tion describes the synthesis of the fourth compound, stibabenzene (antimonin) (**4**).

1,4-Dihydro-1,1-dibutylstannabenzene (**6**)[3] and antimony trichloride reacted exothermally in a THF solution. Distillation gave a waxy crystalline mixture of dibutyltin dichloride (**7**) and 1,4-dihydro-1-chlorostibabenzene (**8**). Recrystallization from heptane afforded pure **8**, mp 115–117° dec. The pmr spectrum[4] ($CDCl_3$) showed a two-proton diallylic multiplet at τ 6.6 and the four vinylic protons as an AB pattern (J_{AB} = 13 Hz) at 3.5 and 3.1 [each peak was split into a triplet (J_{AC} = 3.5 Hz and J_{BC} = 2 Hz, respectively)]. It is convenient to treat a solution of the crude mixture of **7** and **8** in tetraglyme with 1,5-diazabicyclo[4.3.0]non-5-ene to produce stibabenzene. Compound **4** may be isolated by vacuum distillation into a Dry Ice cooled receiver. Stibabenzene is an extremely labile compound and rapidly polymerizes to an intractable brown tar at −80°. Handling appears most convenient in a dilute solution under an inert atmosphere although even these solutions slowly precipitate the brown polymer.

The pmr spectrum of stibabenzene in Figure 1 shows the characteristic pattern of the group V heteroaromatics. The α protons occur as a doublet (J = 11 Hz) at extremely low field while the β and γ protons are in the normal aromatic region. The chemical shift of the α protons is τ 1.9 for pyridine, 1.4 for phosphabenzene, 0.7 for arsabenzene, and −0.7 for stibabenzene. This progressive shift to lower field can probably be associated with the magnetic anisotropy of the increasing large heteroatom.[5] This effect should be attenuated for the more remote β and γ protons and indeed chemical-shift values of these protons do not vary greatly for **1**, **2**, **3**, and **4**. These low-field chemical-shift values are consistent with an appreciable ring current for **1**, **2**, **3**, and **4**.[6]

The mass spectrum of stibabenzene (Table I) like that of **1**, **2**, and **3** shows the molecular ion as the base peak. Also, like **1**, **2**, and **3**, as well as benzene,[7] stibabenzene shows significant fragmentation by loss of acetylene. However, there are some important differences as well. Stibabenzene shows large peaks due to the metal atom[8] as well as from loss of the metal atom.

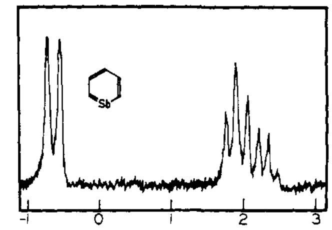


Figure 1. Proton magnetic resonance spectrum of stibabenzene. The spectrum was determined at 60 MHz. τ values are in parts per million relative to internal TMS.

Table I. Mass Spectrum of Stibabenzene Showing Major Ions and Their Relative Abundances[a]

Ion (*m*/*e*)	Rel abundance	Assignment
188	65	$(C_5H_5{}^{123}Sb)^+$
186	100	$(C_5H_5{}^{121}Sb)^+$
162	9	$(P - C_2H_2)^+$
160	16	$(P - C_2H_2)^+$
123	17.5	$({}^{123}Sb)^+$
121	27	$({}^{121}Sb)^+$
65	95	$(P - Sb)^+$
39	95	$(C_3H_3)^+$

[a] The mass spectra were determined on an MS-9 spectrometer at 45 eV using a gas inlet.

The uv spectrum of stibabenzene (cyclohexane) has intense bands at 236 and 312 mμ.[9] These appear to correspond to the intense bands in the spectra of phosphabenzene at 213 and 246 mμ and of arsabenzene at 219 and 268 mμ. If these bands are due to $\pi \rightarrow \pi^*$ transitions, they can be associated with a smaller separation of the bonding and the antibonding energy levels for the heavier heteroaromatics and hence to weaker bonding in stibabenzene relative to arsabenzene and phosphabenzene.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research (Grant No. 5241-AC3-4) and also the National Science Foundation for a grant (GP-8345) to the University of Michigan for the purchase of an MS-9 mass spectrometer. Thanks are also due to Miss Joann Schmidt for help in preparing compound **6**.

Arthur J. Ashe, III
Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48104

Received September 2, 1971

---

(3) A. J. Ashe, III, and P. Shu, *J. Amer. Chem. Soc.*, **93**, 1804 (1971).

