The 1,2-Dithiolium Cation. VII. Methylation of Thiothiophthene No-Bond Resonance Compounds and Their Nitrogen Isosteres[1]

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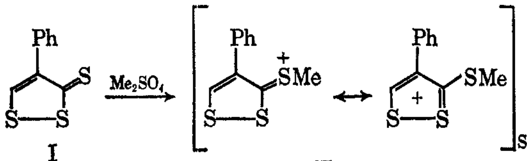
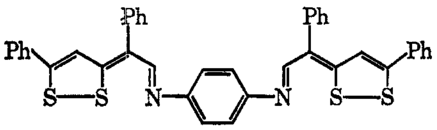
The vinylogous relationship between thiothiophthene no-bond resonance compounds and 1,2-dithiole-3-thiones ("trithiones") is shown by methylation. The dithiolethione I gives the methylthiodithiolium salt II, and thiothiophthenes III and IV give methylthiovinyldithiolium salts V and VI. The latter react with aniline to give anils that have been obtained by two other syntheses and are the first known thiothiophthene isosteres in which sulfur is replaced by a fifth group element. Like thiothiophthenes, anils can also be methylated; both reactions are discussed in terms of the no-bond resonance hypothesis. Electronic absorption characteristics are examined.

Thiothiophthene "no-bond resonance" compounds are vinylogs of the "trithiones" (1,2-dithiole-3-thiones);[2] this relationship is a source of useful insights. Thus, the methylation of trithiones such as I to give "trithionium salts" (3-methylthio-1,2-dithiolium salts) (II) is paralleled by the smooth addition of methyl iodide, under mild conditions, to thiothiophthenes III and IV. The resulting methiodides react readily with primary aromatic amines, eliminating methanethiol to give anils. Since the latter are also obtainable from the carbonyl compounds VIII and IX, they must have structures X and XI, and the thiothiophthene methiodides must have the corresponding structures V and VI. They are vinylogs of the trithionium salts and, like them, can doubtless be considered as hybrid 1,2-dithiolium derivatives[3] in which the positive charge may be withdrawn from the ring by the extracyclic sulfur atom (Va, VIa).



I II

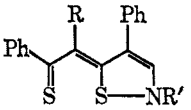
The condensation reaction of VIII and IX with aromatic amines, a new example of carbonyl reactivity in aldehydic compounds in this series, was used to prepare the series of weakly basic anils Xa and XIa; VIII condenses twice with *p*-phenylenediamine to give XIV. As might be expected, ketones in the series[4] are inert. The same anils are obtained from the methiodides V and VI in the form of hydriodides that are converted into the parent base by water or alkali. Alkyl and aralkyl amines react with V (but not with VIII) to give XIIa, b, and c.



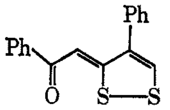
XIV

In a third synthesis, treatment of the thiothiophthene III with sulfur dichloride in benzene gave an insoluble product that reacted with aniline to give a modest yield of anil Xa. This synthesis also parallels the chemistry of 1,2-dithiole-3-thiones, which are converted by sulfur chloride into 3-chloro-1,2-dithiolium salts, highly reactive substrates with amines and other nucleophiles.[3] However, the structure of the thiothiophthene–sulfur chloride reaction product remains obscure at present (see Scheme I).

The question of S–N bonding, *i.e.*, contributions from structure XV, naturally arises from the fact that these imines are nitrogen isosteres of the thiothiophthene no-bond resonance compounds (III, IV), the first known isosteres in which sulfur is replaced by a fifth group element. Bond-length determination by X-ray crystallography is of course needed to determine whether the compounds are best considered as dithioles (X and XI), isothiazoles (XV), or a hybrid of both. The corresponding questions have already been answered for the oxygen[5] and selenium[6] isosteres.



