above way, a crude product was obtained which was chromatographed on neutral alumina using benzene as eluent. 1-Benzamido-2,6-dimethylpyridinium N-betaine was obtained as colorless, irregular needles: 1.80 g (43.5%); mp 150°; nmr ($CDCl_3$), τ 7.35 (s, 6, CH_3), 2.55 (m, 5, phenyl), 2.35 2.25 (d, J = 6.00 cps), 2.22, 2.09 (d, J = 6.00), one aromatic proton, and 1.76 (m, 2, aromatic); $\lambda_{max}^{CH_3OH}$, mμ (log ϵ), 206 (4.22), 230 (4.19), 271 (4.10), 306 sh (3.28); mass spectrum (70 eV) m/e (relative intensity), 226 (36), 211 (100), 181 (12), 149 (59.5), 122 (73.5), 107 (70), 105 (52), 93 (45), 77 (96).

Anal. Calcd for $C_{14}H_{14}N_2O$: C, 74.3; H, 6.2; N, 12.3. Found: C, 74.55; H, 6.2; N, 12.3.

1-Benzamido-2,6-dimethylpyridinium chloride (**7**, $R^2 = CH_3$) was prepared by passing dry HCl gas into a methanolic solution of the pyridinium betaine (**6**, $R^2 = CH_3$). The hydrochloride was isolated as colorless, irregular prisms which decomposed over 265°: nmr ($CDCl_3$), τ 7.13 (s, 6, CH_3) and 2.45–1.75 (m, 8, aromatic); the peak due the imino proton could not be discerned in the spectrum; ir (Nujol), 3350 (NH), 1675 cm^{-1} (C=O); $\lambda_{max}^{CH_3OH}$, mμ (log ϵ), 206 (4.38), 230 (4.26), 271 (4.02), 306 sh (3.21).

Anal. Calcd for $C_{14}H_{14}N_2O \cdot HCl$: C, 64.4; H, 5.85; N, 10.65. Found: C, 64.6; H, 5.8; N, 10.5.

The methiodide of 1-benzamido-2,6-dimethylpyridinium N-betaine was also prepared by standard methods using dry acetone as a solvent. The methiodide (**8**) crystallized from methanol-ether as pale yellow needles: mp 203° dec; ir (Nujol), 1660 cm^{-1} (C=O); nmr ($CDCl_3$), τ 7.07 (s, 6, CH_3), 6.00 (s, 3, N–CH_3), 2.35–1.87 (m, 8, aromatic protons).

Anal. Calcd for $C_{15}H_{17}IN_2O$: C, 48.9; H, 4.6; N, 7.6. Found: C, 48.9; H, 4.6; N, 7.4.

1-Benzamido-2-methylpyridinium N-Betaine.—From 1-amino-2-methylpyridinium iodide (9.0 g), pyridine (15 ml), and benzoyl chloride (5.0 ml), allowed to react in the above way, a crude product was obtained which was chromatographed on neutral alumina using benzene as eluent. 1-Benzamido-2-methylpyridinium N-betaine was obtained as colorless needles: 2.30 g (32%); mp 116°; nmr ($CDCl_3$), τ 7.25 (s, 3, CH_3), 2.50 (m, 5, phenyl protons), 2.30, 2.20 (d, 2, J = 6.00 cps), and 1.76 (m, 2), aromatic protons; $\lambda_{max}^{CH_3OH}$, mμ (log ϵ), 202 (4.47), 233 (4.20), 268 (3.91), 313 sh (3.48); mass spectrum (70 eV) m/e (relative intensity), 212 (53), 197 (100), 170 (17.5), 135 (77.5), 107 (35), 105 (43), 93 (70), 77 (62).

Anal. Calcd for $C_{13}H_{12}N_2O$: C, 73.6; H, 5.7; N, 13.2. Found: C, 73.3; H, 5.9; N, 13.6.

1-Benzamido-2-methylpyridinium chloride (**7**, R^2 = H) was prepared as above: mp 208°; ir (Nujol), 3350 (NH), 1660 cm^{-1} (C=O); nmr ($CDCl_3$), τ 7.12 (s, 3, CH_3), 2.41 (m, 5, phenyl protons), 2.06, 1.94 (d, 2, J = 7.00 cps), 1.67 (m, 2) aromatic protons; the peak due to the imino proton was not visible in the spectrum; $\lambda_{max}^{CH_3OH}$, mμ (log ϵ), 202 (4.36), 233 (4.18), 268 (3.96), 313 sh (3.27).

Anal. Calcd for $C_{13}H_{12}N_2O \cdot HCl$: C, 62.8; H, 5.2; N, 11.3. Found: C, 62.6; H, 5.2; N, 11.1.

Registry No.—3-α-Hydroxyethyl-2-methylpyrazolo-[1,5-*a*]pyridine, 17408-41-2; 3-α-hydroxyethyl-2-methylpyrazolo[1,5-*a*]pyridine picrate, 17408-42-3; **6** (R^2 = Me), 17408-43-4; **7** (R^2 = Me), 17408-44-5; **7** (R^2 = H), 17408-46-7; **8**, 17408-45-6; 1-benzamido-2-methylpyridinium N-betaine, 17408-47-8.

Acknowledgment.—The award of a Grant (NSF GP-6905) from the National Science Foundation for the purchase of the mass spectrometer used in this study is gratefully acknowledged.