(4) The pmr spectra were taken in dilute solutions of the indicated solvent using TMS as an internal standard. They were recorded using a Varian T-60 instrument. The mass spectra were taken on an AEI Model MS-9 spectrometer at 45 eV using a gas inlet. The uv spectra were recorded in cyclohexane using balanced 1-cm cells on a Cary-14 spectrometer.

(5) For pyridine see: J. D. Baldeschwieler and E. W. Randall, *Proc. Chem. Soc., London*, 303 (1961).

(6) J. A. Elvidge and L. M. Jackman, *J. Chem. Soc.*, 859 (1961), and for a brief summary see G. M. Badger, "Aromatic Character and Aromaticity," Cambridge University Press, Cambridge, England, 1969, pp 61–70.

(7) E. Stenhagen, S. Abrahamsson, and F. W. McLafferty, "Atlas of Mass Spectral Data," Vol. 1, Interscience, New York, N. Y., 1969, p 101, 102.

(8) There are few reported mass spectra of stibines for comparison. However, trimethylstibine also shows a large antimony peak: R. E. Winter and R. W. Kiser, *J. Organometal. Chem.*, 10, 7 (1967).

(9) The extinction coefficients for these bands are approximately 10^4. The facile polymerization of **4** makes an exact determination of ϵ difficult.

Nature of Sulfur Species in Fused Salt Solutions[1]

Sir:

A brilliant blue color develops in liquid potassium thiocyanate when it is heated above 300°.[2] Liquid LiCl-KCl eutectic in contact with sulfur also acquires a deep blue coloration.[3] Absorption spectra of the blue thiocyanate and alkali halide melts were found to be virtually identical and the band at 17,000 cm^{-1} giving rise to the blue color was originally thought to be due to a neutral sulfur species, possibly S_2 molecules.[3,4]

By combining electrochemical with spectrophotometric measurements, Bodewig and Plambeck[5] were

---

(1) Work performed under the auspices of the U. S. Atomic Energy Commission and the Environmental Protection Agency.

(2) (a) C. Nöllner, *Pogg. Ann.*, **98**, 189 (1856); (b) E. Paternò and A. Mazzuchelli, *Gazz. Chim. Ital.*, **38**, 137 (1908).

(3) J. Greenberg, B. R. Sundheim, and D. M. Gruen, *J. Chem. Phys.*, **29**, 461 (1958).

(4) H. Lux and H. Anslinger, *Chem. Ber.*, **94**, 1161 (1961).

(5) F. G. Bodewig and J. A. Plambeck, *J. Electrochem. Soc.*, **116**, 607 (1969); 117, 904 (1970).

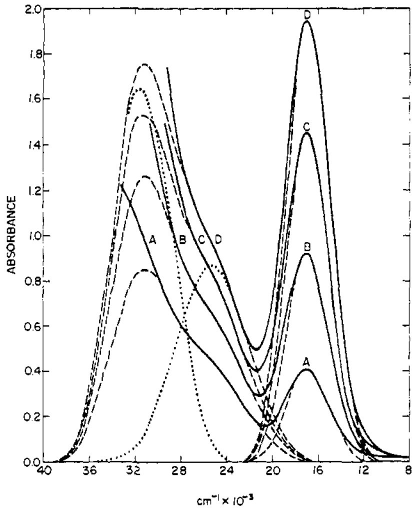


Figure 1. Absorption spectra, taken in 1-cm path-length silica cells, of sulfur species in LiCl–KCl eutectic at 600°; total concentration of $[S^{2-}] = 3.34 \times 10^{-3}$ *M*, partial pressure of S_2 above the melt calculated from the sulfur vapor pressure equation and the data on sulfur vapor species in D. Detry, J. Drowart, P. Goldfinger, H. Keller, and H. Rickert, *Z. Phys. Chem. (Frankfurt am Main)*, **55**, 314 (1967): (A) S_2 pressure, 1.7; (B) S_2 pressure, 4.4; (C) S_2 pressure, 7.3; (D) S_2 pressure, 11.0 mm.

able to show that sulfide ion and elemental sulfur must be present simultaneously to produce the blue color and ascribed its origin to a polysulfide species, S_x^{2-}. More recently,[6] the 17,000-cm⁻¹ band was assigned to the S_2^- ion, while a band at 25,000 cm⁻¹ was assigned to a polysulfide species in potassium thiocyanate melts.

