The Preparation, Structure, and Some Properties of the Sulfoxide of Thiaxanthone

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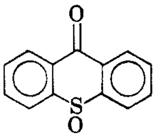
Thiaxanthone was converted to the corresponding sulfoxide (I) by means of selective oxidizing agents of which iodosobenzene diacetate was found to be most suitable. The ultraviolet and infrared spectra of this new sulfoxide were investigated, as well as some chemical properties, in order to ascertain its structure. The sulfoxide function does not inhibit the reactivity of the carbonyl group. All attempts to produce an isomeric sulfoxide failed. On the basis of present evidence it is impossible to distinguish between a coplanar structure of I (with the sulfur–oxygen bond oriented at an angle to the molecular plane), and a moderately folded boat conformation in which the energy barrier toward inversion is too low to permit the isolation of two isomers. Infrared data suggest, however, that the sulfoxide oxygen has an axial orientation. The 2,4-dinitrophenylhydrazone of I is obtained as an orange solid, or as a purple monohydrate. The sulfoxide is reduced by hydrochloric acid–dioxane without the expected chlorination, and in this novel way it is possible to prepare the 2,4-dinitrophenylhydrazone of thiaxanthone which could not be prepared directly.

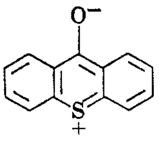
The possibility of transannular sulfoxide–ketone interactions,[2] as well as sulfoxide association phenomena,[3] made it desirable to prepare the sulfoxide of thiaxanthone. Also it is of interest to examine whether this system, like the previously studied thiane 1-oxides[4,5] and 1,4-dithiane *trans*-1,4-dioxides,[6,7] shows a preference for an axial-oriented sulfoxide oxygen conformation, provided, of course, that the molecule is not coplanar.

Surprisingly enough, the sulfoxide (I) of thiaxanthone is not described in the literature. The oxidation of thiaxanthone by means of hydrogen peroxide,[8] of substituted thiaxanthones,[9] and of thiaxanthone analogs,[10] invariably yielded the corresponding sulfones. Chromic acid oxidation,[11] as well as nitration[12] of thiaxanthones, also gave the sulfones. While there is no *a priori* reason for the instability of this sulfoxide, the fact that thiaxanthone resisted oxidation under a mild peroxide treatment led previous investigators[13] to conclude that the unsuccessful attempts to prepare I can be traced to the large dipole moment of the parent compound.

Our attempts to prepare the elusive sulfoxide were centered about three recently reported selective oxidizing agents for the conversion of sulfides to sulfoxides, namely sodium metaperiodate,[14] N-bromosuccinimide,[15] and iodosobenzene diacetate.[16] Of these reagents, the latter was found to be most satisfactory for our purposes since formation of sulfone is negligible. In a similar fashion 2-chlorothiaxanthone was converted by means of iodosobenzene diacetate to the corresponding sulfoxide. In this instance oxidation to the sulfone is more noticeable.

It is well known that typical reactions of the carbonyl function are inhibited[13,17] in thiaxanthone, while the corresponding sulfone exhibits normal carbonyl behavior.[18–20] This difference in behavior has been attributed[21] to the dipolar ion structure II in cyclic ketones containing a heteroatom with nonbonding electrons. This raises the question as to whether I exists in an analogous structure III in spite of the high positive charge at the sulfur atom. In view of the facile formation of the 2,4-dinitrophenylhydrazone of the sulfoxide under discussion one is led to conclude that structure III does not contribute significantly to the ground state of I.


I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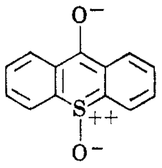
III

The observation that the sulfoxide function of I is reduced by means of dioxane–hydrochloric acid reagent[22] without accompanying chlorination of the ring system (*vide infra*) permitted preparation of the 2,4-dinitrophenylhydrazone of thiaxanthone from the analogous derivative of I. Attempts to prepare the latter compound directly from thiaxanthone under forcing conditions, namely by prolonged heating in amyl alcohol with an excess of 2,4-dinitrophenylhydrazine, gave only thin layer evidence of its formation in small amounts together with decomposition products.

