mp 92–93°). The values for disproportionation per cent of 37–46% mentioned for **13** and **14** (see discussion) were obtained similarly.

C. Equilibration of 13′ and 14′.—A solution of the acid **13** (1.04 g, 4.39 mmol) in H_2O (50 ml) containing NaOH (0.176 g, 4.40 mmol) was heated at 61° (pH ~8). From time to time, 10 ml was withdrawn, saturated with NaCl, and extracted with $CHCl_3$. Removal of $CHCl_3$ gave **3**, which was recrystallized from Me_2CO–Et_2O and then identified by ir and melting point. Compound **14** was treated similarly, and disproportionation per cent was calculated as described above (previous section C). The results based on the weight of **3** isolated are shown in Table III.

D. Disproportionation of Salts 11′–14′.—For the preparation of the sodium salts **11′–14′** of the acids **11–14**, illustratively, a solution of NaOMe in MeOH (2.2 ml of 1.0 *N*) was added to **14** (0.55 g, 2.2 mmol) in MeOH (3 ml) to a pH of 6.8–7.0. Addition of dry Me_2CO then immediately precipitated white **14′**. Decantation and drying at 0.1 mm gave **14**, which was washed with acetone and then was dried again at 0.1 mm under vacuum, mp 188° dec. Compounds **11′**, **12′**, and **13′** were obtained similarly, except that with **11′** and **12′** dry Et_2O was used instead of Me_2CO because **11′** and **12′** are slightly soluble in Me_2CO. Melting points follow: **11′**, 280° dec; **12′**, 120–122°; and **13′**, 215° dec. The purity of **11′–14′** was confirmed by checking absence of any **3** by tlc on alumina.

The disproportionation results of Table IV were obtained using ~1 mmol in 10 ml of H_2O of **11′–14′** (or **11–14** where specified). Illustratively, a solution of **14′** (273 mg, 1 mmol) in 10 ml of H_2O was heated at 61 ± 0.5° in a constant-temperature bath. From time to time, 5 μl was withdrawn by a microsyringe and spotted for tlc on an alumina layer.[23] The spot for disulfide **3** then was observed, and the time was reported in Table IV at which the area no longer increased.

Registry No.—**2**, 34915-80-5; **3**, 638-44-8; **4**, 34915-82-7; **11**, 34915-83-8; **11′**, 34915-84-9; **12**, 34915-85-0; **12′**, 34915-86-1; **13**, 34915-87-2; **13′**, 34915-88-3; **14**, 34915-89-4; **14′**, 34915-90-7.

Electron-Accepting Through-Conjugation Effects in Organosulfur Compounds

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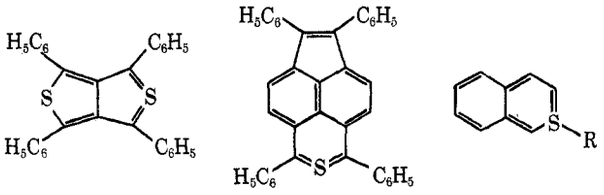
The importance of cyclic conjugation involving (p → d)-π bonding has been investigated in attempted syntheses of thianaphthalene derivatives and in the transmission of substituent effects through sulfur in *S*-phenacyl-*S*-phenyl-*S*-methylsulfonium salts as evaluated from pK_a measurements. No evidence was obtained to support the concept of through-conjugation in the systems chosen for study.

There now exists a large body of experimental evidence regarding the electron-accepting properties of sulfur. These properties are generally described as valence-shell expansion by π bonding in which overlap occurs between a vacant 3d sulfur orbital and a filled 2p orbital of an adjacent first-row atom.[2] The importance, however, of 3d orbitals in supporting electron delocalization *through* sulfur remains a controversial issue. For example, the question of participation of 3d orbitals in the bonding of thiophene has been frequently discussed,[3] and it now appears that 3d and higher energy orbitals contribute very little to the bonding in thiophene in its ground state.[4] Positive evidence for through-conjugation by way of sulfur stems from the synthesis of stable sulfur heterocycles of the type **1**,[5] **2**,[6] **3**,[7] and **4**[8] in which sulfur may be



1 **2** **3**

viewed as quadricovalent in a delocalized π system. However, the stability of thiaaromatic compounds varies widely. For example, thiabenzenes **5**[7,9] and thianaphthalenes **3**[7] vary in stability according to the nature and position of substituents; the thiabenzene 1-oxide **6** is remarkably stable[9] although the chemical behavior of **6** more closely resembles that expected for an ylide structure than for a delocalized benzenoid structure. Likewise, the aromaticity of thiaphenalenes **2** is open to question,[3b] while thiepin dioxide **7** and related compounds, which are formally 6-π-electron systems related to tropone, do not appear to possess aromatic character.[10] The acidity of the cyclic sulfone **8** is unexceptional relative to that of the open-chain analog **9**, and this suggests that the carbanion derived from **8** lacks aromaticity.

