2,2-Dimethyl-1-thiacoumaran was trapped from the vpc and identified by its infrared, nmr, and mass spectra. The infrared showed an *ortho*-substituted benzene ring pattern between 1660 and 1880 cm^{-1}, a split geminal dimethyl group at 1363–1383 cm^{-1}, and an *ortho*-substituted benzene ring pattern at 740 and 695–702 cm^{-1}. The nmr showed a single methyl peak at τ 8.48, a single methylene peak at 6.99, and an aromatic ring at 3.0. The proton integration was consistent. The mass spectrum showed a base peak at m/e 149 and parent peak at m/e 164. The mass and infrared spectra were identical with the data obtained by the Bureau of Mines' workers on an authentic sample isolated from "Wasson Crude Oil."

Pyrolysis of β-Methylallyl Phenyl Sulfide in Refluxing Quinoline for Varying Amounts of Time.—In a three-neck 500-ml flask equipped with magnetic stirrer, nitrogen inlet, water-cooled condenser, and dropping funnel was placed 200 g of pure quinoline. The quinoline was brought to reflux with stirring and under nitrogen and then 36 g of pure β-methylallyl phenyl sulfide added in a period of 3 min. The reaction temperature was kept at 237 ± 3°. Samples (10 ml) were withdrawn at 10-min intervals for 1.5 hr. In all, nine samples were taken. Each sample was diluted with ether, washed with 40 ml of 3 M HCl to remove the quinoline, and dried with anhydrous $MgSO_4$. The ether was removed under vacuum and the resultant liquid analyzed by gas chromatography. The results of the experiment are summarized in Table III.

Pyrolysis of β-Methylallyl Phenyl Sulfide in Quinoline at 300°.—A 15% solution of β-methylallyl phenyl sulfide in quinoline was sealed in a tube and heated for 1.5 hr at 300°. The reaction mixture was diluted with ether and the quinoline removed by washing with 3 M HCl. After the ether solution was dried with anhydrous $MgSO_4$, the ether was removed under vacuum and the resultant liquid was analyzed by gas chromatography. The results of this experiment are summarized in Table III.

Pyrolysis of Diphenyl Disulfide.—About 1 g of diphenyl disulfide was sealed in a small tube and heated in an oil bath for 2 hr at 300°. The tube was then cooled down, opened, and analyzed by vpc. A calibration curve was constructed for this analysis by measuring the intensities of peaks from solutions of known concentrations. From this curve it was determined that the pyrolysate consisted of 48% diphenyl sulfide (and thus 52% unconverted diphenyl disulfide). A silicone oil gas chromatography column was used in this study.

Pyrolysis of Thiophenol.—Thiophenol was also pyrolyzed at 300° for 2 hr in a sealed tube. The pyrolysate was analyzed by vpc in exactly the same way as in the pyrolysis of diphenyl disulfide. This analysis showed that diphenyl sulfide had been formed in the amount representing 13% conversion of the thiophenol.

Registry No.—**1**, 702-00-1; **2**, 6165-59-9; **5**, 13640-71-6; **7**, 6087-88-3.

Acknowledgment.—We are obliged for the support of this work by the National Science Foundation under Grant GP-1177. We are indebted to Professor Henry J Shine for the benefit of several valuable discussions.

Thiapyrone Chemistry. I. The Thermal Rearrangement of 2,6-Dialkylthio-3,5-diphenyl-4-thiothiapyrones[1]

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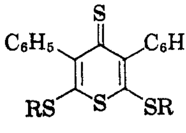
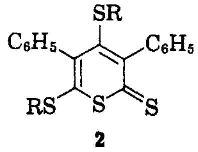
The thermal rearrangement of 2,6-dialkylthio-3,5-diphenyl-2-thiothiapyrones (**1**), first reported by Schönberg, has been reexamined and clarified. The major product of the rearrangement is the isomeric 4,6-dialkylthio-3,5-diphenyl-2-thiothiapyrone (**2**), but, contrary to the earlier reports, this isomerization has been found to be reversible. An equilibrium constant for the reaction has been determined and a structure is suggested for one of the by-products of the thermal process. It has been demonstrated by means of a crossover experiment that the isomerization is intermolecular rather than intramolecular as had been previously proposed by Schönberg. Heating a mixture of two different 4-thiothiapyrones above their melting temperatures produced a complex reaction mixture from which a crossover product was isolated and characterized.

