Organic and Biological Chemistry

The Nature of Sulfur Bonding in α,β-Unsaturated Sulfides and Sulfonium Salts[1,2]

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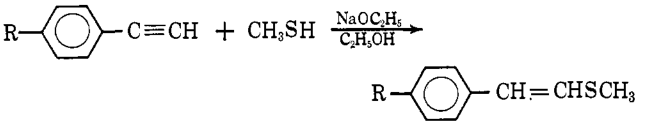
Abstract: The electronic effects of thiomethyl and dimethylsulfonium groups directly bonded to a carbon–carbon double bond have been investigated by nuclear magnetic resonance spectroscopy. A number of compounds of the type $RCH{=}CHSCH_3$ and $RCH{=}CHS^+(CH_3)_2{}^-BF_4$, where R = H or aryl, have been prepared and their nmr spectra recorded. The most striking feature of these spectra is the low-field chemical shift of the vinyl proton β to the dimethylsulfonium group. Comparison with the nmr spectra of analogous nitrogen compounds indicates that d–p π overlap contributes significantly to the bonding of α,β-unsaturated sulfonium salts, and that p–p π overlap is less important in α,β-unsaturated sulfides than in enamines. The observation that the nmr spectra of the sulfonium salts are temperature independent over the range -60 to 114° indicates that d–p π overlap has little or no conformational requirement.

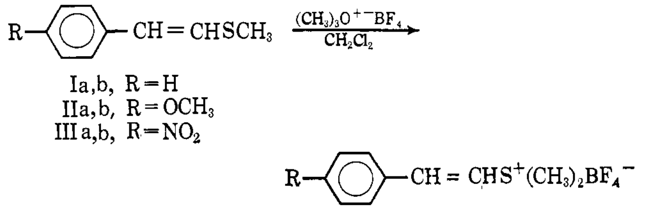
The ability of sulfur to participate in two distinct types of π bonding is well known.[3] For example, overlap of 3p sulfur orbitals with adjacent carbon 2p orbitals is considered responsible for stabilization of thioalkylcarbonium ions, $CH_3\overset{..}{\underset{..}{S}}{-}CH_2^+ \leftrightarrow CH_3\underset{..}{S}^+{=}CH_2$, and must certainly be involved in the double bond of the thiocarbonyl group, C=S. In addition to 3p–2p π bonding, the 3d orbitals of sulfur can, in certain instances, overlap effectively with neighboring 2p orbitals, and 3d–2p π bonding of this type is held partly or wholly responsible for the stabilization of anionic centers adjacent to sulfur.[4–6]

Despite the fact that 3d–2p π overlap can contribute importantly to the bonding in organosulfur compounds, the various steric and electronic requirements of π bonding involving 3d orbitals are not completely understood and have not been investigated as widely as the more common π bonding involving p orbitals. For these reasons we became interested in making a comparative study of inductive and conjugative effects in α,β-unsaturated organosulfur compounds of the type RCH=CH—X, where X is a sulfur-containing substituent, SCH_3, $^+S(CH_3)_2$, $SOCH_3$, SO_2CH_3, CH_3O^+-$S(CH_3)_2$, and $SO(OCH_3)_2$, directly bonded to an unsaturated carbon. Our initial work, which we now report, involved a study of the nuclear magnetic resonance spectra of a number of unsaturated methyl sulfides, I–III, and their corresponding dimethylsulfonium salts, IV–VI. We hoped thereby to evaluate ground-state electronic effects of the thiomethyl and dimethylsulfonium groups insofar as these effects are reflected in nmr spectral parameters.

Synthesis. Two methods of synthesis of the styryl methyl sulfides I–III were employed. In the first of these methanethiol was added to the appropriate arylacetylene in the presence of sodium ethoxide in ethanol. This reaction is reported to lead to a *cis* product *via trans* addition,[7] and this was confirmed for the addition of methanethiol to phenylacetylene and *p*-methoxyphenylacetylene. However, 10–20% of a second component was also formed which was identified from infrared and nmr spectral data as α-thiomethylstyrene from phenylacetylene and α-thiomethyl-*p*-methoxystyrene from *p*-methoxyphenylacetylene. In the case of *p*-nitrophenylacetylene, however, the major product was *trans-p*-nitrostyryl methyl sulfide (IIIb) containing up to 10% of the *cis* isomer IIIa.



Ia, R=H, *cis*
IIa, R=OCH_3, *cis*
IIIb, R=NO_2, *trans*



IVa,b, R=H
Va,b, R=OCH_3
VIa,b, R=NO_2

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[1] Presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 11-16, 1966.

[2] This work was supported in part by the Petroleum Research Fund of the American Chemical Society (PRF-2357-Al, 4).

[3] C. C. Price and S. Oae, "Sulfur Bonding," The Ronald Press, New York, N. Y., 1962.

[4] (a) W. von E. Doering and L. K. Levy, *J. Am. Chem. Soc.*, 77, 509 (1955); (b) W. von E. Doering and K. C. Schreiber, *ibid.*, 77, 514 (1955); (c) W. von E. Doering and A. K. Hoffmann, *ibid.*, 77, 521 (1955).

[5] D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, pp 71–84.

[6] See C. P. Lillya and P. Miller, *J. Am. Chem. Soc.*, 88, 1560 (1966), for a recent report of some strikingly stable sulfonium methylides, $[RR'S{=}CH{=}SRR']^+$.

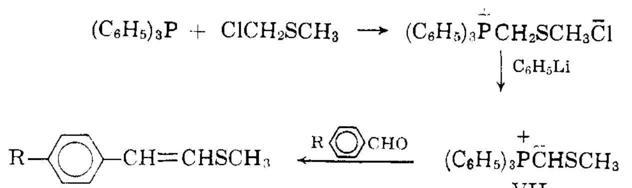
[7] W. E. Truce and John A. Simms, *ibid.*, 78, 2756 (1956).