1-Alkyl-2,5-diphenyl-1,4-dithiinium Salts and Their Ambident Behavior toward Bases[1]

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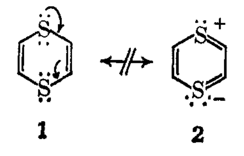
Received March 29, 1968

Alkylation of 2,5-diphenyl-1,4-dithiin (**5**) by methyl, methyl-d_3, and ethyl iodides in the presence of silver 2,4,6-trinitrobenzenesulfonate, mercuric iodide, silver perchlorate, or silver tetrafluoroborate gave high yields of the 1-alkyl-2,5-diphenyl-1,4-dithiinium salts (**6a-g**), while 3-bromo-2,5-diphenyl-1,4-dithiin (**14**) was similarly methylated at the S-1 site. 1-Methyl-2,5-diphenyl-1,4-dithiinium tetrafluoroborate (**6d**) was readily demethylated by common nucleophiles, including dimethyl sulfide and piperidine, and was further attacked at S-4 by *n*-butyllithium with ring scission to form 1-butylthio-2-methylthio-1-phenylethylene (**8**), which was also synthesized by an unambiguous route. Sodium hydride selectively abstracted H-3 of **6d** to yield quantitatively the ring-cleavage product, 1-phenylethynylthio-2-methylthio-1-phenylethylene (**13a**), and the methyl-d_3 analog (**6e**) behaved similarly. The nmr spectra of the salts (*e.g.*, **6a**) revealed that H-3 of the dithiinium ring is strongly deshielded (δ 8.75) *via* d-orbital conjugation of the sulfonium sulfur, while H-6 remains more normally olefinic (δ 6.90) suggesting a lack of cyclic conjugation.

Among heterocyclic sulfur compounds of modern vintage Parham's 1,4-dithiin (1,4-dithiadiene) (**1**)[2,3] was of early interest because of possible sulfur d-orbital participation resulting in valence shell expanded forms such as **2**. However, single crystal X-ray analysis showed that 1,4-dithiin exists in a boat form, and its chemical properties were found to be predominantly olefinic.[3] LCAO-MO calculations by Kreevoy,[4] neglecting d-orbital participation, were in essential agreement with the observed properties of **1**, indicating virtually no contributions from structures such as **2**. This conclusion is hardly surprising, since, as Jaffé and others[5] have argued on theoretical grounds, *a sulfur atom may expand its valence shell only if, in the singly bonded structure, it bears a positive charge.* Hence, it appeared probable to us that 3d–π bonding would be more likely for S-1 of a 1-alkyl-1,4-dithiinium ion (**3**), in which the sulfonium requirement would be fulfilled



1 **2**

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[1] Abstracted in part from the Ph.D. dissertation of R. A. Lazarus, Lehigh University, 1968. This work was supported by Grant GP-5232 from the National Science Foundation to whom we are also indebted for departmental grants for the nmr spectrometer and the mass spectrometer.

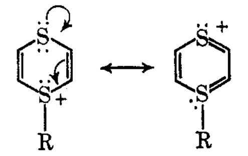
[2] W. E. Parham, H. Wynberg, and F. L. Ramp, *J. Amer. Chem. Soc.*, **75**, 2065 (1953).

[3] W. E. Parham in "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press, Inc., New York, N. Y., 1961, Chapter 22.

[4] M. M. Kreevoy, *J. Amer. Chem. Soc.*, **80**, 5543 (1958).

[5] H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley & Sons, Inc., New York, N. Y., 1962, pp 468–470.

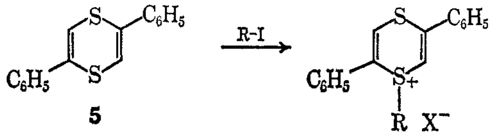
by a σ-tervalent sulfur. Since the remaining, σ-bivalent sulfur (S-4 in **3**) should easily stabilize an onium center (as σ-bivalent sulfur formally conjugates with a carbonium ion in thiapyrylium ions),[6] delocalization *via* structures such as **4** would be more favorable in this case than with neutral dithiin (**1**). For these reasons



3 **4**

we have investigated and now wish to report the synthesis of a series of 1-alkyl-2,5-diphenyl-1,4-dithiinium salts (**6a–g**), along with certain reactions and nmr spectral evidence relevant to the nature of carbon–sulfur π bonding in these interesting compounds.

It has been found that the readily available 2,5-diphenyl-1,4-dithiin (**5**)[7] is easily alkylated with methyl iodide in the presence of silver 2,4,6-trinitrobenzenesulfonate (AgTNBS),[8] mercuric iodide,[9] silver perchlorate, and silver tetrafluoroborate to give high yields of the corresponding 1-methyl-2,5-diphenyl-1,4-dithiinium salts (**6a–d**), which could not be methylated further with excess reagents. The methyl-d_3

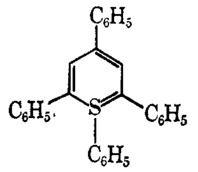


5 **6**

6	R	X⁻
a	Me	TNBS⁻ (2,4,6-trinitrobenzenesulfonate)
b	Me	HgI_3^-
c	Me	ClO_4^-
d	Me	BF_4^-
e	CD_3	BF_4^-
f	Et	TNBS⁻
g	Et	ClO_4^-

compound (**6e**) and the 1-ethylsulfonium salts (**6f, g**) were similarly obtained in high yields, while analogous attempts to alkylate **5** with isopropyl iodide, phenacyl chloride, and benzyl bromide gave unstable products which could not be purified.

These salts (**6**) were well-defined crystalline compounds, and, although the trinitrobenzenesulfonates were light sensitive and the triiodomercurate (**6b**) suffered extensive deterioration on prolonged storage, the tetrafluoroborates and the perchlorates were quite stable under normal ambient conditions, as well as in solutions in acetonitrile or trifluoroacetic acid. Significantly, the tetrafluoroborates and the perchlorates, in which the anions contribute no ultraviolet-visible absorption, were colorless and exhibited electronic spectra differing little from that of **5**, suggesting that the cations in **6** and the parent dithiin (**5**) have similar π-electron systems. Furthermore, the S-alkyl derivatives (**6**) differed markedly from Price's intensely colored S-phenylthia aromatics, *e.g.*, 1,2,4,6-tetraphenyl-1-thiabenzene (**7**), the only known compounds presumably invoking cyclic conjugation *via* σ-tervalent sulfur.[10,11] Consequently, canonical resonance forms such as **4**, which are formally isoelectronic with the thiabenzene structure (**7**), appear to contribute little to the structure of the dithiinium ions (**6**).