While the experimental evidence is both positive and negative on the issue of through conjugation, theoretical arguments are not clear-cut either. Calculations illustrating the importance of cyclic conjugation

(1) The authors wish to gratefully acknowledge the support received for this work from the National Science Foundation (GP 7278 and GP 12828).

(2) For reviews on the topic of sulfur bonding see (a) G. Cilento, *Chem. Rev.*, **60**, 147 (1960); (b) A. B. Burg in "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press, New York, N. Y., 1961, pp 30–40; (c) C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York, N. Y., 1962; (d) D. T. Clark in "Organic Compounds of Sulfur, Selenium, and Tellurium," Special Publication of the Chemical Society, D. H. Reid, Ed., London, 1970; (e) K. A. R. Mitchell, *Chem. Rev.*, **69**, 157 (1969).

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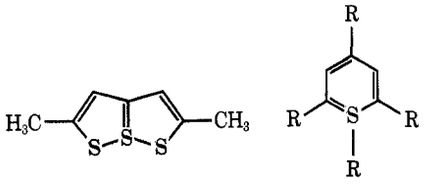
(9) (a) A. G. Hortmann, *J. Amer. Chem. Soc.*, **87**, 4972 (1965); (b) Y. Kishida and J. Ide, *Chem. Pharm. Bull.*, **15**, 360 (1967); (c) B. Holt, J. Howard, and P. A. Lowe, *Tetrahedron Lett.*, 4937 (1969); (d) A. H. Hortman and R. L. Harris, *J. Amer. Chem. Soc.*, **92**, 1803 (1970).

(10) W. L. Mock, *J. Amer. Chem. Soc.*, **89**, 1281 (1967); W. E. Truce and F. J. Lotspeich, *ibid.*, **78**, 848 (1956); V. J. Traynelis and R. F. Love, *Chem. Ind. (London)*, 439 (1958); *J. Org. Chem.*, **26**, 2728 (1961); H. Hofmann and H. Westernacher, *Angew Chem., Int. Ed. Engl.*, **5**, 958 (1966).



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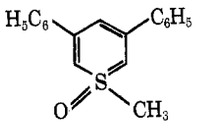

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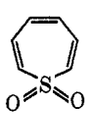

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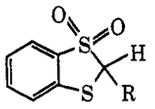


8

$C_6H_5SO_2CH_2SC_6H_5$

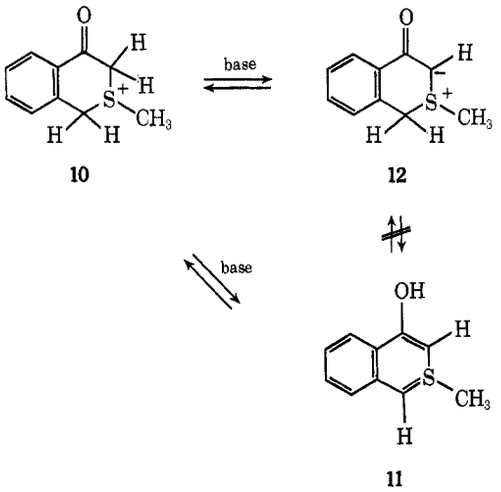
9

through 3d orbitals of second-row elements has been advanced by Craig[11] and questioned by Dewar.[12] Their arguments were initially concerned with the question of delocalization in phosphonitrilic compounds, but they may be applied equally well to other systems which may in principle support (p → d)-π bonding.[13]

A somewhat different approach has been advanced by Price[7c] to explain the benzenoid properties of compounds of type **3**. He has suggested that the delocalized π system of **3** may utilize a sulfur 3p and carbon 2p orbitals with the nonbonding electron pair on sulfur promoted to a 3d orbital. The heterocycle would by this theory be planar and would accordingly be destabilized by bulky substituents ortho to the heteroatom that would force nonplanarity on the ring system. Evidence in support of this theory has been given.[7c]

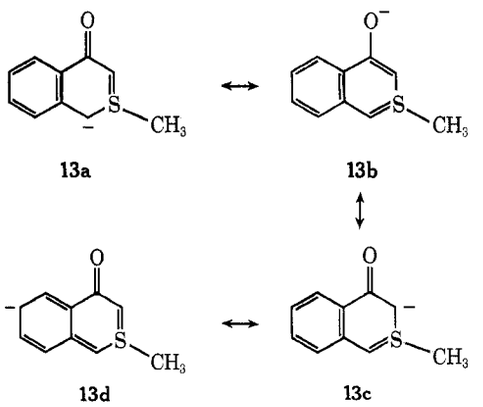
It was with this background to the topic of through-conjugation that we initiated an investigation designed to test the driving force for aromaticity in thianaphthalene derivatives and to measure the transmission of substituent effects in the C–S–C system which we describe in this paper.