Some 20 years ago, Schönberg and Asker[2] described the chemistry of 2,6-dialkylthio-3,5-diphenyl-4-thiothiapyrones (**1**). Included in these earlier investigations was the thermal isomerization of **1** to 4,6-dialkylthio-3,5-diphenyl-2-thiothiapyrones (**2**). Schönberg[3] had previously reported the thermal isomerization of diaryl thioncarbonates (**3**) to diaryl thiolcarbonates (**4**) and suggested that both rearrangements involved a similar mechanistic pathway.[2b] The mechanism proposed for these rearrangements was intramolecular and was explained by assuming that at high temperatures ionic structures make a contribution to resonance stabilization. The rotation of the anion portion of one of the contributing structures about an axis going through the center of the molecule and perpendicular to the plane of the ring was postulated to account for the observed isomerization. These pathways are shown in Scheme I. The mechanism of the carbonate rearrangement, which now bears Schönberg's name, has been carefully elucidated by Tarbell and co-workers.[4] These investigators found the isomerization to be intramolecular, involving nucleophilic displacement by sulfur rather than aryl migration, and requiring a four-membered cyclic transition state (A). An intramolecular rearrangement of this type in the thiapyrone



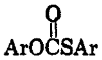
1a, R = CH_3
b, R = C_2H_5
c, R = $(CH_3)_2CH$
d, R = $C_6H_5CH_2$
e, R = p-$NO_2C_6H_4CH_2$



2


$$\mathrm{ArO\overset{S}{\overset{\|}{C}}OAr}$$

3


$$\mathrm{ArO\overset{O}{\overset{\|}{C}}SAr}$$

4

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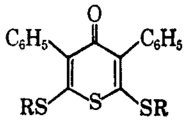
[1] (a) This paper is a portion of a thesis submitted by H. J. T. in partial fulfillment of the requirements for a M.S. degree, May 1967. (b) Presented in part at the 18th Southeastern Regional Meeting of the American Chemical Society, Louisville, Ky., Oct 1966.

[2] (a) A. Schönberg and W. Asker, *J. Chem. Soc.*, 198 (1945); (b) A. Schönberg and W. Asker, *ibid.*, 604 (1946).

[3] (a) A. Schönberg and L. Vargha, *Ber.*, **63**, 178 (1930); (b) A. Schönberg, L. Vargha, and W. Paul, *Ann.*, **483**, 107 (1930).

[4] (a) H. R. Al-Kazimi, D. S. Tarbell, and D. Plant, *J. Am. Chem. Soc.*, **77**, 2479 (1955); (b) D. H. Powers and D. S. Tarbell, *ibid.*, **78**, 70 (1956).

Table I
Properties of 2,6-Dialkylthio-3,5-diphenyl-4-thiapyrones (5)



Compound	Mp, °C	Formula	Calcd, % C	Calcd, % H	Found, % C	Found, % H	Crude yield, %
5a, R = CH_3	163–166[a] (ethyl acetate)	$C_{19}H_{16}OS_3$	*b*				82.5
5b, R = C_2H_5	139–142[c] (benzene–hexane)	$C_{21}H_{20}OS_3$	*b*				79
5c, R = $(CH_3)_2CH$	145–148 (benzene–hexane)	$C_{23}H_{24}OS_3$	66.96	5.86	66.72	5.71	46.4[d]
5d, R = $C_6H_5CH_2$	129–132 (heptane–benzene)	$C_{31}H_{24}OS_3$	73.18	4.75	73.17	4.83	79
5e, R = p-$NO_2C_6H_4CH_2$	200–203 (benzene–chloroform)	$C_{31}H_{22}N_2O_5S_3$	62.19	3.74	62.40	3.76	87

