appreciable amount of alkali-soluble product but boiling it with 70% sulfuric acid gave a black tar from which 0.6 g. of a slightly yellow solid (m. p. 162.5–163°) was obtained after dissolving in sodium carbonate solution, filtering, acidifying, and recrystallizing two times from benzene-ligroin. The ethyl ester melted at 85–86°. The melting points given in literature[8] are 163–164° for bis-(*p*-chlorophenyl)-acetic acid and 88° for its ethyl ester.

Anal. Calcd. for $C_{14}H_{10}Cl_2O_2$: equiv. wt., 281.1. Found: equiv. wt., 284.3.

Reaction with Alkali.—It was observed that when bis-(*p*-chlorophenyl)-acetohydroximyl chloride was warmed with 10% sodium hydroxide solution, it became pasty and then resolidified. Recrystallization of the pale yellow solid from benzene–ligroin gave a white compound melting at 162.5–163°. The same compound was obtained when the hydroximyl chloride was warmed in a sodium carbonate solution. This compound is 3,4-bis-(*p*,*p*'-dichlorobenzohydryl)-furoxan.

Anal. Calcd. for $C_{28}H_{20}Cl_4N_2O_2$: C, 60.24; H, 3.61; N, 5.02; Cl, 25.40; mol. wt., 558. Found: C, 60.80; H, 3.32; N, 4.97; Cl, 25.58; mol. wt. (ebullioscopic in benzene), 574.

The furoxan is unaffected by nitric acid, either dilute or concentrated, or by alkaline permanganate. When 0.25 g. was dissolved in 100 cc. of glacial acetic acid and a solution of 7 g. of chromic oxide in 5 cc. of water and 25 cc. of glacial acetic acid was added, a white crystalline product melting at 144–146° was obtained after warming on the steam-bath for one hour and diluting the solution with water. The melting point of the oxime was 135–135.5°. This compound is identical to the *p*,*p*'-dichlorobenzophenone obtained by the nitric acid oxidation of bis-(*p*-chlorophenyl)-acetohydroximyl chloride.

Acknowledgments.—Microanalyses for carbon, hydrogen and nitrogen were performed by P. Craig, N. Mold, M. Hines and J. Anderson.

Summary

ω-Nitrostyrene and *p*-chloro-ω-nitrostyrene react with benzene or chlorobenzene in the presence of aluminum chloride to yield diarylhydroximyl chlorides. Several reactions of these compounds are presented.

EVANSTON, ILLINOIS RECEIVED APRIL 19, 1950

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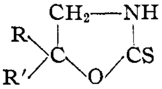
[8] Forrest, Stephenson and Waters, *J. Chem. Soc.*, 336 (1946).

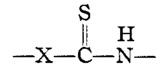
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Infrared Spectra and Tautomerism of 2-Thioöxazolidone and Congeners

BY MARTIN G. ETTLINGER[1]

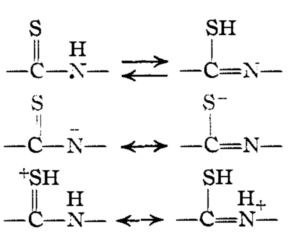
In an investigation of the natural product *l*-5-vinyl-2-thioöxazolidone[2] (I, R = $CH{=}CH_2$, R' = H), the presence of the thioncarbamate group was established by comparison of the infrared absorption spectrum with spectra of known compounds containing the functional group II. These substances, being incompletely N-substituted thioamides, may exist in thione (III) or thiol (IV) forms, which are interconvertible through a common anion (V) and cation (VI). Each tautomer is a resonance hybrid; the dipolar structure VII contributes to III. The position of equilibrium between III and IV has often been discussed for compounds such as thiourea.[3] Chemical reactions, oxidation or alkylation, do not furnish evidence for decision. The weak, phenolic acidity of thioamides accords with either formula; since the less acidic tautomer must predominate, III cannot be excluded by the contention that a substance of such structure should be neutral.