XV



XVI

Like thiothiophthenes III and IV, the anil Xa readily adds methyl iodide; the product must be an S-methyl derivative, since it is different from the N-methyl derivative (VII) obtained unequivocally from V and N-methylaniline. A simple cyclic sulfonium structure seems unlikely, inasmuch as the carbonyl compound VIII is inert to methyl iodide. Evidently the nitrogen atom, though not the site of methylation, is essential to the reaction. (*Cf.* III, where the terminal sulfur atom which is not the site of methylation is essential to the reaction, and carbonyl compound XVI is inert under the same conditions.) Pending investigation by X-ray crystallography, the isothiazolium structure XIII seems probable. On the assumption that the anil has the essentially "normal" dithiole structure Xa, its S-methylation is accompanied by S–S bond cleavage and S–N bond formation, again recalling thiothiophthene III, in which Hordvik, Sletten, and Sletten have recently found that the sulfur atoms are not equally spaced.[7] Both S–S bonds are abnormally weak, but methylation to V *breaks the stronger bond* and

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(1) Paper VI: E. Klingsberg, *J. Org. Chem.*, **31**, 3489 (1966).

(2) E. Klingsberg, in "Organosulfur Chemistry," M. J. Janssen, Ed., John Wiley and Sons, Inc., New York, N. Y., 1967, p 173.

(3) H. Prinzbach and E. Futterer, in "Advances in Heterocyclic Chemistry," Vol. 7, A. R. Katritzky and A. J. Boulton, Ed., Academic Press Inc., New York, N. Y., 1966, pp 39 ff.

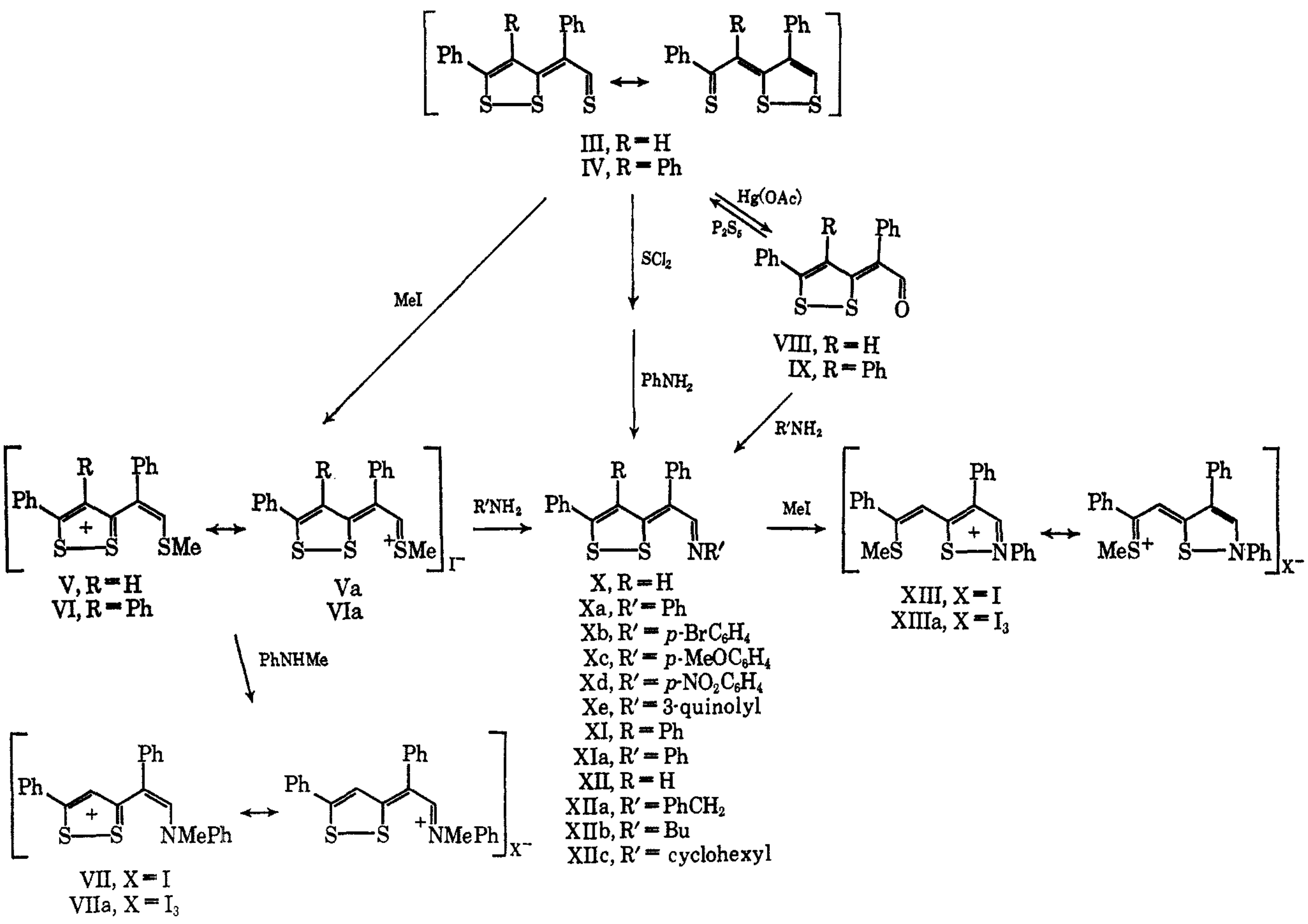
(4) E. Klingsberg, *J. Amer. Chem. Soc.*, **85**, 3244 (1963).