Table I. Nuclear Magnetic Resonance Spectral Data for Styryl Methyl Sulfides, Dimethylstyrylsulfonium Fluoroborates, and Related Compounds[a]

Compd[e]	No.	$\delta(H_\beta)$, ppm	$\delta(H_\alpha)$, ppm	$\delta(H_\beta) - \delta(H_\alpha)$, cps	$\delta(SCH_3)$, ppm	$J(H_\alpha H_\beta)$, cps	$J(H_\beta SCH_3)$, cps	Solvent
$C_6H_5CH{=}CHSCH_3$	Ia	6.34	5.98	19.6	2.01	11	...	Neat
	Ia	6.23	5.93	18.0	2.06	11	...	CCl_4
$C_6H_5CD{=}CHSCH_3$, *cis*		...	5.98	...	2.01	...	...	Neat
	Ib	6.20	6.68	28.9	2.04	16	...	Neat
	Ib	6.11	6.58	28.0	2.06	16	...	CCl_4
$C_6H_5CD{=}CHSCH_3$, *trans*		...	6.68	...	2.04	...	...	Neat
$C_6H_5CH{=}CHS^+(CH_3)_2{}^-BF_4$	IVa	7.82	6.52	78.0	3.13	9.5	...	CH_3NO_2
	IVa	7.83	6.67	70.5	3.10	9.5	...	$(CH_3)_2SO$
	IVa	7.63	6.49	68.4	3.01	9.5	0.2	CH_2Cl_2
$C_6H_5CD{=}CHS^+(CH_3)_2{}^-BF_4$, *cis*		...	6.45	...	3.00	...	...	CH_2Cl_2
	IVb	7.64	6.94	42.0	2.99	14.5	...	CH_2Cl_2
$C_6H_5CD{=}CHS^+(CH_3)^-BF_4$, *trans*		...	6.95	...	2.97	...	...	CH_2Cl_2
p-$CH_3OC_6H_4CH{=}CHSCH_3$	IIa	6.23	5.90	19.5	2.22	11	...	CCl_4
p-$CH_3OC_6H_4CH{=}CHS^+$-$(CH_3)_2{}^-BF_4$	Va	7.53	6.32	72.6	3.05	10	...	CH_2Cl_2
	IIb	6.20	6.47	15.8	2.25	16	...	CCl_4
	Vb	7.64	6.97	39.9	3.04	16	...	$(CH_3)_2SO$
p-$NO_2C_6H_4CH{=}CHSCH_3$	IIIa	6.4[b]	6.4	0	2.43	...	...	CCl_4
	IIIa	6.4[b]	6.4	0	2.37	...	...	$CDCl_3$
p-$NO_3C_6H_4CH{=}CHS^+$-$(CH_3)_2{}^-BF_4$	VIa	8.0[c]	6.95	63	3.18	10	...	$(CH_3)_2SO$
	IIIb	6.25	7.03	46.8	2.38	16	0.4	CCl_4
	IIIb	6.22	7.02	48.2	2.31	16	0.4	$CDCl_3$
	VIb	7.89	7.23	39.6	3.22	15.5	...	CH_3NO_2
	VIb	7.86	7.48	22.8	3.18	15.5	...	$(CH_3)_2SO$
$C_6H_5CH{=}CHN(CH_3)_2$, *trans*	XII	5.11	6.65	92.3	2.63	13.9	0.4	$CDCl_3$
$C_6H_5CH{=}CHN^+(CH_3)_3$-${}^-BF_4$, *trans*	XIII[d]	7.22 (6.96)	6.96 (7.22)	15	3.48	14.5	...	CH_3NO_2

[a] Chemical shifts of aryl and O-methyl protons are not listed. The spectra were recorded with Varian A-60 and HA-60 spectrometers. [b] The chemical shift difference between the vinyl protons of IIIa is virtually zero. [c] Precise chemical shift assignment is uncertain owing to superimposition of resonances of aryl protons. [d] Assignment of the chemical shifts of the vinyl protons is uncertain. From the correlation of Figure 2, it would appear that the resonance at 7.22 ppm is due to the β-vinyl proton. [e] Series a, *cis*; series b, *trans*.

The second method of synthesis utilized a Wittig reaction[8a] between triphenylphosphonium thiomethylmethylide (VII) and an arylaldehyde. This type of reaction is not generally stereospecific,[8b] and mixtures of *cis* and *trans* products were obtained except in the case of *p*-anisaldehyde from which only *trans*-*p*-methoxystyryl methyl sulfide IIb was isolated.



Ia + Ib, R = H, *cis* and *trans*
IIb, R = OCH$_3$, *trans*
IIa + IIIb, R = NO$_2$, *cis* and *trans*

Methylation of the sulfides I–III was achieved with trimethyloxonium fluoroborate and led to the corresponding dimethylstyrylsulfonium fluoroborates IV–VI.

Nuclear Magnetic Resonance Spectra. The proton nmr spectra of the styryl methyl sulfides (Ia b) showed AB quartets for the vinyl protons, the chemical shifts of which were determined in carbon tetrachloride solution as 5.93 and 6.23 ppm with J = 11 cps for the *cis* isomer Ia, and 6.11 and 6.58 ppm with J = 16 cps for the *trans* isomer Ib (see Table I). It was not possible, however, to assign the chemical shift parameters to particular vinyl protons without further information. Deuterium-labeled analogs of Ia and b were therefore prepared by the Wittig reaction[8] using benzaldehyde-d_1 as the aldehyde component. The nmr spectrum of the product mixture showed two broad vinyl resonances, one at 5.98 ppm corresponding to the α-vinyl proton (*i.e.*, α to the thiomethyl group) of the *cis* isomer, and the other at 6.68 ppm corresponding to the α-vinyl proton of the *trans* isomer. The chemical shifts of the β-vinyl protons of Ia and Ib in carbon tetrachloride solution are therefore identified as 6.23 and 6.11 ppm, respectively.

The nmr spectra of the dimethylstyrylsulfonium salts IVa and IVb were particularly interesting in that the chemical shift difference between the two vinyl protons was appreciably greater than in the parent sulfides Ia and Ib (see Table I and Figure 1). Thus, the chemical shift of one vinyl proton of IVa was 68–78 cps downfield from the other depending on the solvent, and this low-field resonance was identified with the β-vinyl proton by comparing the spectrum of the deuterium-labeled salt *cis*-$C_6H_5CD_\beta{=}CH_\alpha S^+(CH_3)_2{}^-BF_4$ with the spectrum of the unlabeled salt IVa.

