxides do not undergo methylation on treatment with methyl iodide or acylation on treatment with acetyl chloride. Finally, the position of equilibrium in protic media is more in favor of the phosphonium salts in the cases of **14** and **16** than the thiinium salts in the cases of **2a–e**, indicating the more basic (carbanionic) nature of the cyclic phosphorus ylides. These comparisons suggest that the pentadienyl carbanion system in the thiabenzene 1-oxides is somewhat more stabilized by overlap with sulfur d orbitals at its termini than the corresponding carbanion system in the phosphabenzenes. However, the data and conclusions regarding ylide-like bonding character in the thiabenzene 1-oxides would still seem to be most reasonably accommodated by the Dewar scheme for $p\pi$–$d\pi$ bonding. Thus, a description of the thiabenzene 1-oxide system might be similar to that proposed for the phosphabenzenes by Märkl, *i.e.*, one in which six π-electrons are distributed in a seven-orbital system in which the bonding in the C_2–S–C_6 moiety is similar to that shown for N–P–N in Figure 3.

Experimental Section[45,46]

Typical Procedure for the Preparation of Dimethyloxosulfonium Methylide.[47] Sodium hydride (0.60 g, 0.025 mol; 56.6% dispersion in mineral oil) was placed in a dry 500-ml three-necked flask. The hydride was washed with several 20-ml portions of petroleum ether (bp 37–42°), and the petroleum ether was removed by means of a suction pipet. Residual petroleum ether was removed under vacuum, nitrogen was introduced into the flask, and 20 ml of anhydrous dimethyl sulfoxide (DMSO) was added *via* a syringe. A solution of trimethyloxosulfonium iodide (5.8 g, 0.026 mol) in 120 ml of DMSO was injected slowly into the resulting suspension of sodium hydride and the ylide was allowed to form while stirring the reaction mixture at room temperature under N_2; evolution of H_2 ceased after 2.25 hr and the resulting solution of ylide was used directly in the preparation of **2a–e**. (For those experiments in which a mixed solvent of tetrahydrofuran–DMSO was used, the specified volume of dry THF was injected into the ylide solution.)

1,3-Diphenyl-2-propyn-1-one (1a).[48] Benzalacetophenone (400 g, 1.92 mol) was converted into dibromobenzalacetophenone as described previously.[49] The entire crude solid dibromo compound was heated for 3 hr at reflux temperature in 1800 ml of EtOH containing 160 g of sodium acetate. The EtOH was distilled over an additional 3-hr period and the residual oil was dissolved in Et_2O–H_2O and worked up in the usual manner. Distillation of the crude product yielded 416.2 g of 2-bromo-1,3-diphenylpropenone, bp 189.5° (1.8 mm). The bromo ketone (380.9 g, 1.33 mol) was dissolved in 600 ml of anhydrous *tert*-butyl alcohol and a hot solution of *tert*-butyl alcohol (1200 ml) containing 52.6 g (1.34 g-atom) of dissolved potassium metal was added under N_2 over a period of 2.5 hr while maintaining the temperature at 25–32°. The reaction mixture was stirred for an additional 12 hr followed by removal of *tert*-butyl alcohol *in vacuo* at *ca.* 70°. The residue was dissolved in Et_2O–H_2O and the organic layer was washed with dilute HCl and brine and dried over $MgSO_4$. Removal of the Et_2O and crystallization of the product from petroleum ether (bp 63–69°) afforded 191 g of crude acetylenic ketone **1a** (52% from benzalacetophenone). Recrystallization of 23.4 g of crude product gave 21.2 g of pure **1a**: mp 49.5–51.5° (lit.[50] mp 46.5–48.0°; lit.[51] mp 49–50°).

1-Phenyl-2-butyn-1-one (1b). Condensed propyne (28.0 g, 0.70 mol) was added at 0° to a solution of ethylmagnesium bromide prepared from 8.5 g (0.36 g-atom) of magnesium and 38.1 g (0.35 mol) of ethyl bromide in 210 ml of Et_2O; a Dry Ice–acetone condensor prevented loss of propyne. The reaction mixture was stirred for 3.25 hr at 0° during which time a two-phase system developed. The resulting acetylenic Grignard reagent was added dropwise during 0.5 hr to a stirred solution of benzaldehyde (37.1 g, 0.35 mol) in 200 ml of Et_2O at 0° and under N_2. After stirring for 1 hr at room temperature, the reaction mixture was cooled to 0° and treated with saturated NH_4Cl solution. Addition of water followed by a normal work-up procedure gave 42.2 g of viscous yellow oil. Distillation at reduced pressure afforded 34.6 g (68%) of

(45) Melting points were determined on a Hoover capillary melting point apparatus and are corrected; boiling points are uncorrected. Infrared spectra were obtained on approximately 10% solutions with a Perkin-Elmer Model 21 (prism) or Model 457 (grating) spectrophotometer; ultraviolet spectra were obtained on either a Cary 11 or Cary 14 spectrophotometer. Nmr spectra were obtained on approximately 20% solutions with a Varian A-60A instrument; chemical shifts are reported in units of δ (parts per million) downfield from tetramethylsilane as an internal standard. Elemental analyses were performed by the Microanalytical Laboratory at the Institute for Physical Chemistry, Vienna, Austria, and by Galbraith Laboratories, Knoxville, Tenn. 37921.

(46) The petroleum ether used was the fraction having bp 63–69° unless stated otherwise.

(47) *Cf.* E. J. Corey and M. Chaykovsky, *Org. Syn.*, **49**, 78 (1969).

(48) *Cf.* C. L. Bickel, *J. Amer. Chem. Soc.*, **69**, 2134 (1947).

(49) C. F. H. Allen, R. D. Abell, and J. B. Normington, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1941, p 205.

(50) M. S. Newman and B. C. Ream, *J. Org. Chem.*, **31**, 3861 (1966).

(51) J. U. Nef, *Justus Liebigs Ann. Chem.*, **308**, 264 (1899).