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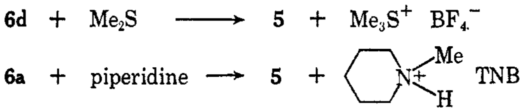
Further evidence for the lack of any special stability of the 1-alkyl-1,4-dithiinium cation was provided by the facile dealkylation of several of the salts (**6**) with various nucleophiles to yield a transalkylated product and to regenerate 2,5-diphenyl-1,4-dithiin (**5**). For example, the reaction of **6d** with excess dimethyl sulfide in acetonitrile at room temperature gave **5** and trimethylsulfonium tetrafluoroborate in yields of 79 and 82%, respectively, while an analogous reaction of **6a** with piperidine yielded 79% **5** and 81% N-methylpiperidinium 2,4,6-trinitrobenzenesulfonate, where *all* products were characterized by comparison with authentic samples. In similar, but qualitative, experiments **6d** was allowed to react with ethoxide, hydroxide, water, iodide, and bromide to yield **5**, although in these cases the transmethylated products were not isolated.



Although 1-alkyl-1,4-dithiinium salts have not been previously isolated, Parham and coworkers had postulated the existence of such compounds as intermediates in the ring scission of **5**[12] and of benzo-1,4-dithiin[13] with *n*-butyllithium in the presence of dimethyl sulfate, since *n*-butyllithium alone did not attack these molecules. As a test of their postulate we have subjected the dithiinium salt **6d** to the action of excess *n*-butyllithium in ether solution. Reaction proceeded above −10° to give a 44% yield of the parent dithiin (**5**), resulting from demethylation of **6d** (*via* attack of the butyl carbanion on the methyl group), along with the ring-cleavage products, phenylacetylene and 1-butylthio-2-methylthio-1-phenylethylene (**8**), in yields of 42 and 44%, respectively. The bissulfide (**8**) after purification by distillation at 115–120° (0.05 mm) was identical with an authentic sample prepared from the reaction of methyl phenacyl sulfide (**9**)[14] and 1-butanethiol in the presence of *p*-toluenesulfonic acid with

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[6] *Cf.* T. E. Young and C. J. Ohnmacht, *J. Org. Chem.*, **32**, 444, 1558 (1967), for pertinent references.

[7] R. H. Barker and C. Barkenbus, *J. Amer. Chem. Soc.*, **58**, 262 (1936).

[8] D. J. Pettitt and G. K. Helmkamp, *J. Org. Chem.*, **29**, 2702 (1964).

[9] J. van der Veen, *Rec. Trav. Chim. Pays-Bas*, **84**, 540 (1965).

[10] C. C. Price, M. Hori, T. Parasaran, and M. Polk, *J. Amer. Chem. Soc.*, **85**, 2278 (1963).

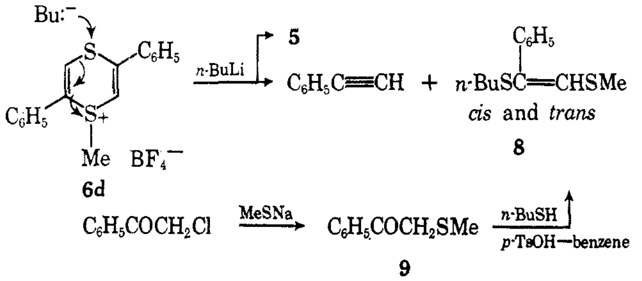
[11] Even in the case of Price's thia aromatics, it is not certain that the cyclic conjugation truly involves carbon 2p to sulfur 3d overlap, and indeed, the intense colors of these compounds suggested to Price that the nonbonding electron pair on sulfur had been promoted to a 3d orbital, leaving an open p_z orbital for π bonding. In the event that there is a special contribution from an S-aryl substituent, we are currently investigating routes to S-phenyl analogs of **6**.

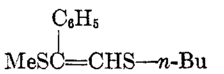
[12] W. E. Parham and M. T. Kneller, *J. Org. Chem.*, **23**, 1702 (1958).

[13] W. E. Parham and P. L. Stright, *J. Amer. Chem. Soc.*, **78**, 4783 (1956).

[14] L. M. Long, *ibid.*, **68**, 2159 (1946).

azeotropic water separation. In addition to comparable infrared spectra, the bissulfide (**8**) samples, as obtained by both methods, exhibited identical nmr spectra which revealed the presence of both *cis* and *trans* isomers (vinyl singlets at δ 6.58 and 6.53; S-methyl singlets at δ 2.30 and 1.97). Although the cleavage reaction (**6d** → **8**) might have been expected to yield solely the *cis* isomer of **8**, the identity of the nmr spectra (including all integrated intensities) suggests that thermal equilibration occurred during the distillations. Surprisingly, there was no evidence for the presence of the isomeric 1-methylthio-2-butylthio-1-phenylethylene (**10**) among the cleavage products from **6d** with butyllithium. Furthermore, since the products **5** and **8**, by actual isolation, account for 88% of the starting material, it is questionable whether significant amounts of **10** are produced at all, as suggested, but not actually demonstrated, in previous reports.[12] Aside from this disparity, our results amply corroborate Parham's postulated mechanism[12] for the scission of **5** by butyllithium and dimethyl sulfate. Although definitive reasons for the remarkably singular cleavage of **6d** along one side of the molecule are not obvious, it is nevertheless clear that the mode of attack by butyl carbanion on **6d** requires that S-4 have some partial, if slight, positive character, as implied by structure **4**.

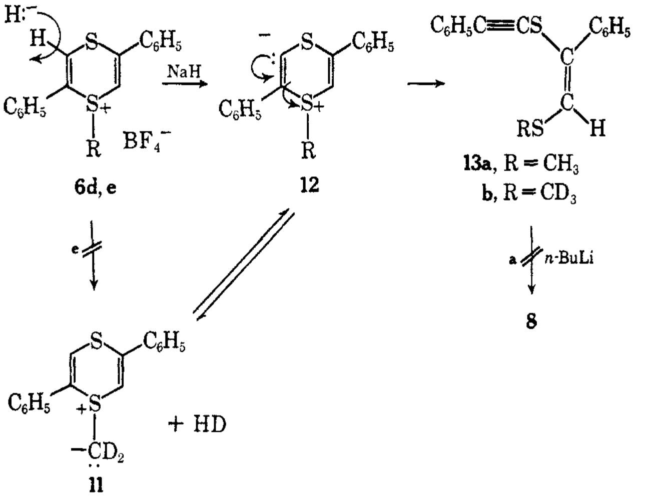




$$\mathrm{MeS}\overset{\displaystyle \mathrm{C_6H_5}}{\overset{|}{\mathrm{C}}}\mathrm{{=}CHS{-}}n\text{-}\mathrm{Bu}$$