A direct comparison of the spectra of Ia with IVa, or Ib with IVb, shows that there is a general shift of the proton resonances of the salts to lower fields relative to the sulfides (see Figure 1). The magnitudes of these shifts are somewhat solvent dependent, but the trends

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(8) (a) G. Wittig and M. Schlosser, *Chem. Ber.*, **94**, 1373 (1961); (b) see A. Maercker, *Org. Reactions*, **14**, 312 (1965).

are unmistakable and are largest for the β-vinyl protons (see Table II). Thus, the downfield shifts of the β-vinyl protons are three to four times greater than the corresponding shifts of the α protons (compare columns 2 and 3 of Table II).

Table II. Chemical Shift Differences between Protons of Styryl Methyl Sulfides and Dimethylstyrylsulfonium Fluoroborates[a]

Compd	$\Delta\delta(H_\beta)$, ppm	$\Delta\delta(H_\alpha)$, ppm	$\Delta\delta(SCH_3)$, ppm
Ia–IVa	1.40	0.56	0.95
Ib–IVb	1.53	0.36	0.93
IIa–Va	1.30	0.42	0.83
IIb–Vb	1.44	0.50	0.79
IIIa–VIa	1.59	0.54	0.75
IIIb–VIb	1.64	0.20	0.74

[a] The data are negative numbers, representing downfield proton shifts of the sulfonium salts relative to the sulfides.

The general shift to lower fields for the proton resonances of the sulfonium salts is consistent with the greater electronegativity of the dimethylsulfonium group relative to the thiomethyl group. We estimated the electronegativity of $^+S(CH_3)_2$ as 3.05 from the chemical shift data of dimethylethylsulfonium fluoroborate (IX; see Table III) and the relationship of Cavanaugh and Dailey[9]

$$\text{electronegativity} = 0.0114[\delta(CH_2) - \delta(CH_3)] + 1.78$$

where $\delta(CH_2) - \delta(CH_3)$ is the difference in chemical shifts in cycles per second at 60 Mcps of the methyl and methylene resonances of the ethyl group of IX. The electronegativity of the thiomethyl group is similarly calculated to be 2.64[9] from the spectrum of methyl ethyl sulfide (VIII; see Table III).

Table III. Nuclear Magnetic Resonance Spectral Data for Methyl Vinyl Sulfide and Related Compounds

Compd	No.	$\delta(H_A)$, ppm	$\delta(H_B)$, ppm	$\delta(H_C)$, ppm	$\delta(SCH_3)$, ppm	$\delta(SCH_2\text{-}CH_3)$ (CH_2), ppm	$\delta(SCH_2\text{-}CH_3)$ (CH_3), ppm	J_{AB}, cps	J_{AC}, cps	J_{BC}, cps	Solvent
$\begin{matrix}H_A & & H_C\\ & >C{=}C< & \\ H_B & & SCH_3\end{matrix}$	X[a]	5.08	4.84	6.35	2.12	...	...	−0.3	10.3	16.4	...
	X[b]	5.18	4.95	6.43	2.25	...	...	...	...	...	CCl_4
$\begin{matrix}H_A & & H_C\\ & >C{=}C< & \\ H_B & & S^+(CH_3)_2{}^-BF_4\end{matrix}$	XI	6.39	6.43	6.73	3.00	...	...	−1.8	10.3	15.5	$(CH_3)_2SO$
$CH_3CH_2SCH_3$	VIII	...	...	...	2.03	2.47	1.23	...	...	...	CCl_4
$CH_3CH_2S^+(CH_3)_2{}^-BF_4$	IX	...	...	...	2.93	3.33	1.47	...	...	...	CH_3NO_2

[a] See ref 16. [b] See Varian Spectra Catalog, Varian Associates, Palo Alto, Calif., Spectrum No. 366.

However, the inductive or electrostatic effect of the dimethylsulfonium group cannot be the only factor influencing the chemical shifts of IVa and IVb since it does not account for the fact that the β-vinyl protons are markedly less shielded than the α-vinyl protons. In order to deshield selectively the β position, the π electrons of the double bond must be delocalized to some extent through overlap of the carbon 2p orbitals with the unoccupied 3d orbitals of sulfur, as shown in the following contributing structures.

$$C_6H_5CH{=}CH{-}S^+(CH_3)_2 \longleftrightarrow C_6H_5C^+H{-}CH{=}S(CH_3)_2$$

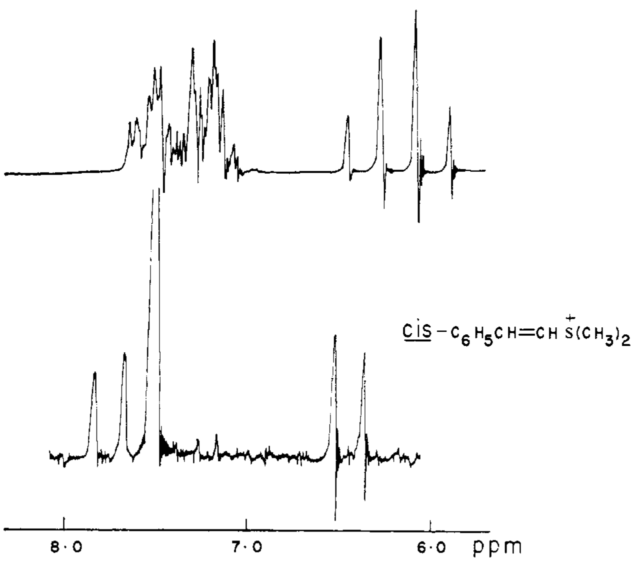

Figure 1. Pmr spectra at 60 Mcps of vinyl and aromatic protons of Ia (top) as the pure liquid and IVa (bottom) in dimethyl sulfoxide.