The 2,4-dinitrophenylhydrazone of I exhibits an unusual property in that it forms, under carefully controlled conditions, a solid hydrate which is deep purple in contrast to the orange "normal" product.

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[2] N. J. Leonard and C. R. Johnson, *J. Am. Chem. Soc.*, **84**, 3701 (1962), and related papers.

[3] (a) R. F. Watson and J. F. Eastham, *ibid.*, **87**, 664 (1965); (b) R. Figueroa, E. Roig, and H. H. Szmant, *Spectrochim. Acta*, **22**, 587 (1966).

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[6] H. M. M. Shearer, *J. Chem. Soc.*, 1394 (1959).

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[15] W. Tagaki, K. Kikukawa, K. Ando, and S. Oae, *Chem. Ind.* (London), 1624 (1964).

[16] (a) A. H. Ford-More, *J. Chem. Soc.*, 2126 (1949); (b) H. H. Szmant and G. Suld, *J. Am. Chem. Soc.*, **78**, 3400 (1956).

[17] M. M. Coombs, *ibid.*, **80**, 4200 (1958).

[18] W. E. Truce and J. A. Simms, *J. Org. Chem.*, **22**, 617 (1957).

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[22] K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, Jr., *J. Am. Chem. Soc.*, **86**, 1452 (1964).

The double-bond character of the ketone function of I is reflected by coincidence of its carbonyl stretching frequency with that of the sulfone (Table I). This point is discussed below in greater detail.

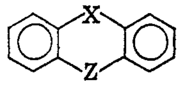
Table I

Carbonyl Stretching Frequencies (cm^{-1}) in Systems IV (X = CO)

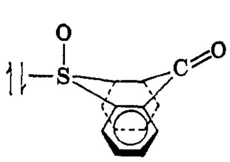
	Z		
Sample in	S	SO	SO_2
CCl_4	1645[a] 1650[b]		1684[c]
CH_2Cl_2	1642[d,e]	1672[d,e]	1672[d,e]
$CHCl_3$		1672[d]	1672[d]
CF_3CH_2OH		1669[d]	
KBr	1640[f]	1672[d]	

[a] A. R. Katrizky and A. P. Ambler, "Physical Methods in Heterocyclic Chemistry," Vol. II, A. R. Katrizky, Ed., Academic Press Inc., New York, N. Y., 1963, p 257. The values when Z = O, NPh, AsPh, and As(O)Ph are 1660, 1632, 1647, and 1662 cm^{-1}, respectively. [b] T. L. Brown, *Spectrochim. Acta,* **18,** 1065 (1962). The value when Z = O is 1668 cm^{-1}. [c] M. M. Coombs, *J. Chem. Soc.,* 4200 (1958). [d] This work. [e] The 2-chloro-substituted sulfide and sulfoxide or sulfone absorb at 1636 and 1675 cm^{-1}, respectively (this work). [f] R. H. Martin, *et al., Tetrahedron,* **21,** 1844 (1965). The value for Z = O is 1667 cm^{-1}.

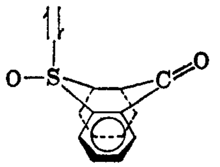
Next, we may inquire into the conformation of the central ring of I. Recently Hosoya[23] has concluded that it suffices that one group (X or Z) be a sulfur, selenium, or tellurium atom in order to produce a folded conformation in IV. The companion group may be O, NH, CH_2, or another S. Also the *trans* disulfoxide of thianthrene (IV, X = Z = SO) has a folded structure[24] with a dihedral angle of approximately 142° (against the corresponding angle of 142° in thianthrene,[28] and 134 ± 5° in phenoxathiine[24]), but one wonders how the presence of the carbonyl function affects the conformation of the molecule since the carbonyl function tends to enforce the coplanarity of the C–CO–C system as well as a bond angle of 120°. Thus it is possible that the effect of the carbonyl group overcomes the usual tendency[23] of the sulfur function to induce a folded structure. Evidence available at this time[25] fails to distinguish between a coplanar structure in which the sulfur–oxygen bond is at an angle to the molecular plane, and a moderately folded structure. If the latter possibility is true then one may visualize the existence of isomers represented by V and VI unless the energy barrier of "flapping" is too low to allow for the separation of the isomers at room temperature.