1-phenyl-2-butyn-1-ol: bp 99.5–103.0° (1.3 mm); ir ($CHCl_3$) 3370 and 2220 cm^{-1}; nmr (CCl_4) δ 1.74 (d, 3, J = 2.1 Hz), 3.31 (d, 1, J = 6.0 Hz), 5.18 (qd, 1, J = 2.1 Hz, 6.0 Hz), and 7.00–7.45 ppm (m, 5). To a rapidly stirring solution of the alcohol (34.1 g, 0.233 mol) in acetone (220 ml) was added Jones–Weedon reagent[52] (3.6 *N*, 130 ml) while the temperature of the reaction mixture was maintained between 2 and 8°. After the solution was stirred for an additional 1.25 hr at 5°, the reaction mixture was diluted with H_2O and extracted with $CHCl_3$. The extract was washed with H_2O, saturated $NaHCO_3$, and NaCl solutions, and dried ($MgSO_4$). Removal of the solvent at room temperature under vacuum left 38.6 g of a colorless oil. An nmr assay indicated that approximately 7% of the starting alcohol was present. A further oxidation of the crude product in acetone with Jones–Weedon reagent (3.6 *N*, 16.0 ml) afforded 32.5 g (97%) of yellow oil. Distillation afforded 27.6 g (82%) of a colorless oil: bp 93.8° (1.3 mm) [lit.[53] bp 133° (12 mm); lit.[54] bp 101° (3 mm)]. Redistillation of the heart cut gave an analytical sample of **1b**: bp 96.5° (1.4 mm); ir (CCl_4) 2240, 2220, and 1640 cm^{-1}; uv max (cyclohexane) 256 (ϵ 15,300) and 213 nm (ϵ 11,100); nmr (CCl_4) δ 2.10 (s, 3), 7.17–7.53 (m, 3), and 7.89–8.15 ppm (m, 2).

Anal. Calcd for $C_{10}H_8O$: C, 83.31; H, 5.59. Found: C, 83.45; H, 5.87.

1-Phenyl-4,4-dimethyl-1-pentyn-3-one (1c). A solution of ethynylbenzene (16.3 g, 0.159 mol) in anhydrous Et_2O (100 ml) was added during 70 min to a suspension of sodium chips (3.45 g, 0.15 g-atom) in 100 ml of Et_2O at 0° under N_2. The reaction mixture was stirred for 2 hr at 0° and then 3 hr at room temperature. The milky white suspension was transferred through a flexible Teflon tube (with the aid of N_2 pressure) into a solution of pivaloyl chloride (30.1 g, 0.25 mol) in dry Et_2O (200 ml) at 0°. The mixture was stirred at room temperature for 0.5 hr and then poured into a mixture of ice and saturated NH_4Cl solution. The Et_2O layer was washed with H_2O and saturated $NaHCO_3$ solution and dried ($MgSO_4$). Evaporation of the Et_2O under vacuum left 23.5 g of a yellow oil; distillation under vacuum gave 15.2 g (55%) of **1c** as a colorless oil, bp 81–82° (1.5 mm). Redistillation of the heart cut afforded an analytical sample: ir (CCl_4) 2200 and 1659 cm^{-1}; uv max (EtOH) 283 (ϵ 12,800), 247 (ϵ 7600 [sh]), 236 (ϵ 6500), and 216 nm (ϵ 11,600); nmr (CCl_4) δ 1.26 (s, 9) and 7.29–7.68 ppm (m, 5).

Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 84.08; H, 7.66.

4-Heptyn-3-one (1d). 1-Butynylmagnesium bromide (1.0 mol) was prepared in the same manner described for propynylmagnesium bromide in the preparation of **1b**. A solution of propanal (87.0 g, 1.5 mol) in anhydrous Et_2O (200 ml) was added to the stirred solution of 1-butynylmagnesium bromide at 0°. The reaction mixture was poured into H_2O and the organic layer was washed with H_2O and saturated $NaHSO_3$ and NaCl solutions and dried ($MgSO_4$). The Et_2O solution was concentrated under vacuum leaving 102.7 g (91%) of a clear yellow oil; distillation of the oil under vacuum afforded 45.8 g (41%) of **4-heptyn-3-ol** as a colorless liquid: bp 58.0–60.8° (5.2 mm); ir (CCl_4) 3440, 2218, and 1720 cm^{-1}; uv max (cyclohexane) 247 (ϵ 84) and 229 nm (ϵ 125); nmr (CCl_4) δ 0.97 (t, 3, J = 6.9 Hz), 1.14 (t, 3, J = 7.5 Hz), 1.66 (p, 2, $J \sim$ 7.5 Hz, and additional splitting of each peak), 2.21 (q, 2, $J \sim$ 6.5 Hz, and minor splitting of each peak), 3.20 (br s, 1) and 4.20 ppm (tt, 1, J = 7.5 Hz, 2.0 Hz). The alcohol (45.8 g, 0.4 mol) was dissolved in acetone (350 ml) and Jones–Weedon reagent[52] (0.88 equiv) was added dropwise during 2 hr while the temperature of the reaction mixture was maintained at 0–8°. After stirring for an additional 1.0 hr at 0°, the mixture was diluted with H_2O and Et_2O; the Et_2O extracts were washed with water and saturated $NaHCO_3$ and Na Cl solutions, and dried ($MgSO_4$). Concentration of the solution under vacuum left 36.6 g (83%) of a pale yellow oil. Distillation under vacuum afforded 33.1 g (75%) of **1d** as a pale yellow oil: bp 71.0–73.3° (27.5 mm); ir (CCl_4) 2205 and 1670 cm^{-1}; uv max (EtOH) 218 nm (ϵ 7000); nmr (50% v/v in CCl_4) δ 1.08 (t, 3, J = 7.5 Hz), 1.20 (t, 3, J = 6.9 Hz), 2.35 (q, 2, J = 7.5 Hz), and 2.48 ppm (q, 2, J = 6.9 Hz).

Anal. Calcd for $C_7H_{10}O$: C, 76.33; H, 9.16. Found: C, 76.31; H, 9.16.

3-Pentyn-2-one (1e). 3-Pentyn-2-ol was prepared in 61% yield by the method outlined by Smith and Swenson.[55] The product had bp 65.5–67.0° (39 mm) [lit.[55] bp 50–55° (16 mm)]; ir (CCl_4) 3379, 2250, and 1740 cm^{-1}; nmr (CCl_4) δ 1.37 (d, 3, J = 6.6 Hz), 1.82 (d, 3, J = 2.0 Hz), 4.16 (s, 1), and a thirteen-line pattern located at 4.42 (qq, 1, $J_{1,2}$ = 6.6 Hz, $J_{2,5}$ = 2.0 Hz). Treatment of the alcohol with Jones–Weedon oxidant,[52] as described previously,[56] afforded the ketone **1e** in 51% yield: bp 67° (95 mm) [lit.[56] bp 73.5–74.5° (95 mm); lit.[57] bp 72–73° (100 mm)]; ir ($CHCl_3$) 2280, 2210, and 1674 cm^{-1}; nmr (CCl_4) δ 2.01 (s, 3) and 2.22 ppm (s, 3).