Thianaphthalene–Ylide Tautomerism.—In order to contribute to the question of thiabenzene aromaticity, an investigation of the behavior of 2-methylisothiachroman-4-one fluoroborate (**10**) with base was undertaken. We reasoned that, if resonance stabilization is significant in a cyclic system of ten π electrons delocalized through sulfur and nine carbons, then treatment of **10** with base might afford the thianaphthol derivative **11**, or an equilibrium mixture of **11** and the cyclic ylide **12**. When **10** was treated with an equivalent of aqueous sodium hydroxide, sodium methoxide in ether–methanol, or sodium hydride in tetrahydrofuran, a single compound was isolated in high yield (90%). This compound was clearly not the thianaphthol derivative **11** but had all the characteristics expected of a β-carbonyl-stabilized sulfonium ylide **12**. Thus, its infrared spectrum showed a strong band at 1510 cm^{-1} typical of β-keto ylides;[14] it was formed from **10** *reversibly* by the addition of appropriate amounts of acid or base, and its nmr spectrum in various solvents listed in Table I leaves no doubt that its structure is correctly assigned as **12**. In particular, the broad temperature-dependent resonance near 3.7 ppm is typical of an exchange-broadened resonance of an ylide proton,[15] and the nonequivalence of the benzylic protons establishes that the structure is nonplanar. No resonances that could be ascribed to the thianaphthol **11** were evident and any rapidly established equilibration between **11** and **12** is ruled out by the observation that the benzylic protons of **12** are coupled (J = 15.8 Hz) and are not exchanged by the addition of D_2O to solutions of **12** in DMSO-d_6 or acetonitrile. In contrast, the methine proton of **12** is exchanged instantly, typical of ylide behavior.[16]



10 12 11

Rapid exchange of the benzylic protons of **12** was observed, however, on addition of aqueous base (NaOD–D_2O) to solutions of **12** in DMSO-d_6. Enhanced acidity of the benzylic protons is anticipated if the resulting anion can support electron delocalization suggested by structures **13a**, **13b**, **13c**, and **13d**. To obtain



13a 13b 13d 13c

(11) (a) D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J. Chem. Soc.*, 332 (1954); (b) D. P. Craig and E. A. Magnusson, *ibid.*, 4895 (1956); (c) D. P. Craig, *ibid.*, 997 (1959); D. P. Craig and N. L. Paddock, *ibid.*, 4118 (1962).

(12) M. J. S. Dewar, E. A. C. Lucken, and M. A. Whitehead, *J. Chem. Soc.*, 2423 (1960); M. J. S. Dewar and V. P. Kubba, *J. Amer. Chem. Soc.*, **82**, 5685 (1960).

(13) Conjugation effects in the related system N–Si–N are discussed by C. H. Yoder and J. J. Zuckerman, *Inorg. Chem.*, **6**, 103 (1967).

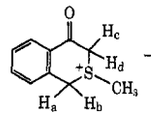
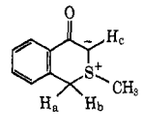
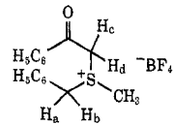
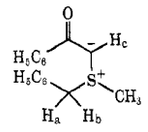
(14) A. J. Speziale and K. W. Ratts, *J. Amer. Chem. Soc.*, **85**, 2790 (1963); H. Nozaki, D. Tunemoto, Z. Morita, K. Nakamura, K. Watanabe, M. Takaku, and K. Kondo, *Tetrahedron*, **23**, 4279 (1967).

(15) S. H. Smallcombe, R. J. Holland, R. H. Fish, and M. C. Caserio, *Tetrahedron Lett.*, 5987 (1968).

(16) H. Nozaki, D. Tunemoto, S. Matubara, and K. Kondo, *Tetrahedron*, **23**, 545 (1967); F. J. Randall and A. W. Johnson, *Tetrahedron Lett.*, 2841 (1968); H. J. Bestman, H. G. Liberda, and J. P. Snyder, *J. Amer. Chem. Soc.*, **90**, 2963 (1968); P. Crews, *ibid.*, **90**, 2961 (1968).

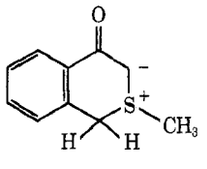
TABLE I

NUCLEAR MAGNETIC RESONANCE SPECTRA OF β-KETOSULFONIUM SALTS AND YLIDES[a]