(5) M. Mammi, R. Bardi, G. Traverso, and S. Bezzi, *Nature*, **192**, 1282, (1961).

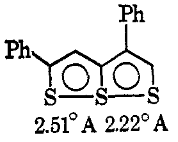
(6) J. H. van den Hende and E. Klingsberg, *J. Amer. Chem. Soc.*, **88**, 5045 (1966).

(7) A. Hordvik, E. Sletten, and J. Sletten, *Acta Chem. Scand.*, **20**, 2001 (1966).

SCHEME I



normalizes the weaker. (In the absence of evidence to the contrary, the S–S bond length in V is assumed normal.)



S–S bond lengths in thiothiophthene III[7]

In the delicately poised thiothiophthene system, the sulfur bonding, which has lost its symmetry under the influence of the unsymmetrical diphenyl substitution, does not govern the chemistry of III but instead accommodates itself to other influences, perhaps steric. The least hindered sulfur atom reacts with mercuric acetate[4] or methyl iodide, despite having a lower degree of thiocarbonyl character than the other terminal sulfur. The same flexibility seems to characterize the N isostere; here perhaps the course of methylation is governed by the greater nucleophilicity of sulfur as against nitrogen, with bonding adjustments corresponding to those observed in the thiothiophthene methylation.

In their electronic absorption spectra, III and V (Figure 1) show the characteristics to be expected of vinylogs of I and II (Figure 2). The more extended systems absorb at higher wavelength, and S-methylation causes a marked hypsochromic shift. S-Methylation of Xa causes a similar hypsochromic shift, whereas N-methylation has almost no effect on the first peak, recalling N-methylation of a π deficient system such as pyridine[8,9] (Figure 3).

Experimental Section

Melting points are corrected. Absorption spectra were determined in alcohol at a concentration of 10 mg/l.

3-(2-Methylthio-1-phenylvinyl)-5-phenyl-1,2-dithiolium Iodide (V).—Stirring and refluxing of a solution of 8.0 g (26 mmol) of *meri*-bicyclo-3,5-epidithio-1,4-diphenyl-2,4-pentadienethione-1 (III)[4] in 120 ml of nitromethane were continued overnight after addition of 80 ml of methyl iodide through the condenser. Filtration, followed by washing with nitromethane or benzene, gave 10.4 g (90%) of brick-red solid, mp 190–191° dec. Nitromethane gave purple crystals, mp 193–194° dec.

Anal. Calcd for $C_{18}H_{15}IS_3$: C, 47.6; H, 3.3; I, 28.0; S, 21.1. Found: C, 47.9; H, 3.4; I, 28.3; S, 21.0.

3-(2-Methylthio-1-phenylvinyl)-4,5-diphenyl-1,2-dithiolium Iodide (VI).—Stirring and refluxing of a solution of 0.60 g (1.5 mmol) of *meri*-bicyclo-3,5-epidithio-1,2,4-triphenyl-2,4-pentadienethione-1 (IV)[4] in 20 ml of nitromethane were continued for 1.5 hr after addition of 5.0 ml of methyl iodide through the condenser. Filtration gave 0.76 g (93%) of an orange-brown solid, mp 188–189°. Acetic acid gave orange crystals, mp 189–191°.

Anal. Calcd for $C_{24}H_{19}IS_3$: C, 54.4; H, 3.6; S, 18.1. Found: C, 54.5; H, 3.6; S, 17.8.