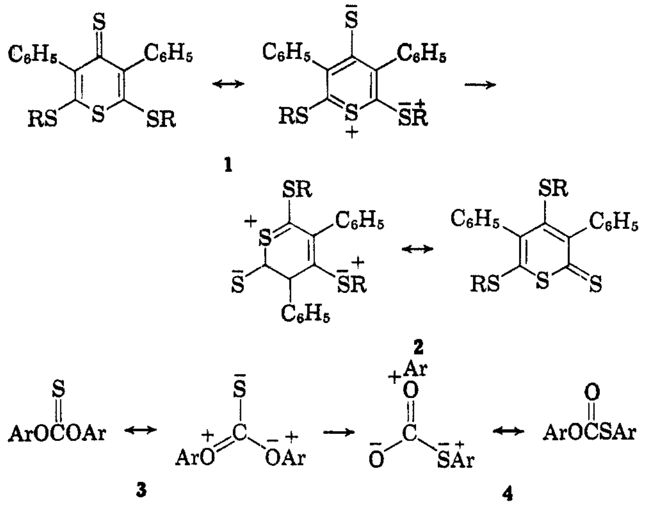
[a] Lit.[5a] mp 167°. [b] Analysis not obtained. [c] Lit.[5a] mp 141.5–142°. [d] Yield after recrystallization.

Table II
Properties of 2,6-Dialkythio-3,5-diphenyl-4-thiothiapyrones (1)

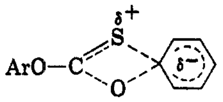
Compound	Mp, °C	Formula	Calcd, % C	Calcd, % H	Found, % C	Found, % H	Yield, %
1a, R = CH_3	245–248[a] (acetonitrile)	$C_{19}H_{16}S_4$					69.0
1b, R = C_2H_5	190–192[b] (acetonitrile)	$C_{21}H_{20}S_4$	62.96	5.03	63.29	5.09	57.0
1c, R = $(CH_3)_2CH$	198–199.5 (benzene)	$C_{23}H_{24}S_4$	64.44	5.64	64.19	5.51	85.0
1d, R = $C_6H_5CH_2$	150[d] (benzene)	$C_{31}H_{24}S_4$	71.15	4.62	70.94	4.52	68.0[e]
1e,[c] R = p-$NO_2C_6H_4CH_2$	140[f] (benzene)	$C_{31}H_{22}N_2O_4S_4$	60.56	3.60	60.47	3.65	19.5

[a] Lit.[2b] mp 252°; recrystallized from toluene. [b] Lit.[2b] mp 209°; recrystallized from toluene. [c] In this case much better yields were obtained when benzene was used as a solvent for the conversion of the pyrone to thiopyrone. This procedure was previously described by Lozac'h and Guillouzo.[7] [d] Color changed from green to red at 150°; melted at 157°. [e] Crude yield. [f] Color changed from green to red at 140°; melted 151–152°.

Scheme I



system appeared unlikely, leading us to reinvestigate the thiapyrone isomerization.



A

Results and Discussion

The 2,6-dialkylthio-3,5-diphenylthiapyrones (**5**) required for the preparation of 4-thiothiapyrones (**1**) were obtained by the method described by Apitzsch.[5] The properties of the thiapyrones are listed in Table I. Conversion of these compounds to their sulfur analogs was accomplished by treatment of the ketones with phosphorus pentasulfide in either pyridine[6] or refluxing benzene.[7] Table II summarizes the properties of the 4-thiothiapyrones.