4-Phenyl-3-butyn-2-one (1f). Prepared in 35% yield by the method of Nightingale and Wadsworth:[58] bp 120–125° (14 mm).

1-Methyl-3,5-diphenylthiabenzene 1-Oxide (2a). A solution of 1,3-diphenylpropynone (6.18 g, 0.030 mol) in anhydrous DMSO (40 ml) was injected by means of a syringe during 10 min into a solution of dimethyloxosulfonium methylide (0.045 mol) in DMSO (150 ml) at 16.5° and under N_2; the temperature of the reaction mixture did not rise above 18.0°. The orange reaction mixture was stirred for 1.7 hr at 17° and then poured into ice water (400 ml). The yellow precipitate which formed was collected by suction filtration, washed with H_2O, and dissolved in EtOAc–CH_2Cl_2; the resulting solution was dried ($MgSO_4$). Evaporation of the solvent under vacuum gave 7.3 g (87%) of a yellow crystalline solid, mp 142–148°. The crude material was dissolved in EtOAc (20 ml), and petroleum ether (bp 63–69°) was added to the boiling solution yielding 6.36 g (76%) of **2a** as yellow needles, mp 149.3–150.3°.

An analytical sample had mp 148.0–148.5°; ir ($CHCl_3$) 1527, 1490, 1385, 1371, 1130, and 697 cm^{-1}; uv max (MeOH) 240 (ϵ 26,200) and 364 nm (ϵ 10,000); nmr (20% w/v in $CDCl_3$) δ 3.50 (s, 3), 5.83(d, 2, J = 1.1 Hz), 6.26 (t, 1, J = 1.1 Hz), and 7.15–7.65 ppm (m, 10); nmr (80 mg of **1a** in 0.25 ml of DMSO-d_6) δ 3.75 (s, 3), 6.28 (m, 3), 7.34–7.89 ppm (m, 10).

Anal. Calcd for $C_{18}H_{16}OS$: C, 77.12; H, 5.75; S, 11.42; mol wt, 280.4. Found: C, 77.15; H, 5.76; S, 11.60; mol wt, 276 (osmometer), 323 (Rast).

Exchange of *S*-Methyl Protons of 2a in NaOD–D_2O–CH_3OD. The 1-oxide **2a** (162 mg) was dissolved in 2 ml of CH_3OD–D_2O (bp 69–70°) containing *ca.* 12 mg of dissolved sodium. After heating at reflux temperature for 21 hr followed by dilution (H_2O) and extraction ($CHCl_3$), 121 mg of **1a**-d_3 was obtained; the nmr spectrum ($CDCl_3$) of the product showed normal absorption peaks for the aryl and S-ring protons and a small residual peak (~0.3 H [brd]) for *S*-methyl protons at δ 3.50 ppm.

Exchange of *S*-Ring Protons of 2a in Deuterated Acidic Media. (A) A solution of 1-oxide **2a** in acetic acid-d_1 was allowed to stand overnight. Removal of the solvent *in vacuo* gave crystalline **2a**-d_3 which showed nearly complete absence of absorption at δ 5.83 and 6.26 in its nmr spectrum ($CDCl_3$); no change in the ratio of S-CH_3 to Ar-*H* protons was evident.

(B) Acetic acid-d_4 (10 mmol) was added to a solution of **2a** (1 mmol) in $CDCl_3$ in an nmr tube. During the first few seconds of agitation 80% of the protons at C-2 and C-6 and about 35% of the protons at C-4 were exchanged for deuterium. The C-4 position continued to incorporate up to 55% deuterium during the next few minutes, while the deuterium content at the C-2 and C-6 positions remained nearly constant. The exchange finally reached a point at which deuterium was statistically distributed in the C-2, C-4, and C-6 positions to the extent of about 85%. (The percentage figures cited are based on comparison of the integrated areas remaining under the still relatively sharp peaks corresponding to H-2, -6, and H-4 with those due to Ar-*H*, and rely on the assumption that no deuterium is incorporated into the phenyl rings.)

(C) Trifluoroacetic acid (20 μl) was added to a solution of **2a** (100 mg) in $CDCl_3$ (400 mg). An nmr spectrum run after 1 min exhibited peaks at δ 3.62 (s, ~3 H) and 7.2–7.7 (s, ~10 H), and a very broad absorption band at 5.3–6.9 ppm (~3 H) which included a one-proton peak ($w_{1/2} \sim$ 8 Hz) at 6.35 ppm. The shape of the Ar-*H* absorption pattern of **2a** had changed considerably.

(D) Deuterium oxide (15 μl) was added to a solution of 40 mg of **2a** in 0.2 ml of DMSO-d_6 in an nmr tube; the exchange was al-

(52) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

(53) G. Martin, *C. R. Acad. Sci., Paris*, **245**, 1933 (1957).

(54) K. E. Schulte, J. Reish, and O. Heine, *Arch. Pharm.*, **294**, 234 (1961); *Chem. Abstr.*, **55**, 16545*b* (1961).

(55) L. I. Smith and J. S. Swenson, *J. Amer. Chem. Soc.*, **79**, 2962 (1957).

(56) E. A. Braude, E. R. H. Jones, F. Sondheimer, and T. B. Toogood, *J. Chem. Soc.*, 607 (1949).

(57) A. A. Petrov and Yu. I. Porfir'eva, *Dokl. Akad. Nauk SSSR*, **90**, 561 (1953); *Chem. Abstr.*, **49**, 12285*c* (1955).

(58) D. Nightingale and F. Wadsworth, *J. Amer. Chem. Soc.*, **67**, 416 (1945).