IV



VI



V

The energy barrier to inversion of the thianthrene molecule (through "flapping" of the benzene rings) was estimated[26] to be a relatively low value of 6–7 kcal/mole. It is reasonable to assume that a higher energy barrier would accompany the presence of more rigid central atoms or groups of atoms, but it is doubtful that this value should reach 16–20 kcal/mole estimated[27] to be necessary to permit the isolation of conformational isomers at room temperature. The energy barrier apparently does not reach this value in the case of *cis*-thianthrene disulfoxide since only one isomer is known.[28] Similarly, in the case of the sulfoxide of phenoxathiin the existence of only one isomer[24] points toward and easy inversion of the structure through "flapping." Our failure to find chromatographic (thin layer) evidence of formation of an isomeric sulfoxide of thiaxanthone, as well as unsuccessful attempts to bring about an isomerization of I, points to either a coplanar structure or one in which conformations V and VI are separated by a relatively low energy barrier.

An attempt to detect the presence of both conformations V and VI in solutions of I was made by examining the infrared spectra.[29]

The frequency of the carbonyl group in heterocycles of type IV (X = CO) is known[30] to vary as a function of the structure of group Z. Table I lists the carbonyl stretching frequencies reported for several heterocyclic systems and the values determined in this study.

As expected, the position of the carbonyl stretching frequency reflects the bond order of the carbon–oxygen bond, and this is primarily a function of the ability of group Z to delocalize its nonbonding electrons into the π system of the heterocycle. We note that the carbonyl group frequency of I coincides with that in the corresponding sulfone. This supports the conclusion concerning the small degree to which electron distribution III contributes to the structure of I. The fact that trifluoroethanol produces a small decrease in the bond order of the carbonyl group in I suggests that hydrogen bonding occurs nearly to the same extent at both functional groups, with the carbonyl group having a slight advantage over the sulfoxide.

Returning to the question of the preference for conformation V or VI, we find no evidence either way from the examination of the stretching frequency of the carbonyl group. It appears clear, however, that a strong transannular interaction[2] which is only possible if the boat conformation VI is steep enough does not seem to occur.

The sulfoxide stretching frequencies of I and related compounds were also examined in an attempt to distinguish between the possible conformation of I in solution. These results are summarized in Table II.

The sulfoxide stretching frequency had to be carefully distinguished from the nearby bands which are also present in the corresponding parent system in which the sulfide exhibits a peak at 1026 cm^{-1} which

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(23) S. Hosoya, *Acta Cryst.,* **16,** 310 (1963).

(24) H. Lumbroso and G. Montaudo, *Bull. Soc. Chim. France,* 2119 (1964).

(25) Arrangements are being made to examine the molecular structure of I by X-ray diffraction method.

(26) A. K. Chandra, *Tetrahedron,* **19,** 471 (1963).

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(28) M. J. Aroney, R. J. W. Le Fèvre, and J. D. Saxby, *J. Chem. Soc.,* 571 (1965).

(29) The dipole moment of I is currently being determined in Professor C. C. Price's laboratory.

(30) See Table I, footnote *a.*

TABLE II

SULFOXIDE STRETCHING FREQUENCIES ($\mathrm{CM^{-1}}$) IN SYSTEMS IV (Z = SO)

	X						
						SO^c	
Sample in	S	O	CHOH^a	CO	CO·DPNPH^b	*cis*	*trans*
KBr			1004–1012^d	1021	1031	1087–1094^d	1070–1079 1018–1044
$\mathrm{CH_2Cl_2}$		1066 1020–1042^d		1038^e			
$\mathrm{CHCl_3}$	1070 1031	1067 1010–1031^d		1040			

[a] Unpublished work from this laboratory. [b] 2,4-Dinitrophenylhydrazone (both yellow and red forms gave the same spectrum in this range). [c] K. Mislow, P. Schneider, and A. L. Ternay, Jr., *J. Am. Chem. Soc.*, **86**, 2957 (1964). [d] Broad bands. [e] The 2-chloro-substituted compound absorbs at 1042 $\mathrm{cm^{-1}}$.