Schönberg[2b] found that heating **1a** (or **1b**) above its melting temperature either alone or in solution caused rearrangement to **2a** (or **2b**). Neither yield nor mention of other products was given and the process was described as irreversible. We were able to confirm the isomerization under the stated conditions and found that the reaction was particularly convenient in refluxing methyl benzoate (bp 200°) and readily monitored by thin layer chromatography (tlc). Thus, heating **1** for less than 2 hr in methyl benzoate gave only a mixture of **1** and **2**, easily separated and isolated by preparative thin layer chromatography (ptlc). Elemental analyses and nuclear magnetic resonance (nmr) spectra showed these products to have the structures assigned to them by Schönberg.[2b]

The reversible character of this reaction was demonstrated by the fact that a mixture of **1** and **2** is always obtained and that the same mixture of products is observed when **2** is subjected to heating in methyl benzoate. The properties of the 2-thiothiapyrones produced by the thermal isomerization are given in Table III.

It was found that in the presence of catalytic amounts of alkyl iodide the rearrangement takes place at much lower temperatures than in Schönberg's original report.[2b] Whereas the uncatalyzed rearrangement of **1b** to **2b** requires temperatures of approximately 200°, with small amounts of alkyl iodide added, the isomerization takes place at 80–100°. The other thiopyrones were similarly affected. The equilibration was followed by visible spectroscopy and a value

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(5) (a) H. Apitzsch, *Ber.*, **37**, 1599 (1904); (b) H. Apitzsch, *ibid.*, **38**, 2888 (1905).

(6) E. Klingsberg and D. Papa, *J. Am. Chem. Soc.*, **73**, 4988 (1951).

(7) N. Lozac'h and G. Guillouzo, *Bull. Soc. Chim. France*, 1221 (1957).

TABLE III

PROPERTIES OF 2,6-DIALKYLTHIO-3,5-DIPHENYL-2-THIOTHIAPYRONES (**2**)

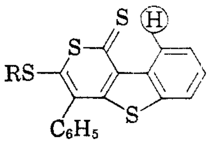
Compound	Mp, °C	Formula	Calcd, % C	Calcd, % H	Found, % C	Found, % H
2b, R = C_2H_5	110[a] (heptane)	$C_{21}H_{20}S_4$	62.96	5.03	62.74	5.09
2c, R = $(CH_3)_2CH$	50[b] (benzene–heptane)	$C_{23}H_{24}S_4$	64.44	5.64	64.25	5.80
2d, R = $C_6H_5CH_2$	148–149.5 (benzene–heptane)[c]	$C_{31}H_{24}S_4$	71.15	4.62	71.13	4.69
2e, R = p-$NO_2C_6H_4CH_2$	175–177 (benzene–heptane)[c]	$C_{31}H_{22}N_2O_4S_4$	60.56	3.60	61.02	3.72

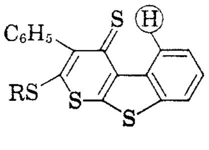
[a] Lit.[2b] mp 200°. [b] Melting point was very poorly defined. [c] Compounds were not heated; they were dissolved in benzene and forced from solution with heptane and cooling.

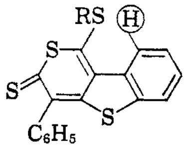
for the equilibrium constant at 100° for the interconversion of **1b** to **2b** was determined to be 0.23.[8]

Prolonged heating of either **1** or **2** in methyl benzoate or without solvent produced an orange by-product not previously noted by Schönberg.[2b] The by-product from **1c** [R = $(CH_3)_2CH$] was chosen for characterization and was isolated and purified by ptlc. The compound analyzed as $C_{20}H_{16}S_4$ and its mass spectrum exhibited a parent peak at 384, indicating the loss of an isopropyl group and a proton during its formation from **1c**.[9] The nmr spectrum confirmed the loss of an isopropyl group.

Several structures (B–D) appear reasonable for this by-product. The choice of structure B as the most likely was made primarily on the basis of nmr and visible spectroscopy. Of particular interest in the nmr spectrum was an unsymmetrical multiplet centered at 9.9 ppm which intergrated for a single proton. This low-field signal did not disappear when the compound was shaken with deuterium oxide but did collapse into a single, sharp peak when decoupled from the aromatic resonance at 7.40 ppm. It appears that this signal is not that of a carboxylic acid or aldehydic proton but is most likely an aromatic proton itself.[10] The visible absorption spectrum of the by-product (λ_{max} 470 mμ) more nearly resembles that of **2** (λ_{max} 500 mμ) than that of **1** (λ_{max} 408 mμ). These data suggest B to be the structure of the by-product. The data for the ethyl analog (by-product from **1b**) are also consistent with structure B.