Table IV. Exchange of S-Ring Protons in 1-Methyl-3,5-diphenylthiabenzene 1-Oxide (**2a**) for Deuterium in D_2O–DMSO-d_6

Time, t, hr	Chemical shift of peak[a] (integrated area)[b] HOD	S–CH_3	H-2, -4, -6
0	3.63 (10.9)[c]	3.75 (70.1)	6.27 (72.8)
9	3.63 (16.9)	3.76 (72.1)	6.27 (65.0)
27	3.63 (58.9)	3.76 (70.9)	6.27 (30.3)
142	3.60 (72.6)	3.75 (72.6)	6.26 (18.8)

[a] All data were obtained using the same instrument settings on a Varian A-60A spectrometer. [b] These values have been normalized to an assigned value of 100 for the area under the peak for the $-C(CH_3)_3$ group of *tert*-butylbenzene (internal standard). [c] Residual HOD in DOD at $t = 0$.

lowed to proceed at room temperature and was monitored by nmr spectroscopy (see Table IV).

1,3-Dimethyl-5-phenylthiabenzene 1-Oxide (2b). Method A. A solution of 1-phenyl-2-butyn-1-one (**1b**) (5.76 g, 0.040 mol) in anhydrous DMSO (10 ml) was injected during 3 min into a solution of dimethyloxosulfonium methylide (0.088 mol) in DMSO (240 ml) at 14° and under N_2. After the deep red reaction mixture was stirred for 4 hr at room temperature and 3 hr at 45°, it was poured into H_2O yielding a rubbery gum. The gum was dissolved (CH_2Cl_2) and the H_2O–DMSO solution was thoroughly extracted (CH_2Cl_2); the combined organic solutions were washed with H_2O and dried ($MgSO_4$). The solvent was evaporated under vacuum leaving 10.8 g of a viscous, red-orange oil. The oil was chromatographed on Woelm neutral alumina (activity grade 1) packed in 1:1 benzene–petroleum ether. Elution with 3:1 benzene–petroleum ether, followed by benzene containing increasing percentages of $CHCl_3$, gave 9.4 g of nearly pure **2b** as a viscous orange oil containing some solvent. Two successive chromatographic separations on Florisil (100–200 mesh) gave an analytical sample of **2b** as a pale yellow gum: ir (CCl_4) 1526, 1492, 1448, 1390, 1240, 1168, 1144, 699, and 642 cm^{-1}; uv max (EtOH) 351 (ϵ 7100), 248 (ϵ 15,200), and 210 nm (ϵ 19,900); uv max (12 *N* HCl–EtOH [1:4]) 330 (very broad), 227, and 208 nm; nmr (CCl_4) δ 2.13 (s, 3), 3.33 (s, 3), AB portion of an ABX pattern with one-proton doublets (of doublets) centered at δ 5.28 and 5.47 (J = 4.3 Hz, 1.4 Hz), 5.67 (t, 1, J = 1.4 Hz), and 7.08–7.60 ppm (m, 5); nmr (10% in 1:1 CD_3COOD–$CDCl_3$) δ 2.20 (s, 3), 3.53 (s, 3), 5.55 (s [br], ~0.25), 5.66 [s [br], ~0.25), 5.88 (s [br], ~0.25), 7.20–7.72 (m, 5), and 10.70 ppm (s, 2.4).

Anal. Calcd for $C_{13}H_{11}OS$: C, 71.52; H, 6.46. Found: C, 71.67; H, 6.40.

Method B. Allylide **3b** (590 mg, 2.5 mmol) was refluxed with NaOMe in MeOH for 24 hr under N_2 to yield 572 mg of yellow gum. Chromatography of the crude product on alumina (40 g) gave 458 mg (84%) of pale yellow gum which was pure **2b** by nmr analysis. Similar results were obtained on refluxing **3b** wth 0.1 *M* NaOEt in EtOH for 4 hr. The allylide **3b** also gave **2b** when refluxed overnight in $CHCl_3$ in the absence of a basic catalyst.

Method C. Condensation of acetylenic ketone **1f** with dimethyloxosulfonium methylide as described for **1b** (see method A) afforded the 1-oxide **2b** in 60% yield as determined by nmr assay of the crude product before chromatography.

1-Methyl-3-phenyl-5-*tert*-butylthiabenzene 1-Oxide (2c). Method A. A solution of 1-phenyl-4,4-dimethyl-1-pentyn-2-one (**1c**) (8.38 g, 0.045 mol) in anhydrous DMSO (20 ml) was injected during 20 sec into a stirred solution of dimethyloxosulfonium methylide (0.099 mol) in DMSO at room temperature. After the yellow reaction mixture was stirred for 17 hr at room temperature, and an additional 1.5 hr at 70°, it was then poured into ice water (100 ml) yielding a small amount of precipitate. The entire suspension was extracted thoroughly with $CHCl_3$, and the combined extracts were washed with H_2O and saturated NH_4Cl solution and dried ($MgSO_4$). Evaporation of the solvent under vacuum at 45° gave 12.7 g of yellow oil. The oil was dissolved in 1:1 Et_2O–petroleum ether (100 ml) and cooled in a Dry Ice–acetone bath yielding 8.83 g (75.5%) of **2c** as fine yellow needles, mp 92.0–94.0°. Recrystallization from petroleum ether (bp 73–75°)–EtOAc gave 7.34 g (three crops, 62.8%) of white needles, mp 97.0–101.0° (first crop). An analytical sample of **2c** was prepared by chromatography (Florisil): mp 97.9–99.6° dec; ir ($CHCl_3$) 1520, 1491, 1370, 1225, 1130, 695, and 640 cm^{-1}; uv max (EtOH) 351 (ϵ 7700), 248 (ϵ 13,400), 222 (ϵ 11,200) [sh]), and 212 nm (ϵ 17,500); uv max (12 *N* HCl–EtOH [1:4]), 320 (ϵ 8800, very broad) and 225 nm (ϵ 10,300); nmr ($CDCl_3$) δ 1.29 (s, 9), 3.44 (s, 3), AB portion of an ABX pattern with doublets (of doublets) centered at δ 5.23 and 5.79 (J = 4.2 Hz, 1.2 Hz), 5.91 (t, 1, J = 1.2 Hz), and 7.18–7.53 ppm (m, 5); nmr (CD_3COOD) δ 1.28 (s, 9), 3.62 (s, 3), 5.7 (s [br], ~0.2), 6.1 (s [br], ~0.1), 7.23–7.65 (m, 5), and 10.94 ppm (s, 3).

Anal. Calcd for $C_{16}H_{20}OS$: C, 73.80; H, 7.74; S, 12.31. Found: C, 73.79; H, 7.63; S, 12.25.

Method B. Allylide **3c** was completely converted to **2c** upon heating a solution of **3c** in $CHCl_3$ at reflux for 36 hr; only partial conversion had taken place after 16 hr (nmr analysis).