TABLE III

SOLVENT EFFECTS ON THE ELECTRONIC TRANSITION OF THE NONBONDING ELECTRONS OF THE SULFOXIDE OXYGEN IN IV (X = SO)

	Z^a				
				SO^b	
Solvent	O	S	CO	*cis*	*trans*
Cyclohexane	220 (*ca.* 32)	247 (18.2)	239 (21)		
Ethanol	221 (*ca.* 34)	239 (34.1)	232 (25.5)	212 (52)	221 (54)
$\mathrm{CF_3CH_2OH}$			225 (*ca.* 27)		

[a] Maxima are given in mμ and molar absorptivities ($\times 10^{-3}$) are cited in parentheses. [b] Reference 31.

overlaps with the sulfoxide peaks. Table II reveals an interesting difference between the spectrum of I and the spectra of the sulfoxides of thianthrene and phenoxathiin. The latter systems exhibit two sulfoxide bands and this is taken to mean that the sulfoxides exist in solution in two conformations of sufficient concentration to be detected by this method, while I is either coplanar or predominantly in conformation VI. Recent work[24] leads to the conclusion that the equatorial orientation of the sulfoxide oxygen in the boat conformation is preferred in the case of the phenoxathiin system because the axial orientation suffers from a repulsion between the nonbonding electrons of both oxygen atoms. The same may be expected to occur between the nonbonding electrons of oxygen and sulfur in the monosulfoxide of thianthrene, but in the case of I, the nonbonding electrons of the axially oriented sulfoxide oxygen confront a receptive p orbital of the carbon terminal of the carbonyl group. The position and shift of the S–O stretching frequency in I under conditions of hydrogen bonding suggest that the axial conformation is preferred as is the case in 1-thiacyclooctan-5-one 1-oxide[2] except that the interaction is not as strong in the aromatic system. The axial orientation is also preferred in the sulfoxide of thiaxanthydrol because of the formation of an intramolecular hydrogen bond. The above interpretations agree with the conclusions of Mislow and coworkers[31] based on the study of the *cis* and *trans* isomers of thianthrene disulfoxides. The preferred conformation of the *cis* isomer has an equatorial conformation for both sulfoxide oxygens, and the band at 1087–1094 $\mathrm{cm^{-1}}$ is associated with this orientation. The *trans* isomer has an axial as well as an equatorial oxygen, and, while the latter again gives a high-frequency band (1070–1079 $\mathrm{cm^{-1}}$), there is a low-frequency band at 1018–1044 $\mathrm{cm^{-1}}$ which is attributed to the axially oriented sulfoxide.

In connection with the attempts to bring about an isomerization, I was treated with a mixture of hydrochloric acid and dioxane[22] but the reduction product was isolated instead. It appears that unlike the case of thianthrene,[32] our parent sulfide resists chlorination under the conditions of this reaction. The deactivating character of the carbonyl group suggests an electrophilic chlorination mechanism.

The electronic spectra of the sulfides and sulfoxides of type IV (X = S or SO; and Z = O, S, or CO) were examined in cyclohexane and ethanol. These results will be discussed in detail elsewhere, but here we wish to point out one aspect of the spectra which relates to the structures of the three sulfoxides. The absorption band associated with the electronic transition of the nonbonding electrons of the sulfoxide oxygen exhibits interesting solvent effects which are summarized in Table III.