Other second row elements show similar effects. For example, the low-field shifts of β-vinyl protons observed in the proton magnetic resonance spectra of several vinylsilanes have likewise been attributed to π bonding involving silicon 3d orbitals.[10] In the case of sulfur, however, electron-accepting conjugation of this kind is apparently more important in the dimethylsulfonium group than in the thiomethyl group. Evidence pertaining to ground-state conjugation effects of divalent sulfur indicates that it can behave as both an electron acceptor and an electron donor, the latter role dominating in the absence of any severe steric restraints.[11,12] This being so, it could be argued that part of the chemical shift differences between the β-vinyl protons of the styryl methyl sulfides and sulfonium salts reflects shielding at the β position of the sulfides due to donation of 3p π electrons of divalent sulfur. However, it has been shown[13] in the case of

$$C_6H_5CH_\beta{=}CH_\alpha{-}\ddot{S}CH_3 \longleftrightarrow C_6H_5CH_\beta{}^-{-}CH_\alpha{=}\ddot{S}^+CH_3$$

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(9) J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, **34**, 1099 (1961).

(10) R. T. Hobgood, Jr., and J. H. Goldstein, *Spectrochim. Acta*, **19**, 321 (1963).

(11) L. Goodman and R. W. Taft, *J. Am. Chem. Soc.*, **87**, 4385 (1965).

(12) R. W. Taft and J. W. Rakshys, Jr., *ibid.*, **87**, 4387 (1965).

(13) W. Drenth and A. Loewenstein, *Rec. Trav. Chim.*, **81**, 635 (1962).

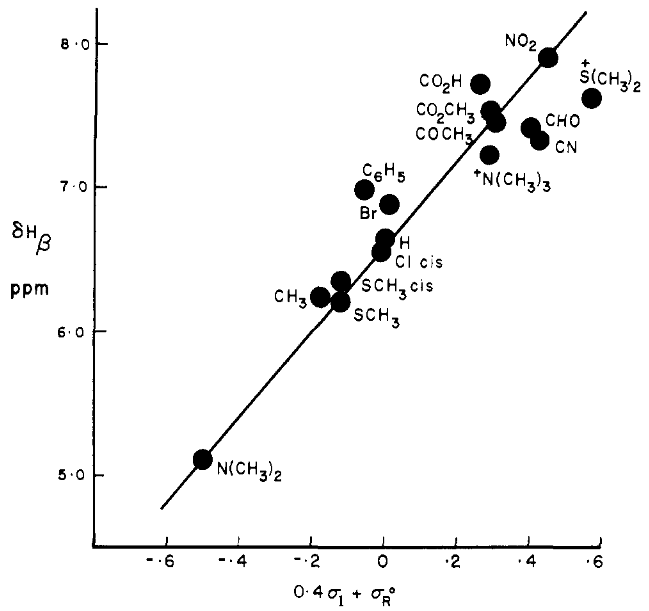

Figure 2. Correlation of chemical shifts of β-vinyl protons of ω-substituted styrenes $C_6H_5CH_\beta{=}CH_\alpha X$, with the inductive and resonance parameters, σ_I and σ_R^0, of the substituent X. Chemical shifts are in parts per million downfield from tetramethylsilane. The σ_I and σ_R^0 values are from fluorine nmr shielding data (*cf.* ref 12 and 15). The chemical shift data are for the *trans* isomers except where indicated (*cf.* ref 14).

acetylenic thioethers $RSC{\equiv}CH$ that the chemical shift of the acetylenic proton is influenced by the inductive effect of the thioalkyl group but not by its resonance effect. To obtain further evidence on this point, we recorded the nmr spectra of the nitrogen analogs of the styryl sulfides and sulfonium salts, namely *trans*-dimethylstyrylamine (XII) and *trans*-trimethylstyrylammonium fluoroborate (XIII). The spectral parameters for XII and XIII are listed in Table I. It is generally recognized that 2p–2p π overlap contributes importantly to the structure of enamines, and this is reflected in the large chemical shift difference (92 cps) between the vinyl protons of XII, the high-field resonance at 5.11 ppm being assigned to the β proton. In contrast, the vinyl protons of the corresponding *cis*- and *trans*-sulfides Ia and Ib are separated by only 19 and 29 cps, respectively (Table I), and the β-vinyl protons of the sulfides are some 60 cps downfield relative to the enamine β proton. Conversion of the enamine XII to the enammonium salt XIII effectively destroys conjugation involving nitrogen orbitals of the p variety, and this is evident in the chemical shifts of the vinyl protons of XIII, which are now separated by only 15 cps. However, conversion of the sulfides to the sulfonium salts IVa and IVb results in a marked *increase* in the chemical shift differences between the α- and β-vinyl protons to 71 and 42 cps, respectively, the β-vinyl protons of IVa and IVb being 25–52 cps downfield relative to the vinyl protons of the enammonium salt. Assuming that electronegativity effects are not widely different between the sulfur and nitrogen compounds, the data indicate that 2p–2p π overlap in the enamine XII is substantially more effective than is 2p–3p π overlap in the sulfides, and that 2p–3d π overlap is more significant in the sulfonium salts than in the sulfides or the nitrogen compounds.

The effect of substituents on the chemical shifts of the vinyl protons of ω-substituted styrenes has been investigated by Kasiwagi and Niwa.[14] These authors report a fair linear correlation between the chemical shift of the β-vinyl proton of $C_6H_5CH_\beta{=}CH_\alpha X$ and the quantity $0.4\sigma_I + 0.7\sigma_R$, where σ_I and σ_R are inductive and resonance parameters obtained from reactivity data for the substituent X. We have attempted to correlate our data similarly, and Figure 2 shows a plot of chemical shift of H_β for a number of ω-substituted styrenes against the quantity $0.4\sigma I + \sigma_{R^0}$, where σ_I and σ_{R^0} are inductive and resonance parameters evaluated from fluorine nmr shielding data of Taft and co-workers.[12,15] The chemical shift data are the results of our own work and that of Kasiwagi and Niwa. Although the plot of Figure 2 shows appreciable scatter, which may be partly due to the fact that we may not have chosen the optimum values for the coefficients of σ_I and σ_{R^0}, it is sufficiently linear to permit the conclusion that the proton shielding at the β position of ω-substituted styrenes can be directly related to the π-electron charge density at hydrogen as determined by the inductive and resonance effects of the ω substituent.