1-Methyl-3,5-diethylthiabenzene 1-Oxide (2d). A solution of 4-heptyn-3-one (**1d**) (4.40 g, 0.040 mol) in anhydrous DMSO (10 ml) was injected into a stirring solution of dimethyloxosulfonium methylide (0.088 mol) in DMSO (150 ml) at room temperature. The red-orange reaction mixture was stirred for 3.5 hr at room temperature and an additional 3.2 hr at 45°, and then poured into ice water. The orange solution was thoroughly extracted (CH_2Cl_2); the organic extracts were washed with H_2O and saturated NaCl solution and dried ($MgSO_4$). Evaporation of the solvent under vacuum at room temperature gave 6.9 g of semicrystalline material. Crystallization from petroleum ether yielded 2.81 g (38%) of **2d** as pale yellow plates, mp 80.8–82.0°. Concentration of the mother liquors gave a yellow oil (3.9 g) which was applied to a column of Woelm neutral alumina (90 g, activity grade 1) packed in 1:1 benzene–petroleum ether. Elution with benzene containing increasing percentages of $CHCl_3$ yielded an additional 0.94 g (13%) of crystalline product. Several recrystallizations from petroleum ether afforded an analytical sample of **2d** as fine white needles: mp 86.7–87.3°; ir ($CHCl_3$) 1533, 1460, 1405, 1311, 1185, 1124, and 642 cm^{-1}; uv max (EtOH) 335 (ϵ 7700), 248 (ϵ 3100 [sh]), 237 (ϵ 4400 [sh]), and 214 nm (ϵ 19,900); uv max (12 *N* HCl–EtOH [1:4]) 330 and 227 nm; nmr ($CDCl_3$) δ 1.18 (t, 6, J = 7.5 Hz), 2.36 (q, 4, J = 7.5 Hz), 3.32 (s, 3), 5.18 (s [br], 2), and 5.32 ppm (s [br], 1); nmr (10% w/v in 1:1 CD_3COOD–$CDCl_3$) δ 1.17 (t, 6, J = 7.5 Hz), 2.42 (q, 4, J = 7.5 Hz), 3.50 (s, 3), 5.37 (s [br], ~0.2), 5.53 ([br], ~0.2), and 10.97 ppm (s, 2.7).

Anal. Calcd for $C_{10}H_{16}OS$: C, 65.17; H, 8.75; S, 17.40. Found: C, 65.35; H, 8.87; S, 17.20.

1,3,5-Trimethylthiabenzene 1-Oxide (2e). A solution of 3-pentyn-2-one (**1e**) (4.1 g, 0.05 mol) in DMSO (10 ml) was injected during 6 min into a solution of dimethyloxosulfonium methylide (0.08 mol) in DMSO (170 ml) at 20° and under N_2. The reaction mixture was stirred at ambient temperature for 4 hr and then poured into H_2O. The resulting mixture was thoroughly extracted with CH_2Cl_2; the extract was washed with H_2O and saturated NaCl solution, dried ($MgSO_4$), and concentrated giving 4.0 g of a red-orange oil. The oil was chromatographed on 175 g of alumina (Woelm, neutral, activity grade 1) packed wet in 1:1 benzene–petroleum ether. Fractions eluted with increasing percentages of chloroform in benzene gave 1.7 g (22%) of **2e** as yellow flakes. Recrystallization from petroleum ether containing a trace of EtOAc afforded 1.3 g (17%) of **2e** as pale yellow prisms: mp 70.3–72.0°; second crop, 0.4 g (4.5%), mp 68.1–69.7°. An analytical sample had mp 70.4–71.0°; ir ($CHCl_3$) 3010, 2920, 1530, 1440, 1392, 1305, 1218, 1125, 1025, 965, 860, 645, and 635 cm^{-1}; uv max (MeOH) 333 (ϵ 7000), 245 (ϵ 4250), and 221 nm (ϵ 5900); nmr ($CDCl_3$) δ 2.12 (s, 6), 3.41 (s, 3), 5.30 (s [br], 1), and 5.47 ppm (s [br], 1); nmr (0.07 ml of CD_3COOD added to 10% w/v of **2e** in $CDCl_3$) δ 2.12 (s, 6), 3.45 (s, 3), 5.32 (s [br], ~1.0), 5.49 (s [br], ~0.5), and 10.54 ppm (s [br], ~1.7).

Anal. Calcd for $C_8H_{12}OS$: C, 61.52; H, 7.74; S, 20.49. Found: C, 61.31; H, 7.78; S, 20.56.

Dimethyloxosulfonium 3-Benzoyl-2-phenylallylide (3a). A solution of 1,3-diphenyl-2-propyn-1-one (**1a**) (6.13 g, 0.03 mol) in anhydrous THF (30 ml) was injected during 6 min into a solution of dimethyloxosulfonium methylide (0.03 mol) in a 4:1 mixture of THF–DMSO (300 ml) which was cooled to −8°. The reaction mixture was stirred for 2 hr and then poured into H_2O (150 ml) and CH_2Cl_2 (100 ml). The aqueous layer was extracted with additional CH_2Cl_2 (100 ml) and the combined organic extracts were washed with cold H_2O and cold saturated NaCl solution and dried ($MgSO_4$). Evaporation of the solvent under vacuum at room temperature left a yellow semicrystalline material which was triturated with Et_2O and filtered, yielding 5.78 g (65.6%) of **3a** as a yellow powder, mp 138.4–139.3°. The product was dissolved in a minimum amount of CH_2Cl_2, petroleum ether was added to the cloud point, and the flask was cooled. In this manner, three crops (5.65 g or 63%) of **3a** were obtained as yellow needles, mp 142.5–143.9° (first crop). An analytical sample was obtained by further recrystallization from CH_2Cl_2–petroleum ether: mp 145.4–147.0°;

ir ($CHCl_3$) 1594, 1584, 1560, 1505, 1475, 1450, 1412, 1170, 1019, and 890 cm^{-1}; uv max (EtOH) 402 (ε 22,200), 251 (ε 15,900), and 209 nm (ε 20,100); uv max (EtOH–10% aqueous HCl [3:2]) 300 (ε 15,500) and 242 nm (ε 8900); nmr ($CDCl_3$) δ 3.02 (s, 6), 5.88 (s, 1), 7.22–7.67 (m, 9), and 7.83–8.00 ppm (m, 2).