I


II


$$-X-\overset{S}{\overset{\|}{C}}-\overset{H}{N}-$$

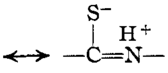
X = O, S or N—



$$\text{III}\quad -\overset{S}{\overset{\|}{C}}-\overset{H}{N}- \rightleftarrows -\overset{SH}{\overset{|}{C}}=N- \quad\text{IV}$$

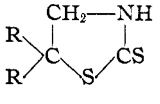
$$\text{V}\quad -\overset{S}{\overset{\|}{C}}-\overset{-}{N}- \longleftrightarrow -\overset{S^-}{\overset{|}{C}}=N-$$

$$\text{VI}\quad -\overset{^+SH}{\overset{\|}{C}}-\overset{H}{N}- \longleftrightarrow -\overset{SH}{\overset{|}{C}}=\overset{H_+}{N}-$$



$$\text{III} \longleftrightarrow -\overset{S^-}{\overset{|}{C}}=\overset{H^+}{N}- \quad\text{VII}$$

Infrared spectra of numerous thioamides in oil suspension have recently been published by Randall, Fowler, Fuson and Dangl.[4] These workers correlated with the group II a "thioureide" absorption band at 6.3–6.9 μ. For one compound, 2-thiothiazolidone (VIII, R = H), the position of the acidic hydrogen could be inferred[5] from the spectrum. The solid absorbs at 3.2 and 6.6 μ, corresponding to hydrogen bonded imino and to dithiocarbamate groups, and not at 3.9 and 6–6.3 μ, required for the sulfhydryl group and carbon–nitrogen double bond of a thiol structure (IV). Hence, 2-thiothiazolidone is a true thione. The present paper supports and generalizes this conclusion.

VIII


In thioamides that contain no hydroxyl group

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[1] Member of the Society of Fellows, Harvard University.

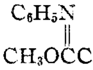
[2] Astwood, Greer and Ettlinger, *J. Biol. Chem.*, **181**, 121 (1949).

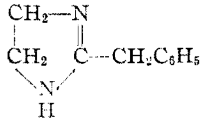
[3] Taylor and Baker, eds., "Sidgwick's Organic Chemistry of Nitrogen," Oxford University Press, New York, N. Y., 1937, pp. 151, 280–291.

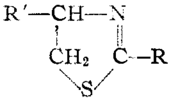
[4] Randall, Fowler, Fuson and Dangl, "Infrared Determination of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1949.

[5] *Ibid.*, p. 66.

and only one mobile hydrogen atom, as do all to be discussed, observation of fundamental absorption at wave lengths less than 3.2 μ, necessarily caused by N–H stretching vibrations, proves the existence of the thione form (III). The sulfhydryl band, which occurs at 3.88 μ in the spectrum of a concentrated solution of thiophenol (C, Fig. 1), is so weak that failure to detect it is not a sensitive criterion for rejection of the thiol (IV). However, the type of carbon–nitrogen double bond in IV absorbs strongly between 6 and 6.3 μ in the compounds methyl N-phenylbenzamidate (IX) (6.00 μ),[4] 2-benzyl-2-imidazoline (X) (6.11 μ)[4] and dimethyl benzylpenillate (6.16 μ),[6] 2-phenyl-2-thiazoline (XI-R = C_6H_5, R′ = H) (6.23 μ)[4] and 2-benzyl-4-carbomethoxy-2-thiazoline (XI, R = $CH_2C_6H_5$, R′ = $COOCH_3$) (6.17 μ),[4] and S,N,N,N′-tetramethylisothiourea[7] (XII) (6.25 μ, D, Fig. 1). Hence, the lack of absorption by a thioamide between 6 and 6.3 μ is excellent reason for elimination of the thiol form.