10

In an attempt to generate a sulfonium ylide (such as **11**), uncomplicated by the nucleophilic displacements encountered in the foregoing reactions, 1-methyl-2,5-diphenyl-1,4-dithiinium tetrafluoroborate (**6d**) was treated with sodium hydride in glyme in the presence of *p*-nitrobenzaldehyde.[15] Reaction ensued at −10°, and, after chromatographic separation of the products on silica gel, afforded a 78% yield of colorless crystals (mp 72–4°) identified as 1-phenylethynylthio-2-methylthio-1-phenylethylene (**13a**) and a 96% recovery of *p*-nitrobenzaldehyde. Repetition of this reaction in the absence of the superfluous aldehyde gave **13a** in 99% yield. This essentially quantitative reaction apparently occurred by abstraction of the 3 proton from **6d** by hydride ion, resulting in smooth, perhaps concerted, cleavage of the dithiinium ring as shown in formula **12**. The interesting enyne (**13a**) was characterized by its mass spectrum (parent peak: *m/e* 282), infrared absorption of the ethynyl group (2160 cm^{-1}), and a well-defined nmr spectrum, which showed an aromatic multiplet *ca.* δ 7.30, vinyl-H as a singlet at 6.55, and a methyl singlet at 2.40, in the correct integrated ratio of 10:1:3, respectively. The singlet vinyl absorption in the nmr spectrum indicates that **13a** was a pure isomer, and its mode of formation provides strong evidence for a *cis* configuration.



As a further probe into possible ylide formation the trideuteriomethyl analog (**6e**) was also subjected to the hydride cleavage reaction, and found to yield 92% **13b** with the methyl-d_3 group fully intact. This product (**13b**) lacked C–H stretching frequencies below 3000 cm^{-1}, possessed a C–D absorption at 2130 cm^{-1}, as well as the acetylenic band at 2160 cm^{-1}, and exhibited an nmr spectrum identical in the vinyl and aromatic regions with that of **13a**, but completely devoid of aliphatic C–H resonance. The parent peak of the mass spectrum at *m/e* 285 confirmed the full retention of the CD_3 group. These results eliminate possible initial formation of an ylide such as **11** with subsequent rapid equilibration to **12**, which would then contain a CHD_2 group. Therefore the ring scission of **6d** and **e** to **13a** and **b** apparently occurs by direct abstraction by hydride ion of the proton at position 3 of the dithiinium ring.

As similar abstraction of the 3 proton by *n*-butyllithium might have been expected, it was of interest to determine whether or not **13a** could be an intermediate in the cleavage of **6d** to **8** by *n*-butyllithium. Although **13a** reacted with a five fold excess of *n*-butyllithium in ether to yield several products, including a yellow solid, mp 200–203°, of as yet unknown constitution, there was no evidence for the formation of **8**. Hence, this alternative pathway for the cleavage of **6d** by *n*-butyllithium is excluded.

The nmr spectra of the dithiinium salts (**6a–d**) were all essentially identical (no difference in cation spectrum due to counterion variation), except that **6a** also exhibited a sharp singlet at δ 8.87 characteristic of the TNBS$^-$ ion. These spectra were especially interesting since they not only corroborate the assigned structures of the cations, but also reveal that, while one of the olefinic protons of cation **6a–d** has shifted far downfield (δ 8.75; *cf.* Figure 1) because of deshielding by the sulfonium center, the remining olefinic proton (δ 6.90) has experienced only a slight displacement compared with the parent dithiin (**5**, δ 6.98; *cf.* Figure 2), and remains, as in the parent, essentially a normal olefinic

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[15] (a) *p*-Nitrobenzaldehyde was intended to serve as an ylide trap by reacting with the transiently stable alkylidenesulfurane to form *p*-nitrophenyloxirane as described by A. W. Johnson, V. J. Hruby, and J. L. Williams, *ibid.*, **86**, 918 (1964); (b) *Cf.* A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966, Chapter 9.

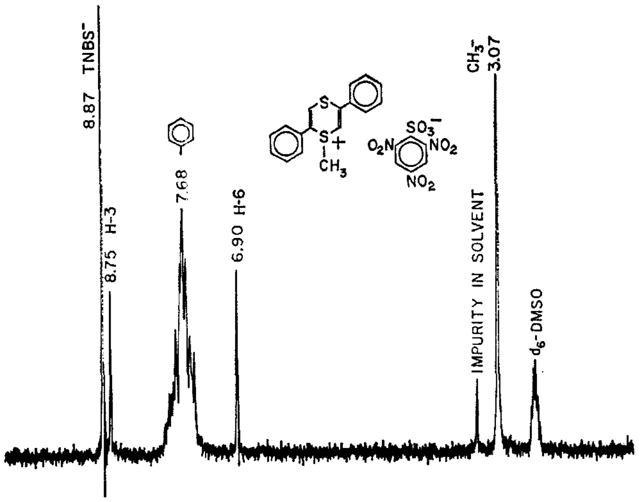


Figure 1.—Nmr spectrum of 1-methyl-2,5-diphenyl-1,4-dithiinium 2,4,6-trinitrobenzenesulfonate (**6a**) in dimethyl-d_6 sulfoxide. δ values are given in parts per million with respect to TMS as internal standard.