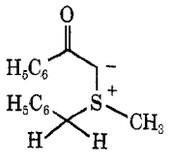
Compd		$\delta_{aromatic}$	δ_{H_a}[b]	δ_{H_b}[b]	$\Delta\nu_{ab}$	J_{ab}	δ_{H_c}	δ_{H_d}	J_{cd}	J_{ac}	δ_{SCH_3}	Solvent
10		7.67 (3 H) 8.05 (1 H)	4.91	4.56	21.2	16.6	4.45[b]	4.09[b]	18.0	2.0	2.83	CH_3CN
		7.58 (3 H) 7.92 (1 H)	4.98	4.64	20.1	16.0	4.59[b,c]	4.27[b]	18.0	*c*	2.80	CH_3SOCH_3
			5.07	4.69	22.4	16.2					2.93	D_2O[e]
12		7.39 (3 H) 8.16 (1 H)	3.93	4.51	34.9	15.8	3.75[d]				2.42	$CDCl_3$
		7.32 (3 H) 7.75 (1 H)	4.16	4.54	22.5	15.8	3.63[d]				2.35	CD_3SOCD_3
		7.40 (3 H) 8.00 (1 H)	4.49	3.97	31.6	15.8	2.53[d]				2.35	CH_3CN
		7.5 (8 H) 8.0 (2 H)	4.8	4.8			5.7	5.7			2.90	CD_3SOCD_3
14		7.3 (8 H) 7.75 (2 H)	4.85	4.42	25.7	12.0	4.11[d]				2.85	$CDCl_3$
		7.28 (8 H) 7.63 (2 H)	4.86	4.30	33.4	12.0	4.03[d]				2.80	CD_3SOCD_3
			4.98	4.00	58.8	12.0	4.00[d]				2.51	C_6H_6

[a] Chemical shifts are in parts per million downfield from TMS as internal standard; coupling constants are in hertz measured at 60 MHz. [b] Part of AB quartet. [c] Broadened line shape of δ_{H_c} obscured long-range coupling J_{ac}. [d] Exchange broadened. [e] External reference, TMS.

evidence on this point, a comparison was made of the acidities of the benzylic protons of **12** and the benzylic protons of the related acyclic ylide **14**, which cannot



12

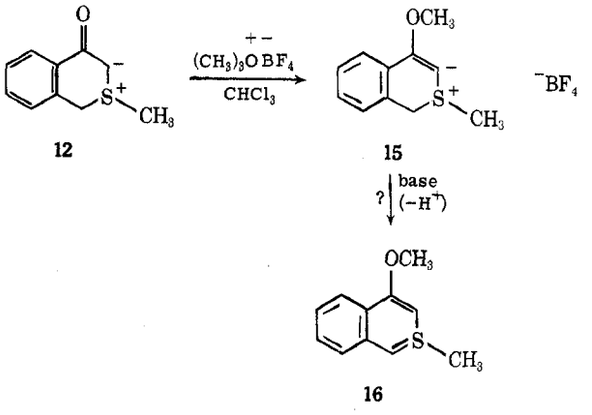


14

form an anion stabilized by cyclic conjugation. Qualitatively, there was no apparent difference in the behavior of **12** and **14** with base. When a mixture of **12** and **14** in DMSO-d_6 was allowed to compete for less than an equivalent amount of NaOD–D_2O, the nmr spectrum of the mixture showed changes in the benzylic AB quartets of *both* ylides. The progressive changes observed in both ylides with increasing added base showed that the exchange rates were not remarkably different and we are forced to conclude that the benzylic protons of **12** are not unusually acidic relative to those of **14**. The significance of delocalization implied in **13** is therefore questionable.

The cyclic ylide **12** was converted to the methyl ether derivative **15** by O-methylation with trimethyloxonium fluoroborate. The behavior of **15** with base is of some importance to the question of cyclic conjugation, since it is conceivable that a stable thianaphthalene derivative **16** might be formed.

No significant reaction occurred on treating **15** with sodium methoxide in methanol or with sodium hydride suspended in dry ether. However, potassium *tert*-butoxide in DMSO and sodium hydride in dry THF both reacted with **15** to give highly colored reaction mixtures from which an amorphous, reddish-brown solid could be isolated. This material defied purification; it could not be recrystallized and its nmr spectrum in chloroform was broad and ill-resolved sug-



12 **15** **16**

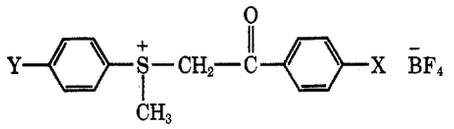
gesting a polymeric composition. On following the exchange of **15** with NaOD–D_2O in acetonitrile–DMSO-d_6 by nmr, it was observed that the *S*-methyl, vinylic, and benzylic protons exchanged at comparable rates. We conclude from these experiments that, if a compound of structure **16** is formed, it is not notably stable and rapidly reprotonates.

Transmission of Substituent Effects in β-Ketosulfonium Ylides.—Several comparative studies of the pK_a values of nitrogen, phosphorus, arsenic, and sulfur onium compounds have been reported.[17–20] The order of ylide stability may be established from the data as N < As < P < S, which parallels the order of increasing importance of (p → d)-π bonding. Linear free energy relationships have also been established from pK_a's of structures **17**,[18] **18**,[19] and **19**.[20] Thus, transmission of the electrical effects of the phenacyl X substituent in **17**, **18**, and **19** follows a Hammett $\rho\sigma$ relationship with ρ = +2.1, +2.3, and +2.3, respectively. It will be noted that there is no direct conjugation of the X sub-

(17) A. W. Johnson and R. T. Amel, *Can. J. Chem.*, **46**, 461 (1968).
(18) K. W. Ratts and A. N. Yao, *J. Org. Chem.*, **31**, 1185 (1966).
(19) S. Fliszar, R. F. Hudson, and G. Salvadori, *Helv. Chim. Acta*, **46**, 1580 (1963).
(20) W. G. Phillips and K. W. Ratts, *J. Org. Chem.*, **35**, 3144 (1970).