IX

$$CH_3O\overset{\displaystyle C_6H_5N}{\overset{\|}{C}}C_6H_5$$

X


XI


XII

$$(CH_3)_2N\overset{\displaystyle SCH_3}{\overset{|}{C}}{=}NCH_3$$

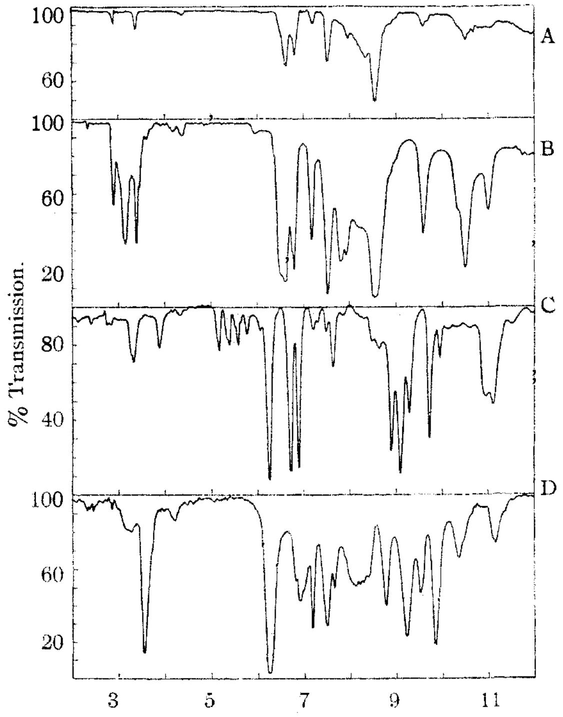


Fig. 1.—Infrared absorption spectra of: A, 2-thiooxazolidone (I, R = R′ = H), 0.5% in chloroform solution; B, 2-thioöxazolidone, 4% in chloroform; C, thiophenol (C_6H_5SH), 10% in chloroform; D, S,N,N,N′-tetramethylisothiourea (XII), 2% in chloroform; liquid thickness *ca.* 0.4 mm.

Spectra of 2-thioöxazolidone[8] (I, R = R′ = H) in chloroform solution are shown in Fig. 1 (A, B). In dilute solution (A) the substance has notable bands at 2.89 μ of the monomeric N–H and 6.61 μ of the thioncarbamate group. In more concentrated solution (B) a new peak appears at 3.15 μ, assignable to the imino groups of molecules associated by hydrogen bonds from the nitrogen to, probably, the negatively charged sulfur. Association of acidic thioamides in solution has been demonstrated cryoscopically,[9] and the spectral result parallels that observed for amides.[10] Other effects of increased concentration of 2-thioöxazolidone are an inflection at 6.5 μ of the 6.6 μ band, and a maximum at 7.8 μ. There is no indication of a thiol.

The spectra of 5,5-dimethyl-2-thioöxazolidone[11] (I, R = R′ = CH_3) (E, Fig. 2) and 5,5-dimethyl-2-thiothiazolidone[11] (VIII, R = CH_3) (F, Fig. 2)

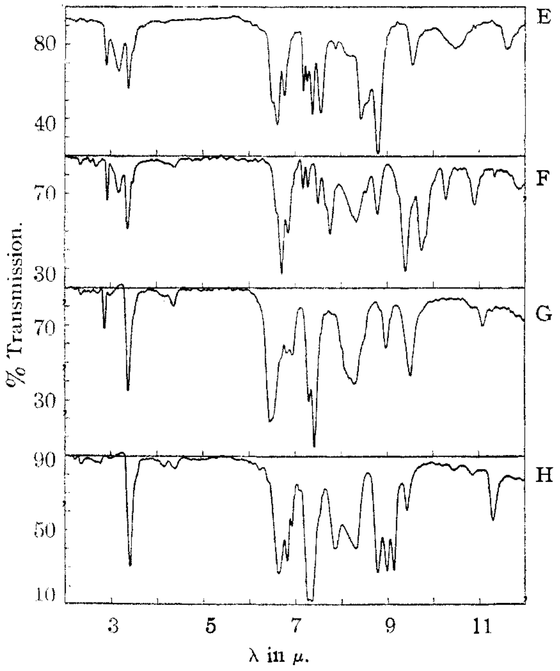


Fig. 2.—Infrared absorption spectra of: E, 5,5-dimethyl-2-thioöxazolidone (I, R = R′ = CH_3); F, 5,5-dimethyl-2-thiothiazolidone (VIII, R = CH_3); G, N,N,N′-trimethylthiourea (XIII, R = H); and H, N,N,N′,N′-tetramethylthiourea (XIII, R = CH_3), all 2% in chloroform solution.