3,5-Epidithio-2,4,5-triphenyl-2,4-pentadienal (IX).—Stirring and refluxing of a solution of 1.50 g (3.9 mmol) of IV in 150 ml of acetic acid were continued for 5 min after addition of 1.50 g,

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[8] A. Albert, "Heterocyclic Chemistry," Athlone Press, London, 1959, p 303.

[9] E. Shaw in "Pyridine and Its Derivatives," part 2, E. Klingsberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1961, p 32.

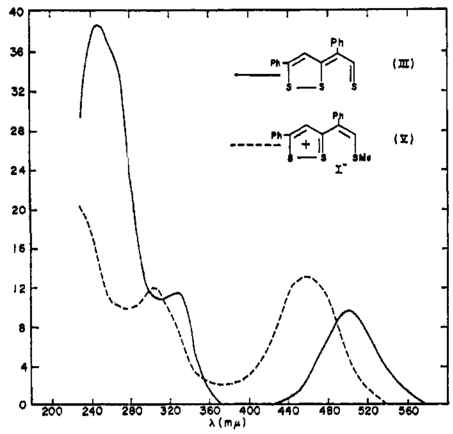

Figure 1.—Electronic absorption spectra of thiothiophthene (III) and its methyl derivative (V).

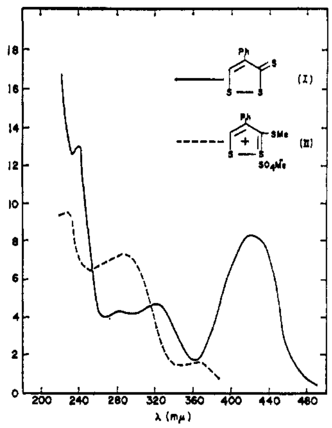

Figure 2.—Electronic absorption spectra of 4-phenyl-1,2-dithiole-3-thione (I) and its methyl derivative (II).

(4.7 mmol) of mercuric acetate.[10] Filtration of the black mixture, followed by cooling and dilution of the orange filtrate, gave 1.25 g (87%) of tan solid, mp 213–215°. Recrystallization from ethanol gave orange crystals, mp 214.5–215.5°. There was a marked melting point depression on admixture with the isomeric 3,5-epidithio-1,2,4-triphenyl-2,4-pentadieneone-1.[4]

Anal. Calcd for $C_{23}H_{16}OS_2$: C, 74.2; H, 4.3; S, 17.2. Found: C, 73.8; H, 4.5; S, 17.2.

Reaction with phosphorus pentasulfide in refluxing toluene rapidly regenerated IV.

3,5-Epidithio-2,5-diphenyl-2,4-pentadienylideneaniline (Xa).—Aniline (1000 ml, 1.02 g, 11.0 mmol) and 2.40 g (5.30 mmol) of V were stirred at reflux for 5 min in 25 ml of acetic acid, cooled, and filtered. The product was digested in warm water, filtered, and dried, giving a quantitative yield (1.96 g) of orange product, mp 199–200°. Crystallization from toluene, nitromethane, or methylcyclohexane did not affect the melting point.

Anal. Calcd for $C_{23}H_{17}NS_2$: C, 74.4; H, 4.6; N, 3.8; S, 17.3. Found: C, 74.4; H, 4.4; N, 3.6; S, 17.3.

Preparation from III.—A solution of 0.62 g (2.0 mmol) of III in 35 ml of warm benzene was treated dropwise with 0.25 ml (0.41 g, 3.9 mmol) of sulfur dichloride. The orange precipitate was filtered and washed with a little benzene or ether to yield 0.75 g. This was warmed on the steam bath for 5 min in 6–7 ml of aniline, cooled, filtered, and washed with a little methanol to yield 0.25 g (33%) of Xa, mp 194–196°. Recrystallization from methylcyclohexane raised the melting point to 198–199°, unaffected by admixture with specimens prepared from V or VIII. The identity was confirmed by elemental analysis.

The same compound was obtained by warming 10.0 g (0.0338 mol) of 3,5-epidithio-2,5-diphenyl-2,4-pentadienal (VIII)[4] and 3.50 ml (3.58 g, 0.0384 mol) of aniline in 50 ml of acetic acid. After 10 min the solution became a slurry, which was kept on the steam bath for 2 hr, cooled, and filtered, yielding 11.8 g (93%) of product, mp 198–200°.

The following analogs were prepared from VIII in comparable yields.

p-Bromoaniline gave Xb, red, mp 196–197° (methylcyclohexane).