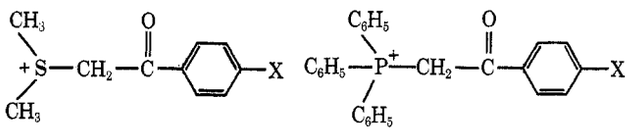
TABLE II

PHENACYLSULFONIUM FLUOROBORATE SALTS[a]

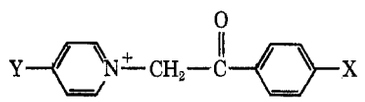


Compd 20	Y	X	Mp, °C	pK_a	δ_{CH_2},[b] ppm	δ_{SCH_3},[b] ppm	δ_{aryl},[c] ppm	δ_X, ppm	λ_Y, ppm	λ_{max},[d] nm	λ_{max},[e] nm
					Series 1						
a	H	H	102–103	7.32	5.86	3.35	7.5–8.3			297	244
b	H	Br	164–166	6.73	5.86	3.36	7.6–8.3			295	268
c	H	Cl	146–147		5.87	3.37	7.6–8.3			305	266
d	H	CH_3	137.5–138.5	7.63	5.86	3.46	7.3–8.3	2.41		299	266
e	H	OCH_3	137–138	8.13	5.82	3.45	7.0–8.3	3.87		305	243
f	H	NO_2	173.5–175.5	5.79	5.92	3.36	7.2–8.4			343	266
					Series 2						
a	H	H	102–103	7.32	5.86	3.35	7.5–8.3			297	244
g	Br	H	133–135	6.89	5.90	3.38	7.6–8.3			297	245
h	Cl	H	123–125		5.92	3.40	7.6–8.3			298	240
i	CH_3	H	135–137	7.59	4.35	3.45	7.4–8.2		2.42	296	253
j	CH_3O	H	105–107	7.79	3.88	3.34	7.2–8.2		3.88	295	251
k	NO_2	H	129–131	6.19	5.96	3.44	7.5–8.2			283	255

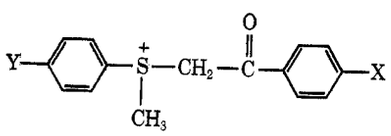
[a] Satisfactory elemental analyses were obtained for all compounds with the exception of X = Br which was consistently 3% high in carbon for no apparent reason. [b] In DMSO-d_6 at 60 MHz; singlet; chemical shift relative to TMS internal standard. [c] Multiplet. [d] Uv of ylide in aqueous base. [e] Uv of salt in aqueous solution.



17 18

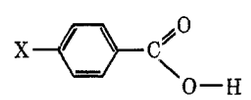


19



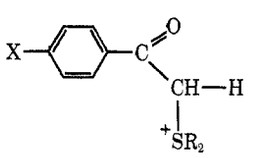
20

stituent with the carbanion center, and in this respect phenacyl ylides parallel substituted benzoic acids (*cf.* **21** and **22**). A linear correlation between the pK_a's of



$\rho = 1$

21



$\rho = 2$

22

phenacylsulfonium ylides and benzoic acids in which there is no enhanced resonance effect is not then surprising.

Of greater interest to the present study is the transmission of substituent effects *through* sulfur in ylides derived from sulfonium salts of type **20**. If the electronic effects of the Y substituent in the ylide derived from **20** can be transmitted through sulfur by d-orbital interactions with the adjacent p–π system, this should be evidenced by an enhanced resonance effect of Y on the acidity of **20**. For example, if resonance stabilization of the nitro-substituted ylide **23** is important due to contributions from the hybrid structure **23b** involving conjugation through sulfur, this should be reflected in a low basicity for **23**, or a low pK_a for its conjugate acid **20** (Y = NO_2).

To test these concepts, we prepared two series of salts of type **20** and determined their pK_a's. In series 1, the Y substituent was held at Y = H as the X substituent was varied from H to CH_3, Br, OCH_3, and NO_2. In series 2, X was held at X = H as Y was varied. The physical and spectral properties of these compounds are summarized in Table II. The pK_a values for the salts in aqueous solution were determined spectrophotometrically and the values obtained are listed in Table II. The acidity data was analyzed by the Ehrenson–Brownlee–Taft dual-parameter equation[21]

$$pK_a = \rho_I\sigma_I + \rho_R\sigma_R$$

where σ_I and σ_R are inductive and resonance substituent constants, respectively, and ρ_I and ρ_R are essentially weighting factors that reflect the relative importance of inductive and resonance effects in the given system. The values of ρ_I and ρ_R were obtained from the best fit of the data to the dual-parameter equation. A reiterative computer procedure was employed to obtain the best fit, which included variation of the substituent constants to include σ_I values, σ_R^+, σ_R, σ_R^0, and σ_R^-.