To elucidate the stoichiometries and stabilities of the sulfur species involved in the production of color in salt melts, it is clearly necessary to study the relevant equilibria as a function of sulfide ion concentration and of sulfur pressure. Consequently, we are measuring the absorption spectra of LiCl–KCl solutions containing known and variable amounts of sulfide ion in a silica apparatus which allows equilibraton of the eutectic solutions with sulfur vapor at known and variable pressures. Furthermore, the temperature of the eutectic can be varied independently of the S^{2-} concentration and the sulfur pressure.

We communicate results on this system early because of their importance to an understanding of the chemistry of sulfur in fused salts. Furthermore, these results have a bearing on solid-state studies of sulfur species doped into alkali halide lattices[7,8] and on the elucidation of the color principle in ultramarine blues.[9]

A typical series of spectra from which the contributions to the absorbances due to LiCl–KCl eutectic solvent and to sulfide ion have been subtracted are shown in Figure 1. The sulfide ion absorption spectrum, measured in separate experiments, has an intense absorption edge at 34,000 cm⁻¹ but makes only a very minor contribution to the total absorbance at energies below 32,000 cm⁻¹. The spectrum of dissolved S_2, also measured in separate experiments, has its maximum at 36,000 cm⁻¹, close to the absorption peak of gaseous S_2 molecules. The tail of the dissolved elemental S_2 absorption band extends to 28,000 cm⁻¹ and is almost entirely responsible for the absorbance in excess of that indicated by the dashed curves in Figure 1 at energies higher than 28,000 cm⁻¹. The spectra shown in Figure 1 are characterized by the following features: (1) a broad complex absorption band (high-energy band) which can be resolved into two Gaussians (dotted curves) with maxima at 31,440 and 25,640 cm⁻¹ and half-widths of 6320 and 7520 cm⁻¹, respectively (the positions and half-widths of the two Gaussians remain unchanged in going from curve A to curve D, showing that a single species gives rise to this complex absorption band) and (2) a band (low-energy band) which is well represented by a single Gaussian with maximum at 16,800 cm⁻¹ and half-width of 4640 cm⁻¹.

It will be noted that the absorbance of the low-energy band increases a factor 2.5 relative to that of the high-energy band in going from low to high sulfur pressures, showing that the two bands are due to two different species. In analyzing the data, we have taken the absorbance values at 26,000 and 16,800 cm⁻¹ as proportional to the concentrations of the two species. We have considered a number of possible reactions but limit the present discussion to the three equilibria

$$2S^{2-} + S_2 = 2S_2^{2-} \qquad (1)$$

$$2S^{2-} + 3S_2 = 4S_2^{-} \qquad (2)$$

$$2S^{2-} + 5S_2 = 4S_3^{-} \qquad (3)$$

If one assigns the low-energy band to the species S_2^- or S_3^- and the high-energy band to the polysulfide species, S_2^{2-}, then it can be shown that a plot of log $[(A_{16,800})^2/A_{26,000}]$ *vs.* log P_{S_2} is a straight line with a slope of 1 or 2, respectively. Our data points plotted according to this expression lie on a least-squares straight line with slope 1.3.

On the other hand, assigning the low-energy band to S_3^- and the high-energy band to the supersulfide ion, S_2^-, implies that a plot of 2 log $[A_{16,800}/A_{26,000}]$ *vs.* log P_{S_2} is a straight line with a slope of unity. Our data obtained as a function of sulfur vapor pressure at 600, 700, and 800° eutectic temperatures when plotted in this way lie on straight lines with slopes equal to 0.90 ± 0.2. Our data, therefore, are best fitted by equilibria 2 and 3 rather than 1 and 2 or 1 and 3.

These results are particularly significant in view of recent epr,[10,11] endor,[12] Raman,[13,14] and ir measurements[9] which have identified the S_3^- ion not only in sulfur-doped alkali halides but also in synthetic ultramarines.[11,13] Interestingly, the intensity of the S_3^- Raman band at 594 cm⁻¹ in sulfur-doped KI crystals was found to increase the more closely the wavelength of the exciting laser radiation was made to approach the S_3^- absorption band centered at 17,000 cm⁻¹.[13,14]

As in the case of the epr spectral parameters,[10,11] so the characteristics of the optical spectrum of the S_3^- ion appear to be closely similar in alkali halide crystals and

---

(6) W. Giggenbach, *Inorg. Chem.*, 10, 1308 (1971).

(7) J. H. Schulman and R. D. Kirk, *Solid State Commun.*, 2, 105 (1964).