Anal. Calcd for $C_{23}H_{16}BrNS_2$: C, 61.3; H, 3.6; N, 3.1; S, 14.3. Found: C, 61.3; H, 3.7; N, 3.3; S, 14.3.

p-Anisidine gave Xc, orange, mp 160–161° (methylcyclohexane or hexane).

Anal. Calcd for $C_{24}H_{19}ONS_2$: C, 72.0; H, 4.7; N, 3.5; S, 16.0. Found: C, 72.3; H, 4.6; N, 3.4; S, 15.9.

p-Nitroaniline gave Xd, purple, mp 216–217° dec (toluene). At a concentration of 10 mg/l. of alcohol, this showed uv absorptions at λ_{max} 510 (ϵ 27,800) and 315 (18,000).

Anal. Calcd for $C_{23}H_{16}O_2N_2S_2$: C, 66.4; H, 3.8; N, 6.7; S, 15.4. Found: C, 66.6; H, 3.6; N, 6.5; S, 15.3.

3-Aminoquinoline gave Xe, red, mp 227–228° dec (toluene).

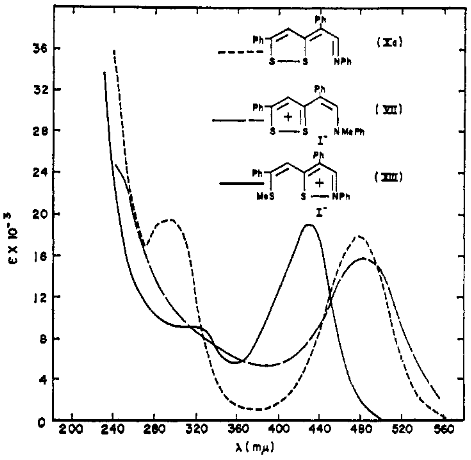

Figure 3.—Electronic absorption spectra of anil Xa, its N-methyl derivative VII, and its S-methyl derivative XIII.

Anal. Calcd for $C_{26}H_{18}N_2S_2$: C, 74.0; H, 4.3; S, 15.0. Found: C, 74.0; H, 4.3; S, 15.0.

p-Phenylenediamine gave XIV, purple, mp 298–299° dec (pyridine).

Anal. Calcd for $C_{40}H_{28}N_2S_4$: C, 72.3; H, 4.2; N, 4.2; S, 19.3. Found: C, 72.1; H, 4.1; N, 4.2; S, 18.9.

3,5-Epidithio-2,4,5-triphenyl-2,4-pentadienylideneaniline (XIa).—A mixture of 0.70 g (1.3 mmol) of VI and 0.30 ml (0.28 g, 3.0 mmol) of aniline in 10 ml of acetic acid was stirred at reflux for 10 min, cooled, and filtered, yielding 0.62 g (82%) of brick-red iodide, mp 210° dec, which was quantitatively converted into the orange base, mp 180–181°, by treatment with alcoholic alkali. Nitromethane or methylcyclohexane gave bright orange crystals of unchanged melting point.

Anal. Calcd for $C_{29}H_{21}NS_2$: C, 77.9; H, 4.7; N, 3.1; S, 14.3. Found: C, 78.0; H, 4.7; N, 3.1; S, 14.0.

The same product was obtained from the corresponding carbonyl compound (IX) and aniline in refluxing acetic acid.

3,5-Epidithio-2,5-diphenyl-2,4-pentadienylidenebenzylamine (XIIa).—A mixture of 0.30 ml (0.29 g, 2.7 mmol) of benzylamine and 1.05 g (2.3 mmol) of V in 5 ml of acetic acid was stirred at reflux for 5 min, cooled, and filtered to yield 1.13 g of the brown-orange iodide of the product, mp 185–187° dec. This was converted into the base by stirring in about 40 ml of ethanol with freshly precipitated silver oxide (from 1.0 g of silver nitrate), followed by evaporation to dryness, extraction of the solids with hot pyridine, filtration, and dilution, yielding 0.63 g (71%) of a yellow solid, mp 208–212°. Methylcyclohexane gave orange-yellow crystals, mp 213–213.5°.

Anal. Calcd for $C_{24}H_{19}NS_2$: C, 74.8; H, 4.9; S, 16.6. Found: C, 74.7; H, 4.9; S, 16.8.