For series 1 in which X is varied and Y = H, the best fit was obtained using σ_R. The ρ_I and ρ_R values were found to be essentially equal and the data corresponds therefore to a straightforward Hammett $\rho\sigma$ relationship in which ρ = +2.0 (Figure 1). This parallels the acidity of the related compounds **17**, **18**, and **19** for which ρ = 2.1–2.3. Transmission of substituent effects through the phenacyl ring as measured by the ρ value

(21) S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, *Prog. Phys. Org. Chem.*, **10**, in press.

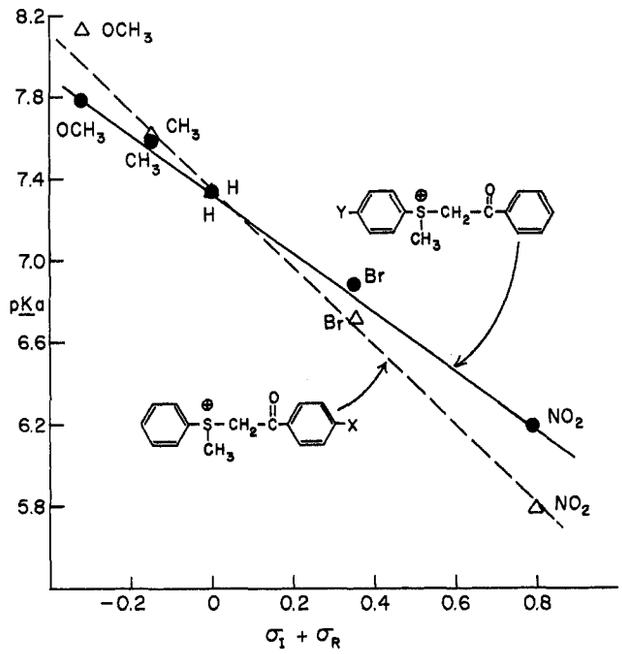
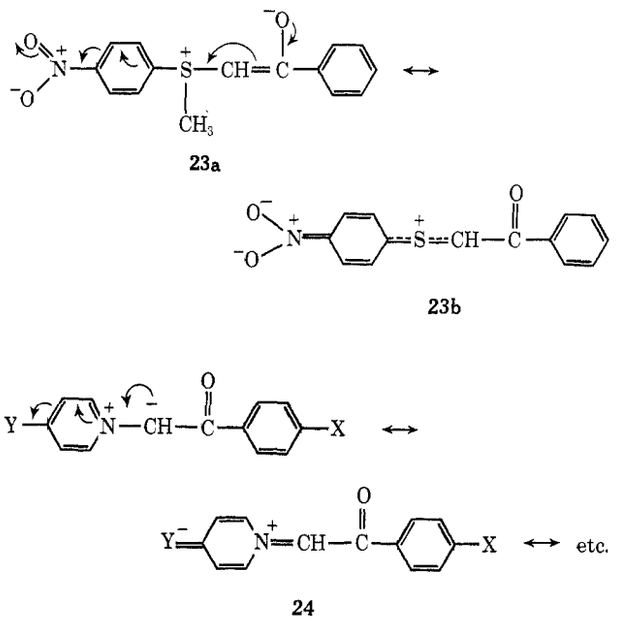


Figure 1.—Plot of pK_a's of substituted β-ketosulfonium salts **20** against inductive and resonance parameters of the substituents X or Y. The data refer to aqueous solutions at 25°, △ to series 1, Y = H, and ● to series 2, X = H.

is therefore independent of the nature of the onium group and is roughly twice as effective as in the benzoic acids (ρ = 1 by definition). However, the pK_a's of the pyridinium salts **19**[20] are higher by about 2.6 pK units than the pK_a's of the structurally related sulfonium salts **20**. This notable difference provides one of the strongest arguments for the involvement of d orbitals in the bonding of sulfonium ylides.

For series 2 in which Y is varied and X = H, the best fit was again obtained using σ_R values. The ρ_I and ρ_R values were also found to be equal and correspond to a Hammett ρ value of +1.4 (Figure 1). The fact that a Hammett type of free-energy relationship for series 2 was observed is inconsistent with the concept of an enhanced resonance contribution due to conjugation through sulfur and indicates that the substituent effects are mainly inductive in nature. Furthermore, the smaller ρ value (+1.4) for series 2 relative to series 1 (+2.0) means that substituent effects are transmitted less effectively through the phenylsulfonium group than through the phenacyl group. In particular the difference of 0.4 pK units in the acidities of **20k** (Y = NO_2, X = H) and **20f** (Y = H, X = NO_2) implies that the ylide **23** derived from **20k** is more basic (less stable relative to **20k**) than the ylide from **20f**, which argues against the importance of structure **23b** in stabilizing the ylide.