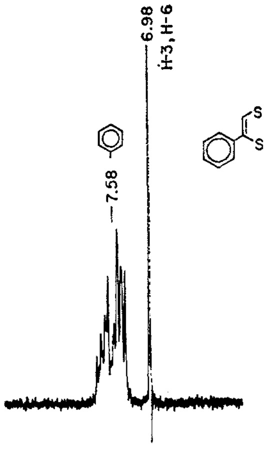
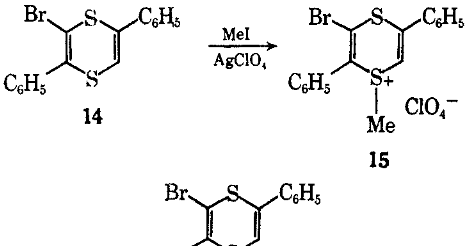


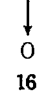
Figure 2.—Nmr spectrum of 2,5-diphenyl-1,4-dithiin (**5**) in dimethyl-d_6 sulfoxide. δ values are given in parts per million with respect to TMS as internal standard.

proton. Since Caserio and her coworkers[16] have recently demonstrated unambiguously that the sulfonium center of vinylsulfonium salts selectively and strongly deshields the protons β to the sulfonium atom, it appears probable that the low-field resonance (δ 8.75) of our 1-methyl-2,5-diphenyl-1,4-dithiinium ion is that of H-3, while the proton at H-6 is responsible for the normal olefinic band at δ 6.90.

These nmr assignments are also consistent with one further observation, *viz.*, that 3-bromo-2,5-diphenyl-1,4-dithiin (**14**)[17] forms an S-methylsulfonium perchlorate which displays only one olefinic proton (δ 7.08) lying on the upfield side of the phenyl resonance; hence, it should have structure **15**. This site of alkylation is consistent with the reported formation of the monosulfoxide (**16**),[18] lending further support to the nmr assignments.

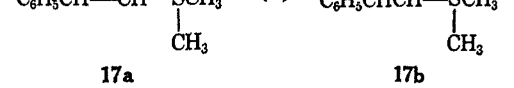


14 **15**



16

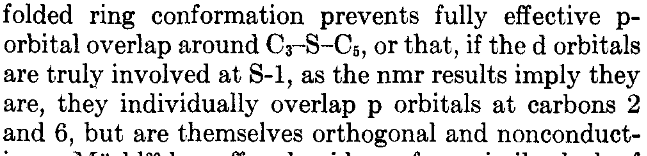
Finally, Caserio[16] has postulated that the strong deshielding of β protons in vinylsulfonium salts (*e.g.*, **17**) is a consequence of d-orbital participation by the sulfonium atom, *e.g.*



$$C_6H_5CH{=}CH{-}\underset{CH_3}{\overset{+}{S}}CH_3 \longleftrightarrow C_6H_5\overset{+}{C}HCH{=}\underset{CH_3}{S}CH_3$$

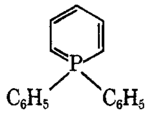
17a **17b**

which places a substantial positive charge on the β carbon (**17b**). Extension of this rationale suggests that contributions from forms such as **18** are then responsible for the strong β deshielding of the dithiinium ion (**6a**). However, since a carbonium ion adjacent to σ-bivalent sulfur is normally stabilized further *via* thionium forms such as **19** (*cf.* thiapyrylium and related ions),[6,19] cyclic conjugation should then occur (canonical form **20**)



18 **19** **20**

resulting in ring-current deshielding of H-6. Such deshielding of H-6 is not observed; hence, the expected cyclic delocalization does not occur, either because a folded ring conformation prevents fully effective p-orbital overlap around C_3-S-C_5, or that, if the d orbitals are truly involved at S-1, as the nmr results imply they are, they individually overlap p orbitals at carbons 2 and 6, but are themselves orthogonal and nonconducting. Märkl[20] has offered evidence for a similar lack of through-conjugation *via* the d orbitals of phosphorus in 1,1-diphenyl-1-phosphabenzene (**21**).



21

Experimental Section[21]

1-Methyl-2,5-diphenyl-1,4-dithiinium Triiodomercurate (6b). —This procedure was analogous with that reported by van der

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[16] M. C. Caserio, R. E. Pratt, and R. J. Holland, *J. Amer. Chem. Soc.*, **88**, 5747 (1966).

[17] W. E. Parham, I. Nicholson, and V. J. Traynelis, *ibid.*, **78**, 850 (1956).

[18] H. H. Szmant and L. M. Alfonso, *ibid.*, **79**, 205 (1957).

[19] R. Zahradník, *Advan. Heterocycl. Chem.*, **5**, 1 (1965).

[20] G. Märkl, *Angew. Chem.*, **75**, 1121 (1963); *cf.* ref 15b, pp 86, 87.

[21] Melting points were determined in capillary tubes using a Mel-Temp apparatus (Laboratory Devices, Cambridge, Mass.) and are corrected. Ultraviolet-visible spectra were recorded on a Beckman DK-2A spectrophotometer, and the infrared spectra were obtained on a Perkin-Elmer 257 instrument. Nmr spectra were determined on a Varian A-60 spectrometer using tetramethylsilane as internal standard, and data are presented in the order δ (multiplicity, number of protons, assignment). Mass spectra were run by Dr. J. E. Sturm (Lehigh University) on a Hitachi 6E high resolution instrument equipped with double focusing sector. Microanalyses were performed by Dr. V. B. Fish (Lehigh University) and by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

Veen[9] for the preparation of dimethylphenylsulfonium triiodomercurate.

To a stirred, refluxing solution of 2.68 g (0.010 mol) of 2,5-diphenyl-1,4-dithiin (5)[7] in 5.0 ml (0.080 mol) of methyl iodide was added 4.54 g (0.010 mol) of mercuric iodide. The red mercuric iodide quickly dissolved to form a yellow solution which gradually changed to orange. After being heated for 40 min, the solution was allowed to stand at room temperature overnight; then anhydrous ether was added to precipitate 7.25 g (84% yield) of crude product, mp 89–94° dec. Recrystallization from acetone–ethanol gave pure **6b** as pale yellow crystals: mp 96–97° dec; nmr (DMSO-d_6), δ 8.77 (s, 1, H-3), 7.73 (m, 10, phenyl), 6.92 (s, 1, H-6), and 3.08 (s, 3, Me) ppm.

Anal. Calcd for $C_{17}H_{15}HgI_3S_2$: C, 23.61; H, 1.75; Hg, 23.20; I, 44.03; S, 7.41. Found: C, 23.59; H, 1.96; Hg, 23.38; I, 43.80; S, 7.23.