We were interested in determining the influence of *para* substituents on 3d–2p π bonding in dimethylstyrylsulfonium salts. We therefore prepared *cis*- and *trans*-p-methoxystyryl methyl sulfides (IIa and IIb) and *cis*- and *trans*-*p*-nitrostyryl methyl sulfides (IIIa and IIIb), and converted them to the corresponding dimethylstyrylsulfonium salts V–VI. The nmr spectral data for these compounds are summarized in Tables I and II. The methoxy and nitro groups evidently influence the chemical shifts of the vinyl protons in accordance with their well-known conjugation effects. Thus, the α- and the β-vinyl protons of both the sulfides and the salts are deshielded by the *p*-nitro substituent and slightly shielded by the *p*-methoxy substituent relative to the unsubstituted compounds. However, the downfield shifts experienced on converting the sulfides to the sulfonium salts (see Table II) were not dramatically different from those observed for the styryl analogs I and IV. The values of $\Delta\delta(H_\beta)$ are 0.1–0.2 ppm larger for the *p*-nitro analogs and 0.1 ppm smaller for the *p*-methoxy analogs. Furthermore, the $\Delta\delta(H_\beta)$ values are *ca.* 0.1 ppm larger for the *trans* isomers than for the *cis*. While these trends are in the direction one might expect for extended conjugation of the aryl ring with the sulfonium group, they are hardly large enough to bear further comment, especially since the values are subject to some uncertainty due to solvent effects.

The nmr spectra of methyl vinyl sulfide (X) and dimethylvinylsulfonium fluoroborate (XI) are of obvious interest. The vinyl region of both compounds are complex ABC patterns, and an analysis of the spectrum of methyl vinyl sulfide has been reported.[16] The spectrum of dimethylvinylsulfonium fluoroborate was not easily obtained owing to the instability of the compound above 0°,[4b] but the spectrum of the vinyl region revealed eight lines of a badly collapsed ABC multiplet. In order to analyze the spectrum by computer methods,

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[14] H. Kasiwagi and J. Niwa, *Bull. Chem. Soc. Japan*, **36**, 405 (1963).

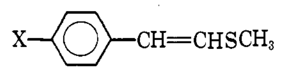
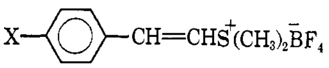
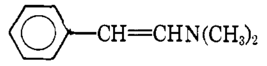
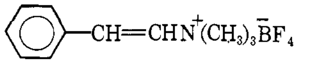
[15] R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Am. Chem. Soc.*, **85**, 709 (1963); **85**, 3146 (1963).

[16] R. T. Hobgood, Jr., G. S. Reddy, and J. H. Goldstein, *J. Phys. Chem.*, **67**, 110 (1963).

an estimate of the coupling constants was made from Schaefer's correlations between electronegativity and vinyl proton couplings.[17] The values obtained using 3.05 as the estimated electronegativity of the dimethylsulfonium group were $J_{gem} = -0.5$ cps, $J_{cis} = +16$ cps, and $J_{trans} = +8.5$ cps. By a reiterative computer technique,[18] a reasonably good fit was obtained with the observed spectrum, the average deviation between observed and calculated transitions being 0.3 cps. The parameters are listed in Table III together with those for methyl vinyl sulfide. The computed coupling constants for the vinylsulfonium salt do not agree individually with those calculated from the electronegativity relationship, but the sum of the coupling constants remains unchanged. A comparison of the chemical shift parameters of methyl vinyl sulfide and dimethylvinylsulfonium fluoroborate shows that the differences in chemical shifts are about the same as observed for the styryl analogs. In particular, the β-vinyl protons of the salt are some 1.2–1.5 ppm downfield relative to the β-vinyl protons of the sulfide, while the α-vinyl and S-methyl protons of the salt are shifted 0.31 and 0.75 ppm downfield relative the sulfide.

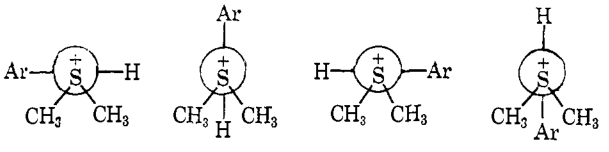
In assigning chemical shifts to the vinyl protons of p-methoxystyryl and p-nitrostyryl derivatives II–III and V–VI, recourse was made to the observation that the S-methyl protons of methyl vinyl sulfide (X) are spin coupled to the β-vinyl protons (J = 0.2–0.4 cps) but not to the α-vinyl proton.[16] This long-range coupling is also evident in the spectra of I and IV (Figure 1) as a broadening of the low-field doublets due to the β-vinyl protons. The line shapes of the high-field doublets are sharp in contrast and show ringing, which is taken as evidence that the α protons are not measurably coupled with the S-methyl protons. Since only one pair of vinyl resonances in each of the compounds II–III and V–VI was broadened, this pair was accordingly assigned to the β-vinyl proton. In some cases, the magnitude of the long-range coupling was directly measurable. Thus, the methyl resonance of IVa was resolved as a doublet, J = 0.2 cps, which appeared as a sharp singlet in the deuterated analog, cis-$C_6H_5CD{=}CHS^+(CH_3)_2{}^-BF_4$. Similarly, the methyl resonance of IIIb was resolved as a doublet, J = 0.4 cps. The magnitude of the coupling is very close to that observed in methyl vinyl sulfide[16] and dimethyl sulfone.[19] A long-range coupling of 0.4 cps was also observed between the N-methyl protons and the β-vinyl proton of the enamine XII.

Table IV. Ultraviolet Spectra of Styryl Sulfides and Related Compounds[a]

No.	X	λ_{max}, mμ	ϵ_{max}	No.	λ_{max}, mμ	ϵ_{max}
						
Ia	H	286	15,500	IVa	261	12,000
IIa	CH_3O	286	25,300	Va	295	13,200
IIb	CH_3O	287	25,000	Vb	304	24,000
IIIb	NO_2[b]	365	13,500	VIb	289	22,400
		246	7,500			
						
XII		299	15,000	XIII	248	15,700

[a] In 95% ethanol. [b] Containing 10% of the cis isomer IIIa.