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[6] Rasmussen and Brattain, *in* "The Chemistry of Penicillin," Clarke, Johnson and Robinson, eds., Princeton University Press, Princeton, N. J., 1949, ch. XIII, pt. II, pp. 409, 411.

[7] Delépine, *Bull. soc. chim.*, [4] **7**, 988 (1910).

[8] Sergeev and Ivanova, *J. Gen. Chem.* (*U. S. S. R.*), **7**, 1495 (1937); [*Chem. Zentr.*, **109**, I, 599 (1938)].

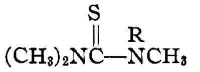
[9] Hopkins and Hunter, *J. Chem. Soc.*, 638 (1942).

[10] Richards and Thompson, *ibid.*, 1248 (1947).

[11] Bruson and Eastes, THIS JOURNAL, **59**, 2011 (1937).

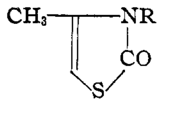
contain a triplet at 2.92, 3.17 and 3.38 μ, of which the first two peaks are caused by N–H and the third by C–H vibrations, and thioamide bands at 6.61 and 6.71 μ, respectively. The N–H band of shortest wave length was not found for solid 2-thiothiazolidone because of increased association in the crystalline state. 4,4-Dimethyl-2-thiothiazolidone (spectrum not reproduced) exhibits in solution the characteristic triplet at 2.9–3.4 μ and a strong maximum at 6.91 μ, inflected at 6.65–6.8 μ. All thioamides examined in this work possess two bands between 6.4 and 7 μ, one at 6.45–6.8 μ and a second, sometimes more intense (K, Fig. 3), at 6.77–7 μ. A third maximum between 7.35 and 7.6 μ is shown by all except 4,4-dimethyl-2-thiothiazolidone. If methylene groups are present, their bending vibrations contribute to the absorption near 6.9 μ. The most intense band of 2-thioöxazolidones occurs at 8.55–8.8 μ and is presumably caused by C–O stretching vibrations, which absorb at 8–8.5 μ in esters[12] and 8.9 μ in aliphatic ethers.[4]

N,N,N′-Trimethylthiourea[13] (XIII, R = H)

XIII 
$(CH_3)_2N\overset{\overset{S}{\|}}{C}-\overset{R}{N}CH_3$

(G, Fig. 2) spectroscopically resembles the thioncarbamates and dithiocarbamates discussed, except that it is not associated in solution. The presence of two adjacent carbon–nitrogen bonds seems not to create unusual features. The N–H peak at 2.86 μ and the thioamide band at 6.45 μ, corresponding to the one at 6.63 μ of N,N,N′,N′-tetramethylthiourea[7] (XIII, R = CH_3) (H, Fig. 2), with the absence of double bond absorption comparable to that of XII furnish evidence that thioureas are pure thiones.

If a thioamide group is embedded in an aromatic ring, the spectrum is complicated. Consider as models the pair of amides[14] 4-methyl-2-thiazolone ("α-methylrhodim") (XIV, R = H) and 3,4-dimethyl-2-thiazolone (XIV, R = CH_3). The dimethylthiazolone absorbs (M, Fig. 3) weakly at 3.47 μ for C–H bonds and strongly at 6.1 μ for the amide group and 6.28 μ for the carbon–carbon double bond.

XIV 

The methylthiazolone (L, Fig. 3) also exhibits the 6.1 μ band, from which the less intense double bond peak is not resolved, and therefore is an amide and not the tautomeric hydroxythiazole. The broad, intense absorption between 3 and 4 μ of the methylthiazolone, contrasted to its N-methyl derivative, must be ascribed to stretching of hydrogen bonded imino groups. The close spectral resemblance (K, Fig. 3) in the 3–4 μ region of 4-methyl-2-thiothiazolone[15] ("4-methyl-2-mercaptothiazole") (XV, R = CH_3) to its oxygenated counterpart