The data for series 2 may be compared with the pK_a data for the pyridinium salt **19** for which ρ = +2.9 as Y is varied with X constant. This ρ value is notably higher than the ρ values for series 1 and 2 as well as for **17** and **18**, and it has been suggested that this relatively high value reflects direct conjugation of the carbanion center with the pyridine ring in the derived ylide **24**. This being so, the validity of related conjugation effects in the sulfonium ylides obtained from **20** is placed further in doubt.



In summary, the evidence at hand does not support conjugation effects transmitted *through* sulfur. An orbital description of (p → d)π bonding need not therefore be invoked to explain the chemistry of the sulfonium salts and ylides described in this paper.

Experimental Section

2-Methylisothiachroman-4-one fluoroborate (10) was prepared in 95% yield by the methylation of isothiachroman-4-one[22] with 1 equiv of trimethyloxonium fluoroborate as a suspension in methylene chloride.[23] Recrystallization of the crude product from absolute ethanol gave colorless crystals, mp 153–154°.

Anal. Calcd for $C_{10}H_{11}BF_4OS$: C, 45.12; H, 4.16. Found: C, 45.01; H, 4.06.

2-Methylisothiachroman-4-one-3-ylide (12) was prepared from **10** on treatment with aqueous sodium hydroxide and extracting with chloroform, or with sodium hydride in dry THF, or with sodium methoxide in methanol–ether solution. The latter method proved to be the most satisfactory. To 1.70 g (7.87 mmol) of sodium methoxide as a 25% solution in methanol was added 2.50 g (9.4 mmol) of **10** and 25 ml of ether. The mixture was stirred for 10 min and the solvents were removed by evaporation at reduced pressure. The residual yellow solid was extracted with 50 ml of chloroform. The chloroform was evaporated and the residue was worked up with pentane and then air dried to give 1.31 g of **12** as a yellow solid, mp 126–128° dec.

Anal. Calcd for $C_{10}H_{10}OS$: C, 65.83; H, 5.66. Found: C, 65.58; H, 5.56.

Methylation of 2-Methylisothiochroman-4-one-3-ylide.—To a solution of 1.31 g of **12** in 50 ml of chloroform was added 1.9 g of trimethyloxonium fluoroborate. The mixture was stirred for 30 min and then decanted from any insoluble material, and the solvent was removed by evaporation at reduced pressure. The residual oil crystallized after washing with pentane and was subsequently recrystallized from absolute ethanol. The product **15** was obtained as almost white crystals, mp 121–122°, and gave an nmr spectrum in $CDCl_3$ showing a complex four-proton aromatic resonance near 7.5 ppm, a one-proton vinylic singlet at 5.75 ppm, a two-proton singlet at 4.55 ppm, a three-proton singlet at 4.00 ppm, and a three-proton singlet at 2.75 ppm. In acetonitrile, the benzylic protons of **15** appeared as an AB quartet (J = 16 Hz) with coupling of the upfield proton to the vinylic proton. On adding a D_2O–OD^- solution to the sample of **15** in CH_3CN in an nmr tube, the exchange of the vinylic, benzylic, and SCH_3 proton was observed.

(22) A. K. Kiang and F. G. Mann, *J. Chem. Soc.*, 1909 (1951).

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

Anal. Calcd for $C_{11}H_{13}BF_4OS$: C, 47.15; H, 4.67. Found: C, 46.95; H, 4.50.

Reaction of **15** (0.2 g in 1 ml of DMSO-d_6) with 1 equiv of potassium *tert*-butoxide was observed directly by nmr. The AB pattern of the benzylic protons disappeared rapidly but there was no significant change in the chemical shift of the vinylic, SCH_3, or OCH_3 resonances of **15**. Attempts to isolate the product(s) of this reaction led only to the isolation of a sticky red solid which could not be recrystallized. Reaction of **15** with sodium hydride in dry THF in an inert atmosphere led to the immediate evolution of hydrogen, precipitation of $NaBF_4$, and formation of a dark red solution which, after evaporating at reduced pressure, gave a red oil which solidified on washing repeatedly with pentane. Analysis by tlc showed the presence of at least three components. Separation was unsuccessful, and the nmr of the crude product in $CDCl_3$ gave very broad signals which were uninformative as to structure.

***S*-Benzyl-*S*-methyl-*S*-phenacylsulfonium ylide (14)** was prepared from the corresponding sulfonium bromide salt by treatment with sodium hydride in THF.[24] The sulfonium bromide was prepared from benzyl methyl sulfide and phenacyl bromide in benzene.