Since overlap of carbon 2p orbitals with sulfur 3d orbitals implies that the carbon–sulfur bond in vinylsulfonium salts has double bond character, we may inquire as to the angular dependence of 3d–2p π overlap. If, as in π systems of 2p orbitals, the steric requirement for effective overlap is critical, the potential barrier to rotation about the carbon–sulfur bond is likely to be appreciable. In the hope of obtaining evidence on this point, we studied the temperature dependence of the nmr spectrum of dimethyl-cis-p-methoxystyrylsulfonium fluoroborate (Va) over the range -60 to 114°. Nonequivalent S-methyl resonances may be expected if the molecule can be "frozen" in conformation Xa (or Xc).



Xa Xb Xc Xd

Since the single S-methyl resonance remained unchanged from 30 to $-60°$, we considered the possibility that the molecule was "frozen" in conformation Xb (or Xd) in which the methyl groups are magnetically equivalent. The spectrum, however, remained unchanged up to 114°. The lack of any observable temperature dependence in the nmr spectrum of Va is further evidence suggestive of little or no angular dependence for effective π overlap involving 3d orbitals.[3,11,20] The reason for the absence of rigid steric requirements undoubtedly lies in the cylindrical symmetry of 3d atomic orbitals. Rotation about a 3d–2p π bond should not then result in diminished overlap.

Ultraviolet Absorption Spectra. The absorption maxima in the ultraviolet spectra of the styryl derivatives of interest are listed in Table IV. Conjugation effects involving the unshared electron pair on sulfur (or nitrogen) in the sulfides (or enamine) are evident as a shift of the absorption maxima to longer wavelengths relative to styrene (λ_{max} 248 mμ (ϵ_{max} 15,000)). When this effect is removed by conversion to a sulfonium salt (or enammonium salt), a shift of 25–76 mμ to shorter wavelengths occurs except in the case of the p-methoxystyryldimethylsulfonium salts Va and Vb, which show shifts of 9 and 17 mμ to *longer* wavelengths. An argument based on stabilization of excited states by d-orbital resonance not only explains the lower energy transitions observed in the sulfonium salts Va and Vb, but also explains why the styrylsulfonium salt IVa absorbs at longer wavelengths than the corresponding enammonium salt XIII.

Experimental Section

***cis*-Styryl methyl sulfide** (Ia) was prepared in 87% yield by the method of Truce and Simms.[7] To a solution of 7.15 g (0.309 g-atom) of sodium in 250 ml of absolute ethanol at 0° was added 17.2 ml (14.9 g., 0.309 mole) of methanethiol. Phenylacetylene (30 g,

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[17] T. Schaefer, *Can. J. Chem.*, 40, 1 (1962).

[18] R. C. Ferguson and D. W. Marquardt, *J. Chem. Phys.*, **41**, 2087 (1964).

[19] G. M. Whitesides and J. D. Roberts, *J. Phys. Chem.*, **68**, 1583 (1964).

[20] R. M. Moriarty, *Tetrahedron Letters*, 509 (1964).

0.294 mole) was added rapidly, and the mixture was refluxed for 20 hr. The ethanol was removed by evaporation at reduced pressure, and the residue was dissolved in water and petroleum ether (bp 30–60°). The organic extract was dried and evaporated to remove the solvent, and the residue fractionally distilled, giving 38.2 g of product as a pale yellow oil, bp 80–85° (1–2 mm), which was identified as *cis*-styryl methyl sulfide (Ia), lit.[7] bp 110–104° (4 mm). About 10% of the reaction product which distilled over in the early fractions was identified as α-thiomethylstyrene. Its nmr spectrum showed resonances centered at 7.4 ppm for the aromatic protons, 4.85 and 5.39 ppm for the vinyl protons (J = 0.5 cps), and 2.05 ppm for the thiomethyl protons. The vinyl resonance at 5.39 ppm may tentatively be assigned to the proton *cis* to the phenyl ring, and that at 4.85 ppm to the proton *trans* to the phenyl ring on the basis that the anisotropy of the phenyl group serves to deshield the *cis* proton more than the *trans* proton of styryl derivatives (*cf.* Table I).

***cis*-Styryldimethylsulfonium Fluoroborate (IVa).** To a suspension of 1.48 g (0.01 mole) of trimethyloxonium fluoroborate[21] in 50 ml of methylene chloride was added all at once 1.65 g (0.011 mole) of *cis*-styryl methyl sulfide. The mixture was stirred magnetically at room temperature until all the oxonium salt had dissolved ($\sim$45 min). The solvent was then evaporated and the residual oil washed with 25 ml of ether. The residue crystallized immediately and was recrystallized from 30 ml of absolute ethanol to yield 2.05 g (80%) of colorless crystals, mp 100–101° (lit.[8] 103–104°).

***cis*-and *trans*-Styryl Methyl Sulfides (Ia, Ib).** The procedure of Wittig and Schlosser[8] was followed. Methylthiomethyltriphenylphosphonium chloride was prepared from a solution of 63.3 g (0.24 mole) of triphenylphosphine in 100 ml of dry benzene and 0.24 mole of methyl chloromethyl sulfide[22] by refluxing the mixture for 48 hr. The cooled mixture was filtered and the crystalline product washed with acetone to yield 60.1 g (70%) of material, mp 213–214° (lit.[22] mp 220–222° after recrystallization from chloroform and ethyl acetate).

To 8.96 g (25 mmoles) of pulverized methylthiomethyltriphenylphosphonium chloride in a 100-ml flask having a long and narrow neck was placed 50 ml of dry tetrahydrofuran. The flask was flushed with a gentle stream of dry nitrogen as 18.5 ml (25 mmoles) of phenyllithium in diethyl ether was added dropwise with shaking. The phosphonium ylide formed exothermically with the development of a deep red color. After 15 min, an ether solution of benzaldehyde (25 mmoles) was added dropwise to the mixture, whereupon the red color faded rapidly. The flask was then sealed under an atmosphere of nitrogen and heated for 52 hr at 55°. At the end of this time the flask was opened and the solvent removed at reduced pressure. The residue was dissolved in 150 ml of ether and 75 ml of water. The ether extract was evaporated and 50 ml of petroleum ether (bp 30–60°) was added to the residue. Triphenylphosphine oxide, which crystallized out, was separated by filtration. The filtrate was evaporated and the residue distilled to give 2.83 g (76%) of product, bp 72–76° (0.5–1.0 mm). Analysis by gas phase chromatography and nmr gave the product composition as 47% *cis*- and 53% *trans*-styryl methyl sulfides.