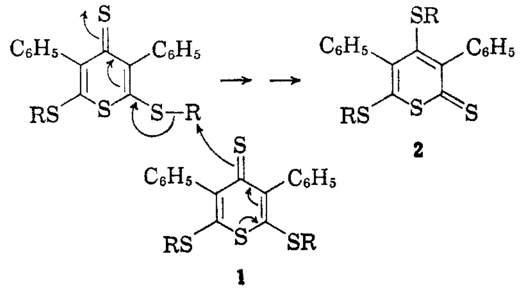

B


C


D

The nature of the primary reaction process, *i.e.*, the isomerization of **1** to **2**, was further investigated. Neither Schönberg's suggestion of ion migration nor Tarbell's mechanism for the rearrangement of diaryl thioncarbonates seemed a likely path by which the thiapyrones might isomerize. A more reasonable pathway appeared to be one which is intermolecular. Such a pathway is depicted in Scheme II. Attack by the γ-sulfur of one molecule on an alkyl group at position 2 of another, followed by a similar loss of alkyl from the attacking molecule, would lead to the rearranged product. The reverse of this rearrangement can be pictured in the same manner.

SCHEME II



Confirmation of the intermolecular character of the isomerization was provided by a crossover experiment. If the rearrangement is inter- rather than intramolecular, a mixture of two different 4-thiothiapyrones should produce at least one and possibly three crossover compounds in addition to the noncrossover equilibrium products. The reaction mixture, therefore, should contain the products shown in Chart I.

The 4-thiothiapyrones **1d** and **1e** were chosen for the crossover experiment. Heating an equimolar mixture of the two compounds in refluxing bromobenzene gave the anticipated complex reaction mixture. Chromatographic separation of this mixture allowed us to identify, by comparison with authentic samples, **1d**, **1e**, **2d**, and **2e**. The preparation and characterization of the authentic samples are described in the Experimental Section and their properties listed in Tables II and III. A fifth component was isolated and on the basis of its visible and nmr spectra and elemental analysis was characterized as the crossover product **6**.[11]

The other two possible crossover products (**7** and **8**)

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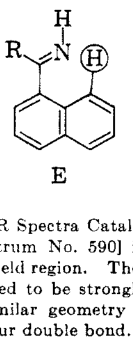
[8] A more complete discussion of the effect of alkyl iodide on the rearrangement and the nature of the thiapyrylium intermediates is given in the following paper by H. J. Teague and W. P. Tucker, *J. Org. Chem.*, **32**, 3144 (1967).

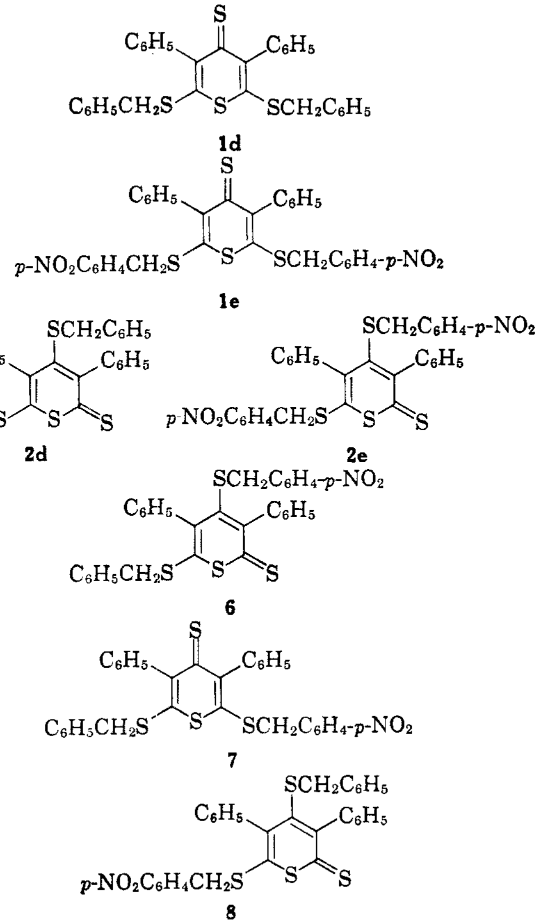
[9] We wish to thank Dr. Maurice Bursey of the University of North Carolina at Chapel Hill for the mass spectral analysis performed on a Perkin-Elmer–Hitachi RMU-6E mass spectrometer.