1-Methyl-2,5-diphenyl-1,4-dithiinium Tetrafluoroborate (6d). General Procedure for Alkylations Employing Silver Salts.[22]—To a stirred solution of 16.9 g (0.0630 mol) of **5** and 44.0 g (0.310 mol) of methyl iodide in 200 ml of methylene chloride and 100 ml of nitromethane was added a solution of 22.3 g (0.0620 mol) of $AgBF_4 \cdot 4CH_3CN$ in 200 ml of nitromethane. The flask was wrapped in aluminum foil to minimize exposure to light, and the reaction mixture was then stirred for 18 hr at room temperature. The yellow precipitate which had formed was removed by filtration, washed with ether, and air dried to give 14.4 g (99.5% yield) of silver iodide. The filtrates were diluted with 1 l. of anhydrous ether to precipitate the crude dithiinium salt, which, after being air dried, weighed 19.4 g (84.5% yield), and had mp 163–164° dec. Recrystallization from acetonitrile–ether (Norit) gave pure **6d** as colorless crystals: mp 163–164° dec; uv max (MeCN), 272 mμ (log ϵ 4.43), 312 (3.94) sh; nmr (CF_3COOH), δ 8.15 (s, 1, H-3), 7.65 (m, 10, phenyl), 6.55 (s, 1, H-6) and 3.02 (s, 3, Me) ppm.

Anal. Calcd for $C_{17}H_{15}BF_4S_2$: C, 55.15; H, 4.08; F, 20.53; S, 17.32. Found: C, 55.11; H, 4.10; F, 20.25; S, 17.55.

Preparations of the remaining dithiinium salts (**6** and **15**) were conducted analogously, but on one-twentieth to one-tenth the above scale, to yield the specific products described individually in the following paragraphs.

1-Trideuteriomethyl-2,5-diphenyl-1,4-dithiinium tetrafluoroborate (6e) was similarly obtained using methyl-d_3 iodide of 99+% isotopic purity (Merck and Co.). This salt (**6e**) had mp 165–166°, caused no depression of the melting point of the protio compound (**6d**), and exhibited an nmr spectrum [CF_3COOD, δ 8.15 (s, 1, H-3), 7.65 (m, 10, phenyl), and 6.55 (s, 1, H-6)] completely lacking absorption in the methyl region.

Anal. Calcd for $C_{17}H_{12}BD_3F_4S_2$: C, 54.70; S, 17.18. Found: C, 54.67; S, 17.27.

1-Methyl-2,5-diphenyl-1,4-dithiinium 2,4,6-trinitrobenzenesulfonate (6a) was obtained in 88% yield from **5**, methyl iodide, and silver 2,4,6-trinitroenzenesulfonate.[8] Recrystallization from absolute ethanol–acetonitrile gave buff crystals which turned orange above 100°, became red up to 150°, then green above 150°, and sharply decomposed at 165°. The nmr spectrum [DMSO-d_6, δ 8.87 (s, 2, TNBS$^-$), 8.75 (s, 1, H-3), 7.68 (m, 5, phenyl), 6.90 (s, 1, H-6), and 3.07 (s, 3, CH_3) ppm] is illustrated in Figure 1.

Anal. Calcd for $C_{23}H_{17}N_3O_9S_3$: C, 47.99; H, 2.98; N, 7.30; S, 16.71. Found: C, 47.89; H, 2.90; N, 7.18; S, 16.66.

1-Methyl-2,5-diphenyl-1,4-dithiinium perchlorate (6c) was isolated in 82% yield from the reaction of **5**, methyl iodide, and silver perchlorate[22] and recrystallized from methylene chloride–acetonitrile–ether to give white crystals: mp 164–165° dec; nmr (DMSO-d_6), δ 8.75 (s, 1, H-3), 7.73 (m, 10, phenyl), 6.90 (s, 1, H-6), and 3.07 (s, 3, Me) ppm; nmr (CF_3COOH), δ 8.17 (s, 1, H-3), 7.67 (m, 10, phenyl), 6.57 (s, 1, H-6), and 3.03 (s, 3, Me) ppm.

Anal. Calcd for $C_{17}H_{15}ClO_4S_2$: C, 53.33; H, 3.95; Cl, 9.26; S, 16.75. Found: C, 53.13; H, 3.86; Cl, 9.14; S, 16.89.

1-Ethyl-2,5-diphenyl-1,4-dithiinium 2,4,6-trinitrobenzenesulfonate (6f), produced in 58% yield as buff crystals, mp 176–177° dec (recrystallized from acetonitrile–ether), showed color changes on heating similar to those observed with **6a**. This ethyl analog (**6f**) showed nmr (DMSO-d_6) at δ 8.88 (s, 2, TNBS$^-$), 8.80 (s, 1, H-3), 7.72 (m, 10, phenyl), 6.97 (s, 1, H-6), 3.58 (q, 2, J = 7.5 Hz, CH_2), and 1.35 (t, 3, J = 7.5 Hz, CH_3) ppm.

Anal. Calcd for $C_{24}H_{19}N_3O_9S_3$: C, 48.89; H, 3.25; N, 7.13; S, 16.31. Found: C, 49.04; H, 3.38; N, 7.30; S, 16.31.

1-Ethyl-2,5-diphenyl-1,4-dithiinium Perchlorate (6g).—This compound was obtained following the general procedure for **6d**, except that the molar proportion of alkylating agent, ethyl iodide, was doubled. The crude product (66% yield) was recrystallized from methylene chloride–ether to give colorless crystals of **6g**: mp 147–148° dec; nmr (CF_3COOH), δ 8.17 (s, 1, H-3), 7.65 (m, 10 phenyl), 6.50 (s, 1, H-6), 3.58 (q, 2, J = 7.5 Hz, CH_2), and 1.51 (t, 3, J = 7.5 Hz, CH_3) ppm.

Anal. Calcd for $C_{18}H_{17}ClO_4S_2$: C, 54.47; H, 4.32; Cl, 8.93; S, 16.16. Found: C, 54.27; H, 4.29; Cl, 8.75; S, 16.02.