Under similar conditions *n*-butylamine gave a 70% yield of hydriodide of XIIb, which was converted into the bright yellow base by treatment with pyridine and crystallized from alcohol or hexane, mp 122.5–123.5°.

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[10] Refluxing with mercuric acetate in acetic acid is a useful technique for desulfurization of thiothiophthenes like IV that resist the usual room temperature conditions. By this technique meribicyclo-2-cyano-3,5-epidithio-1,5-diphenyl-2,4-pentadienethione-1 is converted into 2-cyano-3,5-epidithio-1,5-diphenyl-2,4-pentadienone-1 in good yield.[4] Here the cyano group directs the attack to the nearer of the two sterically equivalent thiocarbonyl groups.

Anal. Calcd for $C_{21}H_{21}NS_2$: C, 71.8; H, 6.0; N, 4.0; S, 18.2. Found: C, 71.8; H, 5.8; N, 3.9; S, 18.2.

Cyclohexylamine gave XIIc, orange, mp 160–161° (methylcyclohexane).

Anal. Calcd for $C_{23}H_{23}NS_2$: C, 73.2; H, 6.1; N, 3.7; S, 17.0. Found: C, 73.1; H, 5.9; N, 3.6; S, 16.9.

Methylation of Xa to XIII.—Methyl iodide (5 ml) was added through the condenser to a stirred refluxing mixture of 1.35 g (3.64 mmol) of Xa in 20 ml of nitromethane. After 1 hr, the solution was cooled, diluted with a little ether, and filtered, yielding 1.85 g (99%) of orange product. In an ordinary capillary melting point determination, it lost methyl iodide around 160° and then gave the melting point (199–200°) of Xa. A melting point of 166° could be observed by insertion into the bath at 160°, but this seems less reproducible. Crystallization occurred readily from ethanol or methanol. Aniline or methylaniline in refluxing acetic acid reversed the methylation reaction, regenerating Xa.

Anal. Calcd for $C_{24}H_{20}INS_2$: C, 56.1; H, 3.9; I, 24.8; N, 2.7; S, 12.5. Found: C, 56.3; H, 3.7; I, 24.7; N, 2.9; S, 12.4.

This combined rapidly with 1 mol of iodine in methanol solution to give the *triiodide* (XIIIa), mp 150–150.5°, which separated as golden crystals from *n*-propyl alcohol.

Anal. Calcd for $C_{24}H_{20}I_3NS_2$: C, 37.6; H, 2.6; I, 49.7; N, 1.8. Found: C, 37.8; H, 2.6; I, 49.6; N, 1.8.

3-(2-N-Methylanilino-1-phenylvinyl)-5-phenyl-1,2-dithiolium Iodide (VII).—A mixture of 2.27 g (5.0 mmol) of 3-(2-methylthio-1-phenylvinyl)-5-phenyl-1,2-dithiolium iodide (V) and 0.65 ml (0.64 g, 6.0 mmol) of N-methylaniline in 50 ml of methanol was stirred at reflux for 5 hr, cooled, diluted with ether, and chilled to −78°, yielding 1.24 g (49%) of greenish product, mp 185–187°. *n*-Propyl alcohol gave dark brown crystals, mp 196.5–197°, showing marked melting-point depression on admixture with XIII.

Anal. Calcd for $C_{24}H_{20}INS_2$: C, 56.1; H, 3.9; I, 24.8; N, 2.7; S, 12.5. Found: C, 56.1; H, 3.8; I, 24.4; N, 2.7; S, 12.4.

When the reaction was continued somewhat longer, the product was obtained in lower yield together with VIII, which separated on cooling before dilution with ether.

The corresponding triiodide VIIa gave bronze crystals, mp 149–150° dec, from *n*-propyl alcohol, showing a marked melting point depression on admixture with XIIIa.