[10] Aromatic absorption is this region, though unusual, has been reported previously. The nmr spectrum of E [N. S. Bhacca, D. P. Hollis, L. P. Johnson, and E. A. Pier, NMR Spectra Catalog, Vol. 2, Varian Associates, Palo Alto, Calif., 1962, Spectrum No. 590] is identical with that of the orange by-product in the low-field region. The absorption is assigned to the circled proton which is believed to be strongly deshielded by the carbon-nitrogen double bond. A similar geometry is apparent in structures B and C involving a carbon-sulfur double bond.


E

[11] The difference in chemical shifts for the protons *ortho* to the nitro groups in **1e** and **2e** allowed assignment of the p-nitrobenzyl group in the crossover products to position 4 (**6**). See Experimental Section and ref 14.

Chart I



did not separate adequately for isolation although tlc analysis gave some evidence for their presence in the reaction mixture.

Experimental Section

All melting points were taken on a Thomas–Hoover melting point apparatus and are uncorrected. Ultraviolet and visible spectra were measured on a Beckman Model DK-2 spectrophotometer. The nmr spectra were determined in $CDCl_3$ on a Varian HA-100 spectrometer and are reported in parts per million downfield from a tetramethylsilane internal standard. Elemental analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn., or in our laboratory on an F & M Model 185 C, H, and N analyzer. Tlc and ptlc were carried out using silica gel as the adsorbent and benzene or chloroform as solvent.

2,6-Dithiol-3,5-diphenylthiapyrone.—The method reported by Apitzsch,[5] slightly modified, was used for this preparation. To a vigorously stirred solution of 50.0 g (0.238 mole) of dibenzyl ketone in 250 ml of carbon disulfide at 0° was added 60 g (1.1 moles) of finely powdered potassium hydroxide. A bright orange mixture resulted and after approximately 1.5 hr at 0°, the mixture became red-brown with evolution of heat. Reaction was completed by refluxing the solution an additional 4 hr on the steam bath.

Excess carbon disulfide was removed with the aid of a water aspirator, and the residual dipotassium salt was dissolved in water. Nonionic material was removed by extraction of the water solution with ether and the crude product was obtained by acidification of the cold aqueous solution with concentrated hydrochloric acid. Precipitation of the oily brown mass was accompanied by evolution of hydrogen sulfide gas. The oil crystallized on standing, affording 60 g (76%) of crude product. Recrystallization from chloroform gave a product melting at 162–165° (lit.[5] mp 165°). The nmr spectrum of this material is consistent with the structure assigned to it by Apitzsch.

2,6-Dialkyl-3,5-diphenyl-4-thiapyrones (5).—The 4-thiapyrones were prepared as described by Apitzsch.[5] The properties of these pyrones are given in Table I.

2,6-Dialkylthio-3,5-diphenyl-4-thiothiapyrones (1).—The method for converting amides to thioamides described by Klingsberg[6] was used to prepare the 4-thiothiapyrones. The conversion of the colorless pyrones (5) to bright green 4-thiothiapyrones (1) was conveniently followed by tlc and the reaction continued until all the thiapyrone had been utilized.