The inspection of the results listed in Table III suggests that the relative position of the absorption bands in the inert solvent is related to the preferred equatorial orientation of the sulfoxide oxygen when Z = O, and the preferred axial orientation when Z = S or CO. We note that this conclusion is in perfect agreement with the differentiation of the isomeric thianthrene disulfoxides by Mislow and co-workers.[31] The lower energy requirement of the excitation of the axially oriented sulfoxide is probably related to transannular interactions involving the p orbital of oxygen. The data of Table III indicate that this interaction occurs most readily with the sulfur atom of thianthrene, less readily with the carbon atom of the thiaxanthone, and least readily with the equatorial sulfoxide of the *trans*-thianthrene disulfoxide. Since the sulfoxide of phenoxathiin is presumed to be equatorially oriented and is therefore less capable of interacting with the rest of the molecule, this compound shows no hypsochromic shifts when one changes to a protic solvent. Such hypsochromic shifts are observed, on the other hand, in the sulfoxides when X = S and SO.

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(31) See Table II, footnote *c*.

(32) H. J. Shine and C. F. Dais, *J. Org. Chem.*, **30**, 2145 (1965).

Experimental Section

Materials.—Commercially available thiaxanthone (Aldrich Chemical Co.) and iodosobenzene diacetate (Eastman) were utilized for the oxidation experiments without further purification. For spectroscopic measurements the thiaxanthone was purified by dissolving in methylene chloride (Spectro Grade), filtration, recovery of the solid by evaporation of the solvent, and crystallizations of the residue from glacial acetic acid, and 95% ethanol and some chloroform. In this way long yellow crystals (mp 213–216°) were obtained, which gave only one spot in thin layer chromatographic assays.

Oxidation of Thiaxanthone.—A solution of 2 g of thiaxanthone (9.4 mmoles) and 3.04 g of iodosobenzene diacetate (9.4 mmoles) in 100 cc of glacial acetic acid was refluxed during 4 hr, allowed to stand overnight, filtered in order to remove a small amount of insoluble impurities, and treated near its boiling point with 450 cc of hot, distilled water. The mixture was allowed to cool overnight and filtered, and the solid was washed with additional amounts of distilled water. Tlc on silica showed the precipitate to consist of a mixture of thiaxanthone and I, while the filtrate and washings contained essentially pure I. The filtrated and washings were concentrated *in vacuo* and the light yellow residue (0.79 g) was recrystallized from ethanol to give I, mp 202–204°.[33]

Anal.[33] Calcd for $C_{13}H_8O_2S$: C, 68.40; H, 3.53; S, 14.05. Found: C, 68.39; H, 3.51; S, 14.03.

The original precipitate (1.10 g) was chromatographed in two portions from 75 × 2 cm silica gel columns using benzene as eluent. After removal of some starting material, the sulfoxide was eluted with chloroform. The product (0.88 g) was recrystallized once from ethanol to give pure I, mp 200–201°. The total yield of crude sulfoxide was 1.67 g of 78% of theory.

Compound I does not depress the melting point of thiaxanthone while it depresses the melting point of the corresponding sulfone.[34]

Attempts to prepare I by means of an equimolar quantity of sodium metaperiodate[14] produced a mixture of the desired sulfoxide and the corresponding sulfone, as well as unoxidized starting material. The oxidation with N-bromosuccinimide[15] gave similar results. An oxidation of thiaxanthone by means of an equimolar quantity of 30% of hydrogen peroxide in *n*-propyl-alcohol gave a negligible amount of I and mainly the corresponding sulfone.

Attempted Isomerization of I.—Compound I distilled without change upon heating at atmospheric pressure. With concentrated sulfuric acid in the cold for 1 day I gave an orange solution with yellow-green fluorescence from which I was recovered unchanged by dilution with water. A treatment of I with a mixture[22] of concentrated hydrochloric acid and dioxane (1:2 parts by volume) gave a precipitate upon standing. The fine needles were identified as thiaxanthone by melting point, mixture melting point, and thin layer chromatography. A treatment with 48% hydrofluoric acid of I for a period of 24 hr at room temperature gave unchanged I. A treatment of I with the boron trifluoride–acetic acid complex[35] gave a solution similar to that produced by sulfuric acid from which I was recovered unchanged.