***cis*- and *trans*-Styryl-d_1 Methyl Sulfide.** Benzaldehyde-d_1 was prepared as described by Wiberg[23] by the reduction of benzil with lithium aluminum deuteride followed by oxidation of the dihydrobenzoin-d_2 with lead tetraacetate. The aldehyde was isolated and stored as the bisulfite addition complex.

To 5.3 g (25 mmoles) of the bisulfite complex was added 33 ml of 10% sodium carbonate solution and 30 ml of ether. The mixture was shaken, and the ether layer was separated, dried, and evaporated to about 10 ml. This solution was added to the phosphonium ylide as described in the preparation of Ia and Ib. There was obtained 2.93 g (78%) of an almost colorless oil, bp 72–76° (1 mm). Nmr analysis gave the product composition as 50% *cis*- and 50% *trans*-styryl methyl sulfides.

The nmr spectrum of the mixture differed from that of the unlabeled material (I) in the absence of resonances due to protons of chemical shifts 6.20 and 6.34 ppm and the appearance of broad triplets ($J \sim$ 1.5 and 2.5 cps) at 5.98 and 6.68 ppm.

***cis* and *trans*-styryldimethylsulfonium fluoroborates (IVa and IVb)** were prepared as an oily mixture by methylation of the *cis–trans* mixture of sulfides Ia and Ib as described for the pure *cis* isomer IVa. The corresponding labeled sulfonium fluoroborates were similarly prepared from the mixture of deuterium-labeled sulfides.

***trans-p*-Methoxystyryl methyl sulfide (IIb)** was prepared as described for the mixture of *cis*- and *trans*-styryl methyl sulfides using *p*-anisaldehyde in place of benzaldehyde. Distillation of the crude product gave 6.8 g (56%) of a colorless oil, bp 110–112° (1 mm), which crystallized on cooling. Recrystallization from petroleum ether gave colorless plates, mp 70–71.5°

Anal. Calcd for $C_{10}H_{12}SO$: C, 66.67; H, 6.71. Found: C, 66.68; H, 6.73.

The nmr spectrum of IIb in carbon tetrachloride showed the aromatic protons as an A_2B_2 multiplet centered at 6.92 ppm and an AB quartet for the vinyl protons having chemical shifts of 6.47 and 6.20 ppm, and J = 16 cps. On the basis of the magnitude of the coupling constants, the compound was assigned the *trans* configuration. The methoxyl protons and thiomethyl protons appeared as single three-proton resonances at 3.70 and 2.25 ppm, respectively.

***trans-p*-Methoxystyryldimethylsulfonium Fluoroborate (Vb).** A suspension of 0.82 g of trimethyloxonium fluoroborate in 50 ml of methylene chloride containing 1.0 g of *trans-p*-methoxystyryl methyl sulfide was stirred magnetically at room temperature for 2 hr, during which time the product separated as a white crystalline mass. The solvent was evaporated and the residue recrystallized from 95% ethyl alcohol, giving 1.0 g (64%) of colorless needles, mp 158–159°.

Anal. Calcd for $C_{11}H_{15}SBOF_4$: 46.83; H, 5.36. Found: C, 46.10; H, 5.34.

The nmr spectrum of Vb in dimethyl sulfoxide showed an A_2B_2 multiplet for the aromatic protons centered at 7.34 ppm overlapping with an AB quartet due to the vinyl protons having chemical shifts 6.97 and 7.64 ppm and J = 15 cps. The methoxyl and dimethylsulfonium protons appeared as single resonances at 3.80 and 3.04 ppm, respectively.

***cis-p*-Methoxystyryl methyl sulfide (IIa)** was prepared by the addition of methanethiol to *p*-methoxyphenylacetylene[24] in the manner described for Ia. There was obtained 24.5 g of product, bp 104–108° (1–2 mm), from 22 g of *p*-methoxyphenylacetylene. The product was analyzed by gas chromatography and nmr and shown to be 80% IIa and 20% a second component which was identified as α-thiomethyl-*p*-methoxystyrene. Fractional distillation gave pure IIa, bp 84–85° (0.01–0.03 mm).

Anal. Calcd for $C_{10}H_{12}SO$: C, 66.67; H, 6.71. Found: C, 66.71; H, 6.76.

The nmr spectrum of IIa in carbon tetrachloride showed the aromatic protons as an A_2B_2 multiplet centered at 7.1 ppm, the vinyl protons as an AB quartet having chemical shifts of 6.23 and 5.90 ppm, J = 11 cps, and methoxyl and thiomethyl protons as three-proton singlets at 3.63 and 2.22 ppm, respectively.

The nmr spectrum of α-thiomethyl-*p*-methoxystyrene showed resonances centered about 7.1 ppm for the aromatic protons, at 4.83 and 5.30 ppm for the vinyl protons (J = 0.5 cps), and at 2.20 ppm for the thiomethyl protons. The vinyl resonance at 5.30 ppm is assigned to the proton *cis* to the phenyl group, and that at 4.83 ppm to the proton *trans* to the phenyl group.

***cis-p*-Methoxystyryldimethylsulfonium fluoroborate (Va)** was prepared by the methylation of *cis-p*-methoxystyryl methyl sulfide with trimethyloxonium fluoroborate in the manner described for IVa. The crude product was recrystallized from 95% ethanol and from a methylene chloride–ether mixture, and had mp 79–82.5°.

Anal. Calcd for $C_{11}H_{15}SBOF_4$: C, 46.83; H, 5.36. Found: C, 46.82; H, 5.33.

The nmr spectrum of Va in methylene chloride showed an A_2B_2 multiplet centered at 7.25 ppm due to the aromatic protons, a one-proton doublet at 7.53 ppm (J = 10 cps), a one-proton doublet at 6.32 ppm (J = 10 cps), a three-proton singlet at 3.80 ppm, and a six-proton singlet at 3.08 ppm.