1-Methyl-3-bromo-2,5-diphenyl-1,4-dithiinium Perchlorate (15).—This compound was obtained from the reaction of 3-bromo-2,5-diphenyl-1,4-dithiin (**14**),[17] methyl iodide, and silver perchlorate[22] in a mole ratio of 1.01:10:1.00. Although silver iodide was isolated in 99% yield, the dithiinium salt (**15**) was obtained in only 31% yield as colorless crystals (from acetonitrile–ether): mp 189° dec; nmr (DMSO-d_6), δ 7.77 (m, 10, phenyl), 7.08 (s, 1, H-6), and 3.27 (s, 3, CH_3) ppm.[23]

Anal. Calcd for $C_{17}H_{14}BrClO_4S_2$: C, 44.22; H, 3.06; Br, 17.30; Cl, 7.68; S, 13.87. Found: C, 44.32; H, 3.14; Br, 17.58; Cl, 7.70; S, 13.64.

Reaction of 6d with Dimethyl Sulfide.—To a solution of 2.26 g (6.10 mmol) of **6d** in 15 ml of acetonitrile was added 2.00 g (35.2 mmol) of dimethyl sulfide. After the solution had been stirred overnight at room temperature, the solvent was evaporated, and the yellow residue was extracted by trituration with ether. The ether-insoluble solid was collected by filtration, washed further with ether, and air dried to give 0.82 g (82% yield) of trimethylsulfonium tetrafluoroborate, which, after recrystallization from acetonitrile–ether, had mp 205–208° (lit.[24] mp 206–211°) and exhibited an nmr spectrum (CD_3CN), showing only a sharp methyl singlet at δ 2.90 ppm.

The ether extract from above was evaporated to leave 1.30 g (79% yield) of 2,5-diphenyl-1,4-dithiin (**5**), mp 110–113°, which, after one recrystallization from absolute ethanol, had mp 112–114° and mmp 112–114° with authentic **5**, mp 112–114°.

Reaction of 6a with Piperidine.—To a solution of 1.00 g (1.74 mmol) of **6a** in 15 ml of acetonitrile was added 0.74 g (8.70 mmol) of piperidine. The resulting solution was stirred at room temperature for 24 hr, then evaporated to dryness, leaving a yellow solid, which was extracted by trituration with ether. The ether extract was evaporated to leave 0.37 g (79% yield) of **5**, which, after one recrystallization from absolute ethanol, had mp 111–114° and caused no depression of the melting point of an authentic sample of **5**.

The ether-insoluble residue from the extraction weighed 0.55 g and melted above 200°. After one recrystallization from acetonitrile–ether, this product had mp 233–237° dec, and was identical with N-methylpiperidinium 2,4,6-trinitrobenzenesulfonate, prepared as follows.

N-Methylpiperidinium 2,4,6-Trinitrobenzenesulfonate.—A solution of 5.23 g (0.010 mol) of silver 2,4,6-trinitrobenzenesulfonate ($3CH_3CN$)[8] in 10 ml of nitromethane and 0.5 ml of acetonitrile was added to a stirred solution of 2.27 g (0.010 mol) of N-methylpiperidinium iodide in 10 ml of methylene chloride and 5 ml of nitromethane. The mixture was stirred for 1 hr, then filtered to remove precipitated silver iodide. The filtrate was diluted with ether to give colorless crystals (3.80 g, 97%) of N-methylpiperidinium 2,4,6-trinitrobenzenesulfonate: mp 235–238°; nmr (DMSO-d_6), δ 8.72 (s, 2, TNBS$^-$), 8.17 (broad low-lying band, 1, N-H), 3.08 (strong s plus m, 7, CH_3 plus two α-CH_2), 1.63 (broad s, 6, two β and one γ-CH_2) ppm.

Anal. Calcd for $C_{12}H_{16}N_4O_9S$: C, 36.73; H, 4.11; N, 14.28; S, 8.17. Found: C, 36.44; H, 4.03; N, 14.39; S, 8.31.

Reaction of 6d with *n*-Butyllithium.—To a well-stirred mixture of 1.46 g (0.210 g-atom) of small pieces of lithium wire and 75 ml of ether (distilled from sodium hydride, kept under a helium atmosphere and precooled to −10°) was added 14.4 g (0.105

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[22] Commercially available silver tetrafluoroborate was fuming, hygroscopic, and ineffective in this reaction. However, after dissolution of this salt in acetonitrile, addition of absolute ether reprecipitated material, which, after being dried at 25° over Drierite, had the composition $AgBF_4 \cdot 4CH_3CN$ (Calcd: Ag, 30.06. Found: Ag, 29.98). This solvate was less hygroscopic and was found effective in the formation of **6d** and **e**. The silver perchlorate employed was similarly obtained as $AgClO_4 \cdot 4CH_3CN$ (Calcd: Ag, 29.03. Found: Ag, 28.94).

[23] For comparison, the nmr spectrum of 3-bromo-2,5-diphenyl-1,4-dithiin (**14**)[17] in DMSO-d_6 showed δ 7.50 (m, 10, phenyl) and 7.32 (s, 1, H-6) ppm.

[24] H. Teichmann and G. Hilgetag, *Ber.*, **96**, 1454 (1963).

mol) of *n*-butyl bromide dropwise during 1 hr. The mixture was stirred for 1 additional hr, and the resulting solution was then cooled to −55°, and 7.79 g (0.0210 mol) of **6d** was added. The cooling bath was removed, and the mixture was allowed to warm to room temperature. A reaction ensued at −10° and became more vigorous at 0°. After 1 hr the reaction mixture was poured, with vigorous stirring, into cold water, and the layers were separated. The water layer was extracted with ether, and then the combined organic layer and ether extract were dried ($MgSO_4$) and distilled through a 24-cm Vigreux column. After removal of the ether at atmospheric pressure, there was obtained a forerun of colorless liquid (1.05 g, bp 25° at water aspirator pressure) and 2.18 g (43.6% yield of **8**) of yellow liquid, bp 115–120° (0.05 mm). Redistillation of the forerun at atmospheric pressure gave 0.90 g (42% yield) of phenylacetylene, which exhibited a boiling point of 142–144° and an infrared spectrum (neat) of 3280 (ethynyl C—H) and 2110 ($C\equiv C$) cm^{-1}, identical with those of an authentic sample.