Conversion of I to the Sulfone.—Compound I was dissolved in glacial acetic acid and treated with potassium permanganate. The solution was heated, treated with sodium bisulfite, and poured into water. The precipitate was recrystallized from glacial acetic acid to give slightly yellow needles of the sulfone of thiaxanthone, mp and mmp 185–187°.[36]

Preparation of the 2,4-Dinitrophenylhydrazone of I.—A solution of 274 mg of I (1.26 mmoles), 250 mg of 2,4-dinitrophenylhydrazine (1.26 mmoles), and 6 drops of concentrated hydrochloric acid in 10 ml of 95% ethanol was refluxed for 3 hr, cooled, and filtered. The product was purified by chromatography on alumina (Merck, acidic) using chloroform as eluent, and crystallized twice from a mixture of chloroform and ethanol to give orange crystals, mp 255.5–256.5° dec.

Anal. Calcd for $C_{19}H_{12}N_4O_5S$: C, 55.88; H, 2.96; N, 13.72; S, 7.85. Found: C, 56.05; H, 3.11; N, 13.63; S, 8.06.

In some experiments the product was a deep purple solid. It melted partially at 164–167° with evolution of water vapor, and the contents of the capillary tube resolidified to melt again at 254–259°. Attempts to crystallize the purple solid from a number of solvents gave the above-mentioned orange crystals. The orange 2,4-dinitrophenylhydrazone could be converted into the purple form by the addition of water to a solution in acetic acid. The infrared spectra of the two solids (KBr pellets) were identical except for the presence of hydroxylic absorption shown by the red form.

The purple 2,4-dinitrophenylhydrazone was analyzed to give C, 53.43; H, 3.38; N, 13.03. Calcd for $C_{19}H_{12}N_4O_5S \cdot H_2O$; C, 53.52; H, 3.31; N, 13.14.

The 2,4-dinitrophenylhydrazone of thiaxanthone sulfone was prepared for comparison, and was obtained as bright orange needles, mp 270.5–271° dec.

Anal. Calcd for $C_{19}H_{12}N_4O_6S$: C, 53.77; H, 2.85; N, 13.20; S, 7.56. Found: C, 53.98; H, 2.98; N, 13.41; S, 7.65.

All attempts to obtain a purple form analogous to that described in the case of the sulfoxide failed.

The 2,4-Dinitrophenylhydrazone of Thiaxanthone.—The 2,4-dinitrophenylhydrazone of I (1.15 g) was stirred at room temperature for 24 hr in a mixture of 20 ml of concentrated hydrochloric acid and 30 ml of dioxane. The suspension was filtered and the resulting solid was washed with water and dried in air. The crude product (0.97 g) was chromatographed using silica gel and chloroform. The desired fraction was obtained from the first colored band which was eluted, and was recrystallized from toluene to give 0.49 g of garnet red crystals, mp 272.5–274° dec.

Anal. Calcd for $C_{19}H_{12}N_4O_4S$: C, 58.16; H, 3.08; N, 14.28; S, 8.17. Found: C, 58.06; H, 3.39; N, 14.11; N, 14.11; S, 8.31

Oxidation of 2-Chlorothiaxanthone.—A solution of 2.47 g of 2-chlorothiaxanthone and 3.22 g of iodosobenzene diacetate in 100 ml of glacial acetic acid was refluxed for 8 hr, allowed to stand overnight, and treated at its boiling point with 350 cc of hot water. The hot solution was decanted from a sticky, yellow residue and allowed to cool in a refrigerator. A light yellow precipitate separated from the solution and it was washed with water and dried in air to give 2.14 g of crude product which was chromatographed (in three portions) from a 75 × 2 cm silica column. First, benzene was used as eluent to remove some impurities, and then the sulfoxide was eluted with dichloromethane. The product was recrystallized from ethanol to give 0.79 g of yellowish crystals, mp 176.5–177°.

Anal. Calcd for $C_{13}H_7ClO_2S$: C, 59.43; H, 2.69; Cl, 13.49; S, 12.25. Found: C, 59.58; H, 2.81; Cl, 13.45; S, 12.05.

The 2,4-dinitrophenylhydrazone was prepared by refluxing 393 mg of the sulfoxide and 299 mg of 2,4-dinitrophenylhydrazine in a solution of 1 ml 6 *N* hydrochloric acid and 30 ml of 95% ethanol for 16 hr. The crude product (554 mg) was crystallized from a mixture of chloroform and ethanol to give orange crystals, mp 268.5–269° dec.