Preparation of Sulfonium Salts 20.—Each of the salts was prepared from the corresponding sulfide by methylation with trimethyloxonium fluoroborate, as described above for **10**. The salts so obtained were recrystallized to analytical purity from absolute ethanol. The sulfides were in turn prepared by the reaction of the appropriate thiophenol under basic conditions (sodium ethoxide in ethanol) with the appropriate phenacyl bromide. The procedure used was typically as follows for the preparation of *p*-methylphenacyl phenyl sulfide. To a solution of 2.88 g (0.125 g-atom) of sodium metal in 250 ml of ethanol was added all at once 13.8 g (0.125 mol) of thiophenol. To this stirred solution was added 26.7 g (0.125 mol) of *p*-methylphenacyl bromide. The mixture was gently refluxed and stirred for 1 hr, during which time sodium bromide precipitated out. The cooled mixture was filtered and evaporated. The residual oil solidified on cooling and was recrystallized from hexane to give 26.3 g (87%) of product.

Determination of pK_a for Sulfonium Salts 20.—Aqueous solutions of each of the sulfonium salts were prepared using oxygen-free distilled water. These stock solutions were diluted accordingly with standard KOH and standard HBF_4 such that 8–10 solutions of a given salt at different pH were prepared, the net concentration of salt + ylide remaining constant. The pK_a value is expressed by the relationship pH = pK_a − log [salt]/[ylide] and a plot of pH *vs.* log [salt]/[ylide] should be linear and of unit slope. The relative amount of salt and ylide present at a given pH was determined spectrophotometrically, and a plot was made of pH *vs.* log [salt]/[ylide]. In each case, the slope was verified as unity. The pK_a was determined directly from the plot for the condition [salt] = [ylide].

Registry No.—**10**, 24806-67-5; **12**, 24310-06-3; **14**, 15876-09-2; **15**, 34881-62-4; **20a**, 34881-63-5; **20b**, 34881-64-6; **20c**, 33043-77-5; **20d**, 34881-66-8; **20e**, 34881-67-9; **20f**, 34881-68-0; **20g**, 33043-72-0; **20h**, 33192-02-8; **20i**, 33043-70-8; **20j**, 34881-71-5; **20k**, 33043-73-1; $PhCOCH_2S(Me)CH_2Ph \cdot BF_4$, 17069-29-3.

(24) K. W. Ratts and A. N. Yao, *J. Org. Chem.*, **33**, 70 (1968).

Mechanisms of Alkaline Hydrolysis of *p*-Nitrophenyl Glucopyranosides

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The alkaline hydrolysis of *p*-nitrophenyl-α- and -β-D-glucopyranosides has been studied by gas chromatographic, uv spectrophotometric, and nmr spectroscopic methods. The α anomer is hydrolyzed to a degradative product of D-glucose whereas the β anomer yields the degradative product of D-glucose and 1,6-anhydroglucopyranose. The formation of the degradative product of D-glucose and the detection of a free radical during the hydrolysis suggest the complexity of the over-all pathways for the alkaline hydrolysis of *p*-nitrophenyl glucopyranosides. *p*-Nitrophenyl-β-D-glucopyranoside is hydrolyzed by mixed mechanisms, C-2 oxyanion participation, and nucleophilic aromatic substitution. In alkaline media, *p*-nitrophenyl-α-D-glucopyranoside forms a Meisenheimer-type complex, 1,2-*O*-*p*-nitrophenylidene-α-D-glucopyranose, as the intermediate which undergoes hydrolysis.

In spite of the general agreement concerning mechanisms of acidic hydrolysis of aryl glucopyranosides,[1,2] alkaline hydrolysis of aryl glucopyranosides has not been successfully rationalized on the basis of generalized mechanisms. In particular, exalted rates of hydrolysis of *p*-nitrophenyl-α- and -β-D-glucopyranosides in alkaline media remain enigmatic.

Previous studies on the alkaline hydrolysis of aryl glucopyranosides[2,3] have shown that β anomers react by a process (Scheme I) which yields 1,6-anhydroglucopyranose (**1**) *via* neighboring C-2 oxyanion participation.[4,5] A trend toward the nucleophilic aromatic substitution (Scheme II) was noted as the electron-withdrawing character of substitutents increased.[6,7]

In the case of aryl-α-D-glucopyranosides, a nucleophilic aromatic substitution mechanism analogous to Scheme II was proposed.[8] This mechanism explains the fact that 1,6-anhydroglucopyranose is not formed when the α anomers are treated with alkali. However, it does not explain the formation of *p*-nitrophenol when the experiment is carried out with sodium methoxide in methanol. To resolve some of these uncertainties, the present work was undertaken. The knowledge concerning mechanisms of hydrolysis of *p*-nitrophenyl-α- and -β-D-glucopyranosides is desirable because they have been extensively used as substrates in the studies of α- and β-glucosidases.[9,10]

Results

In the range of alkaline concentrations studied, the rate of *p*-nitrophenol liberation was first order in substrate concentrations until the hydrolysis is 50% completed. Figure 1 shows that the specific rate of alkaline hydrolysis of *p*-nitrophenyl-β-D-glucopyranoside (**3**)

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(2) B. Capon, *Chem. Rev.*, **69**, 407 (1969).
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