The higher boiling fraction was redistilled to give 1.80 g of yellow oil, bp 118–120° (0.05 mm), which showed nmr and ir spectra identical with those of authentic 1-butylthio-2-methylthio-1-phenylethylene (**8**), prepared as described in the next experiment.

Anal. Calcd for $C_{13}H_{18}S_2$: C, 65.49; H, 7.61; S, 26.90. Found: C, 65.66; H, 7.59; S, 26.92.

The residual semisolid from the original distillation of products was triturated with ethanol to give 2.50 g (44% yield) of yellow solid, which, after recrystallization from absolute ethanol, had mp 116–118° and an infrared spectrum identical with that of authentic 2,5-diphenyl-1,4-dithiin (**5**); a mixture melting point with **5** was also undepressed.

1-Butylthio-2-methylthio-1-phenylethylene (**8**).—A mixture of 13.0 g (0.0781 mol) of methyl phenacyl sulfide (**9**),[14] 7.08 g (0.0781 mol) of butanethiol, and 0.75 g of *p*-toluenesulfonic acid in 100 ml of benzene was refluxed under a Dean–Stark trap for 6 hr, during which 1.0 ml (72% of theory) of water was collected. The benzene solution was evaporated to 50 ml, then washed with water, with 5% sodium bicarbonate solution, then again with water, and dried ($MgSO_4$). After removal of the benzene on a rotary evaporator, the residual oil was distilled at 0.01 mm to give four fractions as follows: (1) 0.9 g (bp below 75°); (2) 7.5 g (bp 75–77°; largely unreacted **9**); (3) 2.9 g (bp 95–100°); and (4) 6.0 g (bp 120–125°; crude product **8**). Fraction 4 was twice redistilled to give pure **8** as a pale yellow liquid: bp 110–111° (0.005 mm); ir (neat), 3070, 3050, 3010 weak (vinyl and aromatic C–H), 2950, 2920, 2870, 2850, all strong (aliphatic (C–H), and other strong bands at 1595, 1540, 1484, 1462, 1440, 1273, 1223, 815, 755, and 695 cm^{-1}; nmr (CCl_4), δ 7.40 (m, 5, phenyl), 6.58 and 6.53 (two singlets, total 1, vinyl C–H), and the remaining 12 aliphatic protons distributed among the following, 2.60 (m), 2.30 (s), 1.97 (s), 1.40 (m), 0.90 (m) ppm. Among this last group the nmr bands were not well enough resolved to permit distinct integrations.

Anal. Calcd for $C_{13}H_{18}S_2$: C, 65.49; H, 7.61; S, 26.90. Found: C, 65.66; H, 7.83; S, 26.61.

Sodium Hydride Cleavage of 6d to 1-Phenylethynylthio-2-methylthio-1-phenylethylene (**13a**).—To a slurry of 0.41 g (10 mmol) of a 59.6% mineral oil dispersion of sodium hydride in 30 ml of glyme (predried and distilled from sodium hydride) cooled to −55° was added 3.70 g (10 mmol) of **6d**. The resulting mixture was allowed to warm slowly with continuous stirring. At −10° a noticeable reaction began and continued for 45 min, during which the temperature rose to 25° and the mixture became yellow-green. The reaction mixture was stirred an additional 15 min, then filtered to remove a white solid which was washed on the filter with ether. The ether in the filtrate caused precipitation of more of this material, which was combined with the first crop and dried to yield 1.10 g (100%) of sodium tetrafluoroborate, which decomposed above 380° and had an infrared spectrum (KBr) displaying only a broad set of three peaks centered at 1080 cm^{-1} (and identical with that of authentic sodium tetrafluoroborate). The glyme–ether filtrate was then evaporated to give 2.80 g (99% yield) of crude **13a** as an oil which solidified on cooling and had mp 68–72°. Recrystallization from absolute ethanol gave pure **13a**, colorless crystals: mp 72–74°; ir (KBr), 3065, 3045, 3000 (aromatic and vinyl C–H), 2940 sh, 2915, 2845 (CH_3), 2160 ($C\equiv C$), and strong bands at 1590, 1545, 1479, 1435, 1318, 1249, 906, 811, 750, and 685 cm^{-1}; nmr (CCl_4), δ 7.40 (m, 5, phenyl), 7.17 (s, 5, phenyl), 6.55 (s, 1, vinyl C–H), and 2.40 (s, 3, CH_3) ppm; mass spectrum, *m/e* 282 (parent peak) and 267 (parent minus CH_3).

Anal. Calcd for $C_{17}H_{14}S_2$: C, 72.30; H, 5.00; S, 22.70. Found: C, 72.50; H, 5.28; S, 22.60.

Sodium Hydride Cleavage of 6e to 1-Phenylethynylthio-2-trideuteriomethylthio-1-phenylethylene (**13b**).—By a procedure exactly parallel with that of the foregoing experiment, 0.137 g (3.24 mmol) of 56.9% mineral oil dispersion of sodium hydride and 1.20 g (3.24 mmol) of **6e** in 15 ml of glyme reacted to yield 0.84 g (92%) of the trideuterio compound (**13b**): mp 69–71°; ir (KBr), 3065, 3045, 3005 (aromatic and vinyl C—H), 2160 ($C\equiv C$), 2130 (C—D), and strong bands at 1590, 1548, 1480, 1438, 1254, 1010, 940, 911, 820, 750, and 690 cm^{-1}; nmr (CCl_4), δ 7.40 (m, 5, phenyl), 7.17 (s, 5, phenyl), and 6.55 (s, 1, vinyl C–H) ppm only; mass spectrum, *m/e* 285 (parent peak) and 267 (parent minus CD_3). This compound caused no depression of the melting point of the protio analog.

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Registry No.—**6a**, 17245-09-9; **6b**, 17250-78-1; **6c**, 17245-10-2; **6d**, 17250-79-2; **6e**, 17250-80-5; **6f**, 17245-11-3; **6g**, 17245-12-4; **8** (*cis*), 17245-13-5; **8** (*trans*), 17245-08-8; **13a**, 17278-23-8; **13b**, 17244-46-1; **15**, 17245-14-6; N-methylpiperidinium 2,4,6-trinitrobenzenesulfonate, 17245-15-7.