***p*-Nitrostyryl Methyl Sulfide (III). Method I.** Compound III was prepared by the Wittig reaction as described for I with the following modifications. *p*-Nitrobenzaldehyde (9.9 g) was added as the solid to a solution of the phosphonium ylide prepared from 74 mmoles of phenyllithium in 70 ml of ether and 25.9 g (75 mmoles) of methylthiomethyltriphenylphosphonium chloride in 150 ml of tetrahydrofuran. The mixture was stirred and refluxed in an atmosphere of nitrogen for 24 hr. The product was isolated as described for I except that, since the product was sparingly soluble in petroleum ether, it was separated from triphenylphosphine oxide by

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(21) H. Meerwein, G. Hinz, P. Hofmann, E. Kroning, and E. Pfeil, *J. Prakt. Chem.*, **147**, 257 (1937).

(22) H. Böhme, H. Fischer, and R. Frank, *Ann.*, 563, 54 (1949).

(23) K. Wiberg, *J. Am. Chem. Soc.*, **76**, 5371 (1954).

(24) A. D. Allen and C. D. Cook, *Can. J. Chem.*, 41, 1084 (1963).

continuous extraction with petroleum ether (bp 30–60°) in a Soxhlet apparatus. The crude product thus obtained was distilled at 110° (1 mm) in a Hickman still and recrystallized from hexane to give 5.6 g of intense yellow crystals, mp 57–83°. The nmr spectrum of the product showed it to be a mixture of 45% *trans*- and 55% *cis*-*p*-nitrostyryl methyl sulfides. The vinyl protons of the *cis* isomer have virtually coincident chemical shifts (6.4 ppm).

Anal. Calcd for $C_9H_9SNO_2$: C, 55.38; H, 4.65. Found: C, 55.31; H, 4.70.

Method II. *p*-Nitrophenylacetylene was prepared by the method of Cristol and Begoon.[25] This required the preparation of *p*-nitrocinnamic acid dibromide[26] which was converted to the acetylene *via cis*-*p*-nitro-β-bromostyrene.

To a solution of 0.71 g (0.03 g-atom) of sodium in 25 ml of absolute alcohol was added 2 ml of methanethiol at 0°, followed by 3.0 g (0.02 mole) of *p*-nitrophenylacetylene. An exothermic reaction took place and the mixture darkened perceptibly. After 30 min, the ethanol was evaporated at reduced pressure and the residue taken up in water and ether (150 ml). The ether extract was dried and evaporated, and the crude product was distilled in a Hickman still at 110–170° (1 mm), giving 2.1 g (52%) of product, mp 76–84°. The nmr spectrum of the product showed it to be predominantly (90%) *trans*-*p*-nitrostyryl methyl sulfide (IIIb) and 10% *cis* isomer IIIa.

p-**Nitrostyryldimethylsulfonium fluoroborate** (VI) was prepared from a *cis–trans* mixture of III as described for IVa except that the reaction time was extended to 2 hr. The crude product was crystallized successively from ethanol and acetone–ether to give sparingly soluble almost colorless crystals, mp 172–173°, identified by nmr as the *trans* isomer VIb.

Anal. Calcd for $C_{10}H_{12}SBNO_2F_4$: C, 40.42; H, 4.07. Found: C, 40.44; H, 4.11.

A more soluble fraction, mp 120–155°, was isolated; this was identified similarly as a *cis–trans* mixture.

Dimethylethylsulfonium fluoroborate (IX) was prepared from methyl ethyl sulfide by methylation with trimethyloxonium fluoroborate, and was isolated as hygroscopic crystals. The nmr spectrum of the product was entirely consistent with the structure as IX.

Dimethylvinylsulfonium fluoroborate (XI) was prepared by alkylation of methyl vinyl sulfide with trimethyloxonium fluoroborate at 0° or below. The salt proved to be very unstable above 0°, rapidly discoloring. Hence it was not isolated in pure form. It showed no absorption maximum in the ultraviolet above 200 mμ. The nmr spectrum of the product was consistent, however, with the assigned structure XI.

Dimethylstyrylamine (XII) was prepared by the method of Mannich and Davidson.[27] To a mixture of 90 g (0.75 mole) of freshly distilled phenylacetaldehyde and 75 g of anhydrous potassium carbonate cooled to −60° was added with stirring 67.5 g (1.50 moles) of anhydrous dimethylamine in a 15-min period. The reaction mixture was allowed to warm to room temperature and was stirred for 15 hr. An equal volume of anhydrous ether was added and the potassium carbonate filtered off. The ether was removed by evaporation and the residue was fractionally distilled. About 10 ml of forerun was discarded and the main fraction (55 g) distilled as a colorless oil, bp 75–78° (1 mm) (lit.[28] 105–110° (20–22 mm)).

The nmr spectrum XII in deuteriochloroform showed a complex five-proton resonance centered at 7.1 ppm for the aromatic protons, a broadened one-proton doublet at 5.11 ppm, $J = 13.9$ cps, a one-proton doublet at 6.65 ppm, $J = 13.9$ cps, and a six-proton singlet at 2.63 ppm. Under high resolution, the singlet at 2.63 ppm was resolved as a doublet, $J = 0.4$ cps. The *trans* configuration was assigned to XII from the magnitude of the vinyl proton coupling constant.

Trimethylstyrylammonium Fluoroborate (XIII). To 22 g (0.148 mole) of trimethyloxonium fluoroborate was added a solution of 21 g (0.143 mole) of XII in 200 ml of methylene chloride. The mixture was stirred magnetically at room temperature for 20 hr. About 100 ml of solvent was removed at reduced pressure, and the residual suspension was filtered and washed twice with 50 ml of methylene chloride and 50 ml of ether. There was obtained 28 g (0.112 mole, 79%) of a white crystalline solid, mp 197–200°. Recrystallization from acetone gave material, mp 200–203°.

Anal. Calcd for $C_{11}H_{16}BNF_4$: C, 53.04; H, 6.47. Found: C, 53.31; H, 6.58.

The nmr spectrum of XIII in nitromethane had a complex five-proton resonance centered at 7.5 ppm, a broadened AB quartet for the vinyl protons with chemical shifts at 7.23 and 6.96 ppm, $J = 15$ cps, and a nine-proton singlet at 3.48 ppm. The compound was assigned the *trans* configuration from the magnitude of the vinyl proton coupling constant. The broadening observed for the vinyl resonances may be attributed to electrical quadrupole relaxation of ^{14}N.

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