Anal. Calcd for $C_{18}H_{18}O_2S$: C, 72.45; H, 6.08; S, 10.75. Found: C, 72.74; H, 6.15; S, 11.00.

Dimethyloxosulfonium 3-Benzoyl-2-methylallylide (3b). 1-Phenyl-2-butyn-1-one (**1b**) (5.8 g, 0.04 mol) was added neat during 1 min to a solution of dimethyloxosulfonium methylide (0.09 mol) in a mixture of 4:1 DMSO–THF (100 ml) at 2° and under N_2. The resulting red mixture was stirred for 1.25 hr at 10–20°, and then an aliquot (50 ml) was removed *via* syringe and injected into ice water. The aqueous solution was extracted with cold CH_2Cl_2 and the organic extract was washed with H_2O and dried ($MgSO_4$). Removal of the solvent under vacuum at room temperature gave an orange oil which crystallized upon trituration with CCl_4. The yellow solid was collected and washed with Et_2O–petroleum ether affording 2.8 g (60%) of **3b** as a yellow powder, mp 131.3–134.3°. The remaining 50 ml of the reaction mixture was worked up in the same manner after 24 hr yielding 3.2 g (69%) of **3b**, mp 129.3–131.3°. An analytical sample, obtained after several recrystallizations from CH_2Cl_2–petroleum ether (cold), had mp 142.9–143.6°; ir ($CHCl_3$) 1594, 1584, 1560, 1500, 1482, 1412, 1264, 1171, 1018, 980, 920, 855, and 690 cm^{-1}; uv max (EtOH) 395 (ε 22,200), 250 (ε 8000), and 212 nm (ε 13,900); uv max of a solution of **3b** in 3.3 ml of EtOH containing 4 drops of 10% HCl appeared at 350 (ε 1250), 262 (ε 10,800), and 212 nm (ε 10,500); nmr ($CDCl_3$) δ 2.24 (s, 3), 3.30 (s, 6), 5.85 (s, 1), 7.17–7.48 (m, 4), and 7.64–7.98 ppm (m, 2).

Anal. Calcd for $C_{13}H_{16}O_2S$: C, 66.07; H, 6.82; S, 13.57. Found: C, 66.19; H, 6.65; S, 13.60.

Dimethyloxosulfonium 3-Pivaloyl-2-phenylallylide (3c). A solution of 1-phenyl-4,4-dimethyl-1-pentyn-3-one (**1c**) (3.7 g, 0.02 mol) in DMSO (10 ml) was injected during 1.5 min into a solution of dimethyloxosulfonium methylide (0.03 mol) in 5:1 DMSO–THF (180 ml) at 10°. The pale yellow mixture was stirred for 1.25 hr at 11–14° and then poured into 150 g of crushed ice. Water was added to the slurry, and the white precipitate was collected and washed with H_2O yielding 4.6 g (83%) of **3c** as a pale yellow powder. A portion (2.6 g) of the crude material was recrystallized by dissolving the material in a minimum amount of methylene chloride, treating with charcoal, and adding petroleum ether to the cloud point; the yield of pale yellow needles was 2.3 g, mp 148.4–150.6°. An analytical sample of **3c** was obtained as white needles, mp 157.4–158.4°, after several recrystallizations from the same solvent mixture: ir ($CHCl_3$) 1597, 1464, 1405, 1153, 1070, and 950 cm^{-1}; uv max (EtOH) 353 (ε 7900), 249 (ε 14,000), and 213 nm (ε 17,400); uv max (EtOH–12 *N* HCl [3:2]), 322 (very br) and 224 nm; nmr ($CDCl_3$) δ 1.13 (s, 9), 2.98 (s, 6), 5.38 (s, 1), 7.13 (s, 1), and 7.30–7.65 ppm (m, 5).

Anal. Calcd for $C_{16}H_{20}O_2S$: C, 69.02; H, 7.96; S, 11.51. Found: C, 68.95; H, 7.95; S, 11.68.

A solution of **3c** in THF was treated with D_2O followed by removal of the solvent mixture *in vacuo*. Nearly complete loss of absorption at δ 7.13 (H-1) and 2.98 ($S-CH_3$) and partial loss of absorption at δ 5.38 (H-3) was observed in a spectrum of the residue dissolved in $CDCl_3$.

1-Ethyl-3,5-diphenylthiabenzene 1-Oxide (6a). To a solution of 1-methyl-3,5-diphenylthiabenzene 1-oxide (**2a**) (1.7 g, 0.006 mol) in anhydrous THF (30 ml) at 0° and under N_2 was added *tert*-butyllithium (1.24 *M*, 4.84 ml) in pentane. The orange reaction mixture was stirred for 30 min at 0° and then treated with CH_3I (4.3 g, 0.03 mol). The resulting yellow reaction mixture was stirred overnight at room temperature and then poured into H_2O and extracted with CH_2Cl_2. The organic extracts were washed with H_2O and saturated NaCl solution, and dried ($MgSO_4$). The solvent was removed under vacuum leaving 1.8 g of yellow solid. Nmr analysis showed the material to be composed of 80% *S*-ethyl, 11% *S*-isopropyl, and 7% *S*-methyl derivatives. The crude material was recrystallized from 1:4 EtOAc–petroleum ether giving 1.33 g (76%) of yellow needles which contained a 16:1 ratio of *S*-ethyl to other *S*-alkyl derivatives (nmr analysis). Several recrystallizations from the same solvent pair and two recrystallizations from ethyl acetate gave **6a**, mp 180.6–182.4°, which contained only traces of the *S*-methyl compound.

A mixture (415 mg) of 1-alkyl-3,5-diphenylthiabenzene 1-oxides obtained from a similar preparation was carefully chromatographed on 50 g of alumina (Woelm, neutral, activity grade 1) packed wet in 1:1 benzene–petroleum ether. Recrystallization of **6a** obtained in this manner gave an analytical sample: mp 181.5–182.8°; ir ($CHCl_3$) 1525, 1489, 1373, 1125, 699, and 649 cm^{-1}; uv max (EtOH) 366 (ε 10,000), 240 (ε 28,800), and 210 nm (ε 30,000); nmr ($CDCl_3$) δ 1.27 (t, 3, J = 7.5 Hz), 3.58 (q, 2, J = 7.5 Hz), 5.57 (d, 2, $J \simeq$ 1.2 Hz), 6.25 (t, 1, J = 1.2 Hz), and 7.20–7.80 ppm (m, 10).