Anal. Calcd for $C_{19}H_{11}ClN_4O_5S$: C, 51.53; H, 2.50; Cl, 8.01; N, 12.65. Found: C, 51.75; H, 2.62; Cl, 7.89; N, 12.84.

For comparison the 2,4-dinitrophenylhydrazone of the corresponding sulfone (prepared as described for the preparation of the sulfone of I) was prepared by refluxing 558 mg of 2-chlorothiaxanthone 10,10-dioxide (mp 227.5–229.5°) with 436 mg of 2,4-dinitrophenylhydrazine in a solution of 3 ml of concentrated hydrochloric acid and 100 ml of 95% ethanol. The bright orange crystals (mp 278–278.5° dec) were crystallized from toluene without causing a change in the melting point.

Anal. Calcd for $C_{19}H_{11}ClN_4O_6S$: C, 49.74; H, 2.42; Cl, 7.73; N, 12.21; S, 6.99. Found: C, 49.96; H, 2.50; Cl, 7.67; N, 12.03; S, 6.91.

Determination of the Spectra.—The infrared and ultraviolet spectra were determined using a Perkin-Elmer 237 and a Cary 14-K spectrophotometer, respectively.

Registry No.—I, 7605-15-4; 2,4-dinitrophenylhydrazone of I, 7648-77-3; 2,4-dinitrophenylhydrazone of thiaxanthone sulfone, 7605-16-5; 2,4-dinitrophenylhydrazone of thiaxanthone, 7605-17-6; 2-chlorothiaxanthone

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[33] All microanalyses were by Dr. Alfred Bernhardt, Max Plank Institute, Mülheim (Ruhr), Germany. All melting points are uncorrected and were determined by means of a Mel-Temp apparatus.

[34] The formation of solid solutions between thiaxanthone and I may be partially responsible for the failure to detect the sulfoxide by some previous investigators.[13] Mixed crystals are commonly formed by related sulfoxides and sulfones but are not expected in sulfide–sulfoxide pairs; see H. Rheinboldt and E. Giesbrecht, *J. Am. Chem. Soc.*, **68**, 913 (1946), and preceding papers; S. C. Abrahams and J. V. Silverton, *Acta Cryst*, **9**, 281 (1956).

[35] C. A. Johnson, *J. Am. Chem. Soc.*, **85**, 1020 (1963).

[36] H. Heymann, *ibid.*, **71**, 260 (1949).

sulfoxide, 7605-18-7; 2,4-dinitrophenylhydrazone of 5, 7605-19-8; 2,4-dinitrophenylhydrazone of corresponding sulfone, 7649-30-1; IV ($X = CO$, $Z = SO_2$), 3166-15-2; IV ($X = CO$, $Z = S$), 492-22-8; IV ($Z = SO$, $X = S$), 2362-50-7; IV ($Z = SO$, $X = O$), 948-44-7; IV ($Z = SO$, $X = CHOH$), 7605-20-1; IV ($Z = SO$, $X =$ SO-*cis*), 2748-51-8; IV ($Z = SO$, $X =$ SO-*trans*), 2748-50-7.

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The Reaction of Active Methylene Compounds with Carbon Disulfide in the Presence of Ammonia. I. The Reaction of Cyclohexanone

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Cyclohexanone, in the presence of ammonia, easily reacted with carbon disulfide to give a characteristic sulfur compound containing nitrogen. Cyclohexylideneammonium 2-cyclohexylideneamino-1-cyclohexene-1-dithiocarboxylate (I) was proposed for this compound. Compound I was easily converted into its isomer, for which 1′-amino-1′-cyclohexyl 2-cyclohexylideneamino-1-cyclohexene-1-dithiocarboxylate (II) was proposed. Both I and II easily gave a derivative of thiazine which was assigned 4-thiono-1,2,5,6,7,8-pentahydro-3,1,2-benzothiazine-2-spirocyclohexane (III). Compound I was remarkably sensitive to cupric and a few other metal ions. In relation to the present reaction, several new compounds are described. It is suggested that two of these compounds, 2,4-dithiono-1,2,5,6,7,8-pentahydro-3,1,2-benzothiazine (IV) and 9-thiono-10-azanonahydroanthracene (V), may have *meso*-ion structure.