(8) L. E. Vanotti and J. R. Morton, *Phys. Rev.*, 161, 282 (1967).

(9) U. Hofmann, E. Herzenstiel, E. Schonemann, and K. H. Schwarz, *Z. Anorg. Allg. Chem.*, 367, 119 (1969).

(10) L. Schneider, B. Dischler, and A. Rauber, *Phys. Status Solidi*, 13, 141 (1966).

(11) R. Bottcher, S. Wartewig, W. Windsch, and A. Zschunke, *Z. Naturforsch. A*, 23, 1766 (1968).

(12) J. Suwalski and H. Seidel, *Phys. Status Solidi*, 13, 159 (1966).

(13) W. Holzer, W. F. Murphy, and H. J. Bernstein, *J. Mol. Spectrosc.*, 32, 13 (1969).

(14) W. Holzer, W. F. Murphy, and H. J. Bernstein, *Chem. Phys. Lett.*, 4, 641 (1970).

melts and in ultramarines. The color of ultramarine blue is known to be due to an intense absorption band with maximum at 17,000 cm^{-1}. In the LiCl–KCl eutectic, this band has now been found to have a molar absorptivity in excess of 10^4. The identification of the band as due to the S_3^- ion, based on a quantitative analysis of chemical equilibrium measurements from which the stoichiometry was deduced, strongly supports the suggestion[9,15,16] that this is the sulfur species primarily responsible for the color of ultramarine blue. Furthermore, the identification of the higher energy band in LiCl–KCl eutectic with the S_2^- ion suggests that the absorption feature at 26,000 cm^{-1} in ultramarines[9] is due to the S_2^- species. The oxidation of ultramarine green to ultramarine blue can be rationalized, on the basis of this analysis, as due to an increasing S_3^-/S_2^- ratio in going from the former to the latter pigment.

(15) J. R. Morton, *Proc. Colloq. AMPERE (At. Mol. Etud. Radio Elec.) 1968*, **15**, 299 (1969).

(16) S. D. McLaughlan and D. J. Marshall, *J. Phys. Chem.*, **74**, 1359 (1970).

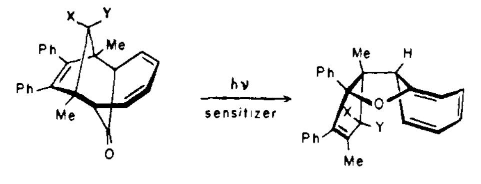
D. M. Gruen,* R. L. McBeth, A. J. Zielen
Chemistry Division, Argonne National Laboratory
Argonne, Illinois 60439
Received August 25, 1971

Photochemistry of Tricyclo[4.4.1.1^{2,5}]dodeca-3,7,9-trienes. I. Selective Photochemically Forbidden Processes

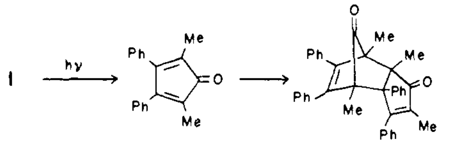
Sir:

Recent interest in the photochemistry of multichromophoric molecules[1] and in the application of orbital symmetry considerations to photochemical reactions[2] prompts us to report a number of new photochemical reactions observed in tricyclo[4.4.1.1^{2,5}]dodeca-3,7,9-triene derivatives.[3–5] Remarkably, the new photochemical reactions reported here are all of the photochemically forbidden variety.[5]

Photolysis of **1** in acetone solution produces **2** (67%) as the only major product.[6a] Similar results were obtained with the sensitizers benzophenone and triphenylene.[6b] By contrast, direct photolysis[6c] of **1** in acetonitrile or methanol solution leads to [6 + 4] photodissociation, as evidenced by formation of the cyclopentadienone dimer, **6** (66%).[7] Thermal dissociation of **1** has also been observed at room temperature at a much slower rate than is observed in the photochemical reaction.