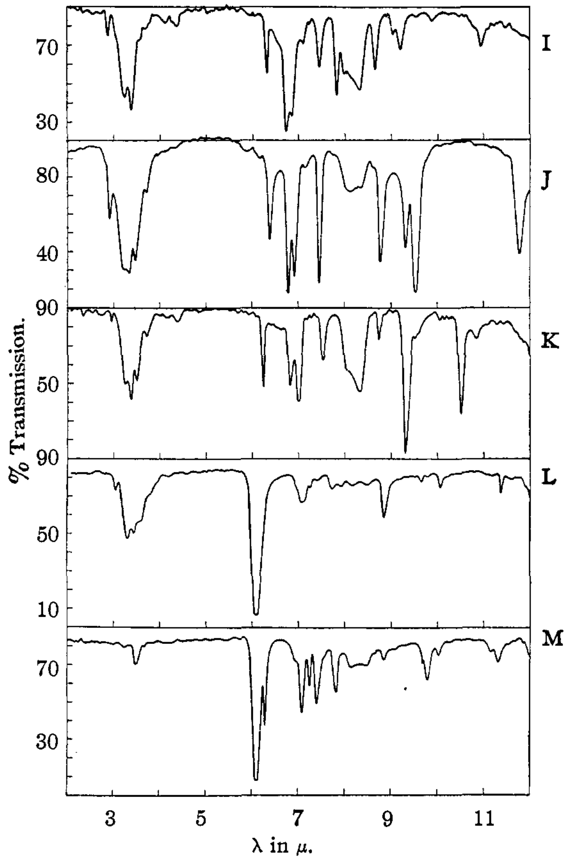
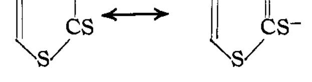


Fig. 3.—Infrared absorption spectra of: I, 1-methyl-2-thioimidazolone (XVI); J, 2-thiothiazolone (XV, R = H); K, 4-methyl-2-thiothiazolone (XV, R = CH_3); L, 4-methyl-2-thiazolone (XIV, R = H); and M, 3,4-dimethyl-2-thiazolone (XIV, R = CH_3), all 2% in chloroform solution.

XV  XVII

proves the existence of an imino group in the thiothiazolone. Of the other absorption bands of 4-methyl-2-thiothiazolone, that at 6.23 μ can be attributed to carbon–carbon double bond stretching of XV, and those at 6.81 μ and, probably, 6.99 μ to the dithiocarbamate group. The absence of other double bond absorption in the 6–6.7 μ region implies that the mercaptothiazole tautomer is imperceptible. The spectrum (J, Fig. 3) of 2-thiothiazolone[16] (XV, R = H) contains a triplet at 2.91, 3.3 and 3.47 μ with a broad central member, and maxima at 6.3 μ of the double bond and 6.78 and 6.90 μ of the dithiocarbamate group. The bands (I, Fig. 3)

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(12) Thompson and Torkington, *J. Chem. Soc.*, **640** (1945).

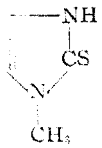
(13) Dixon, *ibid.*, **67**, 556 (1895).

(14) Tcherniac, *ibid.*, **115**, 1071 (1919); Hantzsch, *Ber.*, **61**, 1776 (1928).

(15) Miolati, *Gazz. chim. ital.*, **23**, I, 575 (1893).

(16) Backer and Buisman, *Rec. trav. chim.*, **64**, 102 (1945).

of 1-methyl-2-thioimidazolone[17] ("1-methyl-2-mercaptoimidazole") (XVI) at 2.88, 3.25, 3.40, 6.32, 6.72 and 6.86 μ can be assigned in exactly corresponding fashion, the last two to the thiourea system.

XVI 

The thiothiazolone spectrum was differently interpreted by Randall, *et al.*,[4] who considered the 4,5-dimethyl derivative as a mercaptothiazole. Examination of this substance in chloroform solution during the present investigation showed that it absorbed almost indistinguishably from the 4-methyl compound between 2 and 9 μ, notably in the 3–4 μ region which suffered no interference from mineral oil. The positions of the two bands previously observed between 6.5 and 7 μ were confirmed, but instead of the reported doublet at 6.16 and 6.23 μ a single sharp peak was found at 6.12 μ. In the solid state association would be increased and the N–H stretching bands further obscured. The additional resonance caused by the double bond in the thiothiazolone ring augments the contribution of dipolar structures such as the aromatic XVII corresponding to VII and therefore promotes hydrogen bonding. Probably a great tendency to association exists in 2-thiopyridone and analogs and accounts for the failure of a recent infrared spectroscopic study[18] of certain 2- and 4-thioquinolones to reach a structural decision. The difficulty may be alleviated as present results show.