The present investigation was directed to exploring the reaction of active methylene compounds with carbon disulfide in the presence of ammonia. Here, cyclohexanone was chosen as one of the model active methylene compounds.

Cyclohexanone readily reacted with the above reagents to give a characteristic and rather unstable compound, $C_{19}H_{30}N_2S_2$ (I), which formed yellow needles and melted at 115–116° (slow heating) and 135–136° (rapid heating) and was very sensitive to cupric ion. Compound I, when treated with acidic reagents, was readily converted into long orange plates, $C_{13}H_{19}N_2S_2$ (III), mp 197–198°, and cyclohexanone (Scheme I). The same compound, on treatment with methanol or such as dimethylformamide for a short time was converted into an isomeric compound, short orange prisms, $C_{19}H_{30}N_2S_2$ (II), mp 143–144° dec (slow heating) and 162° dec (rapid heating). In these transformations I was sensitive to trivial conditions and other complex compounds have been obtained from the former; these problems will be reported in a separate paper. When I was heated with morpholine, elimination of dithiocarboxyl group occurred to give a dithiocarbamate.[3]

Compound II, on treatment with acid, also changed into III and cyclohexanone.

Generally, III was most easily obtained in these transformations. When the crude product mentioned above was treated with acetic acid, III was obtained in almost quantitative yield. The compound was rather stable and easily soluble in hydrochloric acid or alcoholic alkali; the greater part could be regenerated from the solution by neutralization.

In order to determine the structure of these compounds, III was subjected to oxidation and desulfuration. Oxidation with permanganate gave cyclohexanone and cyclohexanedione. Desulfuration afforded 2-methylcyclohexanone and N-cyclohexyl-2-methylcyclohexylamine (VII). Picryl and benzoyl derivatives of III, and methyl, ethyl, and benzylidene derivatives of II were also prepared.

The presence of a thiocarbonyl group in I, II, and III was inferred from their ultraviolet absorption spectra. The presence of an amino group in II and an imino group in III was considered from their infrared absorption spectra. It seemed that I had neither amino nor imino group and broad bands which may be assigned to $^{+}NH_2{=}$ or $-^{+}NH{=}$ group were observed.

When II was alkylated (the methyl derivative, IIa, and the ethyl derivative, IIb), one of the two NH_2 stretching bands disappeared; the benzylidene deriva-

TABLE I

APPEARANCE AND MELTING POINTS OF THE COMPOUNDS INVESTIGATED

Compd[a]	Appearance	Mp, °C (cor)
I	Yellow needles	115–116 (slow heating) 135–136 (rapid heating)
II	Short orange prisms	143–144 dec (slow heating) 162 dec (rapid heating)
IIa	Yellow needles	204–205
IIb	Yellow needles	201–202
IIc	Orange-red plates	183–184
III	Long orange plates	197–198
IIIa	Yellow crystals	136–138
IIIb	Yellow needles or plates	165–166 dec
IIIc	Orange thick plates	194–195
IV	Lustrous red plates	202–203 dec
V	Light flesh colored crystals	*ca.* 250 dec
VI	Light pink needles	275–276
Hydrochloride of VII	Colorless thick plates	265–266 (in sealed tube)

[a] IIa, methyl derivative of II; IIb, ethyl derivative of II; IIc, benzylidene derivative of II; IIIa, benzoyl derivative of III (hydrochloride); IIIb, picryl derivative of III (hydrochloride); IIIc, the compound prepared from 4-methylcyclohexanone (corresponds to III).

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(3) Colorless needles, mp 233–234° (in sealed tube), possibly $O(CH_2CH_2)_2NCSS^- \cdot H_2N^+(CH_2CH_2)_2O$. Details may be reported in a separate paper.