Anal. Calcd for $C_{24}H_{20}I_3NS_2$: C, 37.6; H, 2.6; I, 49.7; N, 1.8; S, 8.3. Found: C, 37.6; H, 2.6; I, 50.1; N, 1.7; S, 8.5

At a concentration of 10 mg/l. in ethanol containing a little Cellosolve, VII showed an absorption band at λ_{max} 480 (ϵ 16,100) (Figure 3). Absorption in the same region is reported in a recent brief communication on salts of similar type.[11]

Registry No.—I, 3354-37-8; II, 16717-54-7; III, 16717-55-8; V, 16717-56-9; VI, 16717-57-0; VII, 16717-58-1; VIIa, 16717-59-2; IX, 16717-60-5; Xa, 16753-66-5; Xb, 16753-67-6; Xc, 16753-68-7; Xd, 16753-69-8; Xe, 16753-70-1; XIa, 16753-71-2; XIIa, 16753-72-3; XIIb, 16753-73-4; XIIc, 16753-74-5; XIII, 16717-61-6; XIIIa, 16717-62-7; XIV, 16717-63-8.

Acknowledgment.—The author is greatly indebted to Mrs. Maryellen Kish for technical assistance, to J. J. Kobliska and his staff for microanalyses, and to Miss Vera Jordan for absorption spectra.

[11] R. Meyer and H. Hartmann, *Z. Chem.*, **6**, 312 (1966).

Preparation of Silylalkanethiols

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Silylalkyl ethanethiolates with chloro, acetoxy, hydroxy, and alkoxy substituents attached to silicon were prepared by the reaction of ethanethiolic acid with corresponding alkenylsilanes. The effects of the substituents on silicon on the reactivity of vinylsilanes toward thiols or ethanethiolic acid were found to be additive. Ethanethiolic acid reacts with most vinylsilanes to give two adducts, $\equiv SiCH_2CH_2SAc$ (major) and $\equiv SiCHCH_3SAc$ (minor). Silylalkanethiols were prepared by methanolysis or ammonolysis of some of these esters. Several new types of silylalkanethiols prepared in this manner are $HN(SiMe_2CH_2CH_2SH)_2$ and $Me_2XSiCH_2CH_2SH$ where X is Cl-, MeO-, HO-, and AcO-. The log of the relative rate constants (the rate constant for hexene-1 ÷ 1) for addition of thiols and also of silicon hydrides was found to show a linear correlation with the sum of substituent constants C for the groups R, R′, and R″ in compounds of the formula $RR'R''SiCH{=}CH^2$.

Ethanethiolic acid adds to the double bond of olefins by a free-radical process with great efficiency. Olefins substituted in nearly all possible ways form corresponding alkyl ethanethiolates in good yields. A few examples of silicon-containing olefins of the types $R_3SiC_nH_{2n-1}$ and $O(SiR_2C_nH_{2n-1})_2$ have been used in which R was either an alkyl or phenyl group.[1-6]

We have found that alkenylsilanes with chloro, alkoxy, and acetoxy substituents on silicon can be converted into corresponding silylalkyl ethanethiolates in excellent yield. We observed no interference from any of these substituents. Aminosilylalkyl ethanethiolates could not be prepared in the same manner, however, because ethanethiolic acid reacts rapidly with amino groups on silicon to form thionoacetoxysilanes.[7]

Ethanethiolic acid reacts with vinylsilanes to form two isomeric adducts (eq 1). Only terminal adducts to

$$\equiv SiCH{=}CH_2 + AcSH \longrightarrow \underset{\text{major}}{\equiv SiCH_2CH_2SAc} + \underset{\text{minor}}{\equiv SiCH(CH_3)SAc} \qquad (1)$$

vinylsilanes had been reported by workers previous to Wetterlin[8] who was the first to report that two adducts analogous to the above form during the reaction of vinylsilanes with some thiols.

Silylalkyl ethanethiolates were converted into silylalkanethiols by methanolysis or ammonolysis. Methanolyses were run in an excess of methanol containing

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(1) P. V. Bonsignore, C. S. Marvel, and S. Bonerjee, *J. Org. Chem.*, **25**, 235 (1960).

(2) P. W. Gawrys and H. W. Post, *ibid.*, **27**, 634 (1962).

(3) W. Stamm, *ibid.*, **28**, 3264 (1963).

(4) C. S. Marvel and H. N. Cripps, *J. Polym. Sci.*, **9**, 53 (1953).

(5) V. F. Mironov and N. A. Pogonkina, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **85**, (1959).

(6) A. D. Petrov, V. F. Mironov, and V. G. Glukhontsev, *J. Gen. Chem. USSR*, **27**, 1535 (1957).

(7) G. A. Gornowicz and J. W. Ryan, *J. Org. Chem.*, **31**, 3439 (1966).

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