Experimental

Infrared absorption spectra were determined with a Baird Infrared Recording Spectrophotometer, Model B. Dr. E. B. Astwood generously supplied the majority of compounds examined from his collection of antithyroid drugs. 2-Thioöxazolidone was prepared by a synthesis to be described in another paper, and S,N,N,N′-tetramethylisothiourea (b. p. 62° (11 mm.)) by methylation of N,N,N′-trimethylthiourea according to a general method.[19] The solvent chloroform was anhydrous or U. S. P. Several spectra show small, spurious peaks at 4.1–4.4 μ, caused by cell impurities or imperfect compensation of the solvent absorption band in that region. The intense chloroform band at 8–8.4 μ also appears frequently.

Summary

The infrared absorption spectra of certain potentially enolic heterosubstituted thioamides have been measured and interpreted. Even if the functional group is incorporated in a five-membered aromatic ring, the substance exists solely in thione form.

CAMBRIDGE, MASSACHUSETTS RECEIVED MARCH 6, 1950

[17] Wohl and Marckwald, *Ber.*, **22**, 1353 (1889).

[18] Hannan, Lieblich and Renfrew, THIS JOURNAL, **71**, 3733 (1949).

[19] Lecher, Graf and Gnaedinger, *Ann.*, **445**, 61 (1925).

[CONTRIBUTION NO. 497 FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY]

Some Reactions of Phenylsilane

BY W. H. NEBERGALL

The use of lithium aluminum hydride[1] makes the alkyl hydrides of silicon and the other elements of the fourth group of the periodic system readily obtainable by virtue of its power to reduce the halides to the corresponding hydrides in ether solution. Accordingly, phenylsilane was prepared in this investigation by the action of lithium aluminum hydride upon phenyltrichlorosilane. The phenyltrichlorosilane was produced by the interaction of phenyllithium and an excess of tetrachlorosilane.

$$4C_6H_5SiCl_3 + 3LiAlH_4 \longrightarrow 4C_6H_5SiH_3 + 3LiCl + 3AlCl_3$$

$$C_6H_5Li + SiCl_4 \longrightarrow C_6H_5SiCl_3 + LiCl$$

Phenylsilane, $C_6H_5SiH_3$, is a colorless, volatile liquid boiling at 120° and possessing an odor suggesting that of toluene, $C_6H_5CH_3$. This silane may be distilled at atmospheric pressure without noticeable decomposition and it was not found to be spontaneously inflammable in air at the boiling point.

In its chemical reactions, phenylsilane resembles the corresponding halides, the hydrogen atoms exhibiting a negative character much like that of the halogens, but less so. Previous reports[2] have shown that the trialkylsilanes react with organolithium compounds in ether to form tetrasubstituted silanes and lithium hydride. The above reaction appears to be one case of a more general reaction[3] since it was found in the present investigation that phenylsilane may be alkylated with ethyllithium to form phenyltriethylsilane and with phenyllithium to form tetraphenylsilane.

$$R_3SiH + R'Li \longrightarrow R_3SiR' + LiH$$

$$C_6H_5SiH_3 + 3RLi \longrightarrow C_6H_5SiR_3 + 3LiH$$

Diethyl ether was found to be a suitable reaction medium, but when low boiling petroleum

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[1] (a) Finholt, Bond, Wilzbach and Schlesinger, THIS JOURNAL, **69**, 2692 (1947); (b) Johnson and Nebergall, *ibid.*, **71**, 1720 (1949); (c) Nebergall and Johnson, *ibid.*, **71**, 4022 (1949).

[2] Gilman and Massie, *ibid.*, **68**, 1128 (1946); Meals, *ibid.*, **68**, 1880 (1946); Gilman and Melvin, *ibid.*, **71**, 4050 (1949).

[3] The reaction of diphenylsilane with organolithium compounds will be reported in a later paper.