Anal. Calcd for $C_{19}H_{18}OS$: C, 77.51; H, 6.16; S, 10.89. Found: C, 77.47; H, 6.31; S, 10.73.

1-Isopropyl-3,5-diphenylthiabenzene 1-Oxide (6b). A solution of *tert*-butyllithium (1.24 *M*, 0.6 ml) in pentane was added at room temperature to a solution of 1-ethyl-3,5-diphenylthiabenzene 1-oxide (95% pure; 200 mg, 0.68 mmol) in anhydrous tetrahydrofuran (15 ml) under N_2. The orange reaction mixture was refluxed for 30 min and then treated with purified CH_3I (4.68 g, 0.022 mol). The resulting yellow reaction mixture was refluxed for an additional 30 min, cooled, poured into H_2O, and extracted with CH_2Cl_2. The extract was washed with saturated NaCl solution, dried (Na_2SO_4), and evaporated under vacuum to leave 0.260 g of a yellow-brown solid containing 80% of **6b** by nmr analysis. Recrystallization from ethyl acetate gave 110 mg (52%) of the *S*-isopropyl derivative **6b** containing a small amount of the *S*-ethyl compound (**6a**). An analytical sample of **6b** was prepared by chromatographing the 110-mg crop on 15 g of alumina (Woelm, neutral, activity grade 1) packed wet in 1:1 benzene–petroleum ether. Continuous elution of the column with the same solvent mixture gave 75 mg of pure **6b** which, after recrystallization from ethyl acetate, had mp 181.5–182.4°; ir ($CHCl_3$) 3058, 2930, 1600, 1580, 1324, 1288, 1256, 1122, 698, and 648 cm^{-1}; uv max (EtOH) 370 (ε 9700), 243 (ε 26,800), and 212 nm (ε 31,000); nmr ($CDCl_3$) δ 1.41 (d, 6, J = 7.0 Hz), 3.65 (heptet, 1, J = 7.0 Hz), 5.53 (d, 2, J = 1.3 Hz), 6.23 (t, 1, J = 1.3 Hz), and 7.22–7.83 ppm (m, 10).

Anal. Calcd for $C_{20}H_{20}OS$: C, 77.88; H, 6.54; S, 10.40. Found: C, 77.83; H, 6.58; S, 10.33.

1-Carboethoxymethyl-3,5-diphenylthiabenzene 1-Oxide (7). The anion of **2a** (2 mmol) was generated as described in the preparation of **6a**. Treatment of the reaction mixture with diethyl carbonate (20 mmol) followed by a normal work-up afforded 460 mg of orange oil containing **2a** and **7** in a ratio of *ca.* 1:1 (nmr analysis). The carboethoxy compound **7** exhibited characteristic nmr (CCl_4) signals at δ 1.13 (t, 3, J = 7.2 Hz), 4.08 (q, 2, J = 7.2 Hz), 4.38 (s, 2), 5.75 (d, 2, J = 1.2 Hz), and 6.12 ppm (t, 1, J = 1.2 Hz).

2,3-Dibromo-1-cyclooctene and 1,3-Dibromo-1-cyclooctene. Distilled 1-bromocyclooctene (120.0 g, 0.639 mol), prepared in 66% overall yield *via* bromination of cyclooctene[59] followed by treatment of the distilled product with KOH in refluxing 2-butanol,[60] was combined with *N*-bromosuccinimide (124.4 g, 0.699 mol), benzoyl peroxide (1.0 g), and CCl_4 (1.0 l.) in a 2-l. flask. The mixture was placed under N_2 and heated on a steam bath; after the initial exothermic reaction subsided (*ca.* 15 min), the resulting suspension was refluxed for 45 min, cooled, and filtered. The filtrate was washed with H_2O, saturated $NaHSO_3$, $NaHCO_3$, and NaCl solutions and dried (Na_2SO_4). Evaporation of the solvent under vacuum at 45° left 171.5 g (86.2%) of viscous yellow oil, which contained a 1:4 ratio of 2,3-dibromo- to 1,3-dibromocyclooctene by nmr analysis. The isomers could not be readily separated by distillation using a 24-in. spinning band column (Nester–Faust), and therefore the mixture was used in the preparation of 1-bromo-3-hydroxy-1-cyclooctene without further purification or separation of isomers. The nmr spectrum of the product mixture exhibited low-field multiplets (1 H each) for the 2,3-dibromo compound at δ 5.10 (dd, J = 6 Hz, J = 10 Hz) and 6.18 ppm (t, J = 6 Hz) and for the 1,3-dibromo compound at δ 4.67 (ddd, J = 10 Hz, J = 8.8 Hz, J = 5.5 Hz) and 6.18 ppm (d, J = 8.8 Hz).

1-Bromo-3-hydroxy-1-cyclooctene. The 1:4 mixture of 1,3-dibromo- and 2,3-dibromo-1-cyclooctenes (75.0 g, 0.280 mol), $NaHCO_3$ (41.4 g, 0.560 mol), acetone (450 ml), and H_2O (250 ml) were refluxed for 1.5 hr. The mixture was cooled, diluted with H_2O (300 ml), and extracted with Et_2O (900 ml). The extract was washed with H_2O and saturated NaCl solution and dried ($MgSO_4$). The solution was concentrated under vacuum leaving 59.5 g of clear yellow oil which contained 65% or the desired alcohol and 15% of 2,3-dibromo-1-cyclooctene by nmr analysis. Attempts to separate the compounds efficiently by distillation under vacuum were unsuccessful. The alcohol and dibromo compound were separated by chromatography on alumina (230 g, Alcoa, F-20

(59) A. C. Cope and G. W. Wood, *J. Amer Chem. Soc.*, **79**, 3885 (1957).

(60) L. I. Zakharkin and G. G. Zhigareva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **8**, 1402 (1965); *Chem. Abstr.*, **63**, 16206*d* (1965).

grade) and the alcohol (obtained in the later fractions) was distilled under vacuum yielding 17.8 g (47% recovery) of colorless, viscous oil, bp 107° (1.8 mm). Redistillation of a portion of the product yielded an analytical sample of the bromo alcohol: bp 107° (1.8 mm); ir (CCl_4) 3300 and 1655 cm^{-1}; nmr (CCl_4) δ 1.1–2.2 (m, 10), 4.36 (s [superimposed on a broad m], 2), and 5.86 ppm (d, 1, J = 7.0 Hz).