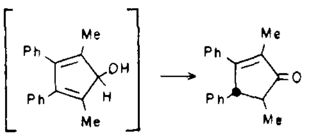


1 (X,Y = O) **2** (X,Y = O)
3 (X = H, Y = OH) **4** (X = H, Y = OH)



5 **6**
+
Tropone

Sensitized photolysis of **3**[6a] produces **4** (45%) as the only major product. Direct photolysis[6c] of **3** produces several unidentified minor products and polymer, but neither the triplet product **4** nor the product expected from dissociation, **8**, are observed in the direct photolysis.[8]



7 **8**

The formal [8 + 2] adduct **2** was previously isolated by Houk and Woodward as a minor product of the thermal reaction of **5** with tropone.[4] At that time the possibility of formation of **2** by either a direct [8 + 2] combination of reactants, or by a [3,3] sigmatropic shift from [6 + 4] adduct **1** was noted. The previously unknown stereochemistry of the tropone–cyclopentadienone fusion has now been resolved by NOE experiments[9] and by chemical evidence. Thus, sodium borohydride reduction of **2** produced alcohol **4**, the result of borohydride attack from the less hindered side of the carbonyl. Chromic anhydride–pyridine oxidation of **4** regenerated **2** quantitatively. Furthermore, heating **4** for 7.5 hr in refluxing benzene solution or in the crystalline state for 3 days at 100° produced **3** in nearly quantitative yield. The intramolecular nature of this [3s,3s] sigmatropic shift is indicated by the stereospecific formation of **3** uncontaminated by epimer and by the absence of competing formation of **8** which would be expected to be the ultimate product of dissociation of **4** in solution.

Both the reverse Claisen rearrangements of **1** to **2** and of **3** to **4** are photochemically forbidden [3s,3s]

---

(1) H. Morrison, J. Pajak, and R. Peiffer, *J. Amer. Chem. Soc.*, **93**, 3978 (1971); H. E. Zimmerman and R. D. McKelvey, *ibid.*, **93**, 3638 (1971); D. O. Cowan and A. A. Baum, *ibid.*, **93**, 1153 (1971), and references therein.

(2) W. van der Lugt and L. J. Oosterhoff, *ibid.*, **91**, 6042 (1969); J. J. C. Mulder and L. J. Oosterhoff, *Chem. Commun.*, 305, 307 (1970); R. C. Dougherty, Southeast–Southwest Regional Meeting, American Chemical Society, New Orleans, La., Dec 2–4, 1970, ORGN 430; L. Salem, *J. Amer. Chem. Soc.*, **91**, 3793 (1969); **90**, 553 (1966); D. Bryce-Smith, *Chem. Commun.*, 806 (1969); J. A. Berson and S. S. Olin, *J. Amer. Chem. Soc.*, **92**, 1086 (1970); W. C. Herndon and J. B. Giles, *Chem. Commun.*, 497 (1969); I. Haller, *J. Chem. Phys.*, **47**, 1117 (1967); H. E. Zimmerman, *Accounts Chem. Res.*, **4**, 272 (1971); K. Fukui, *ibid.*, **4**, 57 (1971); J. Michl, *J. Amer. Chem. Soc.*, **93**, 523 (1971), and references therein.

(3) K. N. Houk and R. B. Woodward, *ibid.*, **92**, 4143 (1970).

(4) K. N. Houk and R. B. Woodward, *ibid.*, **92**, 4145 (1970).

(5) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

(6) $[\lambda_{\max}^{C_6H_{12}}]$: **1**, sh 224 ($\epsilon$ 9600), 250 (ϵ 12,700), sh 268 (ϵ 9600), sh 320 (ϵ 500), sh 335 (ϵ 300); **3**, sh 220 (ϵ 18,500), sh 259 (ϵ 9900), sh 268 nm (ϵ 8200); **10**, sh 229 nm (ϵ 17,000), 269 nm (ϵ 9700); (a) Rayonet RPR reactor, RUL 2537-Å lamps, quartz vessel, 10–20°, $\sim 10^{-3}$ *M* in acetone (absorbing ~95% light); (b) RUL 2537-, 3000-, or 3500-Å lamps, $\sim 10^{-3}$ *M* in acetonitrile containing added sensitizer (absorbing >90% light); (c) RUL 2537-, 3000-, or 3500-Å lamps, $\sim 10^{-3}$ *M*.

(7) C. F. H. Allen and J. Van Allan, *J. Amer. Chem. Soc.*, **64**, 1260 (1942); C. F. H. Allen and J. A. Van Allan, *ibid.*, **72**, 5165 (1950).

(8) Formation of **7** by other methods results in rapid tautomerization to **8**: M. A. Ogliaruso, M. Romanelli, and E. I. Becker, *Chem. Rev.*, **65**, 261 (1965); K. N. Houk, Ph.D. Dissertation, Harvard University, Cambridge, Mass., 1968.

(9) Irradiation of the high-field methyl in **2** results in ~30% enhancement of the intensity of the allylic proton resonance. We thank Professor N. S. Bhacca for carrying out this experiment.