Anal. Calcd for $C_8H_{13}BrO$: C, 46.85; H, 6.39; Br, 38.96. Found: C, 46.89; H, 6.61; Br, 38.92.

Treatment of the alcohol with Jones–Weedon oxidant[52] gave 3-bromo-2-cycloocten-1-one which underwent isomerization to the β,γ olefinic ketone on distillation at reduced pressure.[61] Distillation (evaporative-still) at <0.1 mm afforded nearly pure 3-bromo-2-cycloocten-1-one [nmr (CCl_4) δ 6.34 (s, 1)] which contained about 5% of minor impurities by nmr analysis.

2,4-Diphenyl-1,4-pentadienyl Methyl Sulfoxide (12) or 2,4-Dienyl Isomer (11). Method A. By Catalytic Hydrogenation of 2a. A suspension of 10% palladium on charcoal (0.5 g) in absolute ethanol (15 ml) was prereduced under hydrogen, and a solution of **2a** (0.73 g, 0.0026 mol) in ethanol (35 ml) was added to the suspension of the prereduced catalyst. The reduction was stopped after uptake of 1 mol equiv of hydrogen had occurred. The catalyst was removed by filtration and the ethanol evaporated under vacuum, leaving 0.76 g of pale green crystalline solid which was recrystallized from methanol, giving 0.30 g (41%) of **12** (or **11**) as long white needles, mp 117.2–118.2°. An analytical sample had mp 119.2–119.7°; ir ($CHCl_3$) 1492, 1445, 1415, 1405, 1397, 1220, 1130, 910, and 698 cm^{-1}; uv max (MeOH) 252 nm (ϵ 29,700); nmr ($CDCl_3$) δ 2.37 (s, 3), an AB pattern (J = 13 Hz) centered at δ 3.73 and 4.21, 5.51 (t, 1, J = 1.1 Hz), 5.72 (s [br], 1), 6.82 (s [br], 1), and 7.10–7.69 ppm (m, 10).

Anal. Calcd for $C_{18}H_{18}OS$: C, 76.57; H, 6.43; S, 11.33. Found: C, 76.55; H, 6.41; S, 11.33.

Method B. By Reduction of 2a with Zinc in Acetic Acid. A solution of **2a** (4.20 g, 0.015 mol) in glacial acetic acid (30 ml) was added to a suspension of zinc dust (1.96 g, 0.026 g-atom) in glacial acetic acid (20 ml). The reaction mixture was stirred at room temperature for 1.0 hr, $CHCl_3$ was added, and the mixture was filtered. The filtrate was washed with H_2O and saturated $NaHCO_3$ and NaCl solutions, and dried ($MgSO_4$). Evaporation of the solvent under vacuum at room temperature gave 3.88 g (92%) of a pale yellow crystalline solid; recrystallization from $CHCl_3$–petroleum ether yielded 2.94 g (70%) of **12** (or **11**) as long white needles: mp 118.7–121.2°. A second crop amounted to 0.45 g (11%) of a mixture of the starting material and the reduction product.

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(61) *Cf.* N. Heap and G. Whitham, *J. Chem. Soc. B*, 164 (1966).

Synthesis of Cyclobutenone

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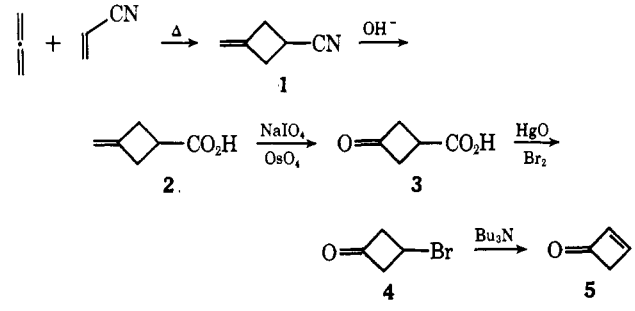
Abstract: Cyclobutenone was prepared from 3-bromo- and 3-chlorocyclobutanone, which were synthesized by independent routes from allene and ketene, respectively.

Cyclobutenone (**5**) has thus far escaped isolation,[1] although numerous examples of substituted cyclobutenones have been reported. We wish to report the synthesis and isolation of **5**, which was obtained by two independent routes, both converging to a 3-halocyclobutanone as the immediate precursor.

3-Bromocyclobutanone. Cyclobutenone was first prepared as shown in Scheme I. Compounds **1**, **2**, and **3** were prepared according to literature methods.[2,3] The precursor **4** was prepared by a modification[4] of the Hunsdiecker reaction. The structure of **4** was proved by spectral and elemental analyses (see Experimental Section). A limitation of Scheme I is the conversion of **2** to **3**, because crude **3** is obtained as a black, water-soluble solid which is difficult to purify. Ozonolysis of **2** would probably be preferable on a small scale.

Scheme I



3-Chlorocyclobutanone. A preferable route to **5** (Scheme II) resulted from our work on the thermal cycloaddition of ketene to vinyl ethers,[5] where **6** was easily prepared in large quantities. Treatment of **6** with carbonyl fluoride[6] gave **7** in quantitative yield. This was converted to **8**, which liberated **9** on hydrolysis. The intermediacy of **8** is based on two facts: (1) glpc showed **9** to be absent in the crude reaction mixture be-

(1) A. C. Cope, S. F. Schaeren, and E. R. Trumbull, *J. Amer. Chem. Soc.*, **76**, 1096 (1954); E. Vogel and K. Hasse, *Justus Liebigs Ann. Chem.*, **615**, 22 (1958); E. F. Silversmith, Y. Kithara, and J. D. Roberts, *J. Amer. Chem. Soc.*, **80**, 4088 (1958).

(2) H. N. Cripps, J. K. Williams, and W. H. Sharkey, *ibid.*, **81**, 2723 (1959).

(3) J. D. Roberts and F. F. Caserio, *ibid.*, **80**, 5837 (1958).

(4) S. J. Cristol and C. W. Firth, Jr., *J. Org. Chem.*, **26**, 280 (1961).

(5) J. B. Sieja, *J. Amer. Chem. Soc.*, **93**, 130 (1971).

(6) F. S. Fawcett, C. W. Tullock, and D. D. Coffman, *ibid.*, **84**, 4275 (1962).