A mixture of 2.0 g of thiapyrone and excess phosphorus pentasulfide in 40 ml of dry pyridine was vigorously stirred and refluxed. The time required for complete reaction varied with the thiapyrone but ranged from 0.5 to 2 hr. After complete reaction, the hot mixture was poured into 200 ml of water forming a viscous green precipitate. Recrystallization followed. The properties of the 4-thiothiapyrones are given in Table II.

4,6-Dialkylthio-3,5-diphenyl-2-thiothiapyrones (2).—The 2-thiothiapyrones were formed by the thermal rearrangement of the 4-thio isomers (1) in a reaction catalyzed by alkyl halide.

A solution of 4-thiothiapyrone (1) and bromobenzene containing a few drops of the corresponding alkyl halide was refluxed for 15 min. After removal of the solvent the resulting mixture of 2- and 4-thiothiapyrones was separated by preparative thin layer chromatography. Yields for the conversion were not calculated. Properties of the 2-thiothiapyrones (all bright red) are listed in Table III.

Thermal Rearrangement of 2,6-Dialkylthio-3,5-diphenyl4-thiothiapyrones.—The procedure described by Schönberg[2b] was used for this isomerization. The 4-thiothiapyrone **1b** was heated in a test tube at 220–230° (sand bath temperature) for 10 min. Tlc analysis showed that a mixture of three compounds, including the 4- and 2-thiothiapyrones, was obtained. Separation of this mixture was achieved by column chromatography (alumina) and the 2-thiothiapyrone identified by elemental analysis and nmr spectroscopy. Its melting point and other properties are consistent with those reported for it by Schönberg.[2b] Other 4-thiothiapyrones were similarly isomerized.

The isomeric change was also effected by dissolving the 4-thiothiapyrone in ethyl benzoate or phthalate and boiling the solution for 10 min. Results obtained were similar to those above. The properties of the 2-thiothiapyrones obtained are given in Table III.

Catalyzed Thermal Rearrangement of 2,6-Dialkylthio-3,5-diphenyl-4-thiothiapyrones.—This rearrangement was carried out in a variety of solvents including methyl benzoate, bromobenzene, benzene, toluene, xylene, and mesitylene. The general procedure is described below.

To a solution of 4-thiothiapyrone was added 1 or 2 drops of the corresponding alkyl iodide. No rearrangement was noted after 4 hr at 50°, but at 80° the presence of 2-thiothiapyrone was detected (color of solution and tlc) after approximately 1 hr.[12] The progress of the reaction was followed by periodic sampling of the reaction mixture and spectrophotometric determination of the 4- and 2-thiothiapyrone concentrations.[13] When the ratio of these concentrations no longer changed, equilibrium was assumed to be established.

Orange By-Product of Thermal Rearrangement of 4-Thiothiapyrones. A. Pyrolysis of 2,6-Diisopropylthio-3,5-diphenyl-4-thiothiapyrone (1c).—Prolonged heating of 4-thiothiapyrone (1c) at approximately 200–210° without solvent gave an orange compound in addition to the mixture of thiapyrone isomers. The thiapyrone was heated until a red-brown gas began to be evolved. Analysis of the resulting mixture by tlc indicated that a large amount of an orange by-product had formed. This by-product (smallest R_f) was isolated by ptlc and recrystallized from hexane as bright orange crystals, mp 155–156.5°.

Nmr and mass spectral analysis (parent peak 384) of this material suggested that the original thiapyrone had lost the

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[12] At the reflux temperatures of the aromatic hydrocarbons (toluene, xylene, and mesitylene) there was apparently some reaction between solvent and a pyrone species. Bromobenzene proved to be a good solvent for the rearrangement.

[13] The visible absorption spectra of **1** and **2** were quite different and permitted determination of the concentration of each pyrone in mixtures of the two. The thiapyrone curves had the following characteristics: **1b**, λ_{max} 408 mμ (log ϵ 2.14 $\times$ 10^4) and λ_{min} 500 mμ (log ϵ 0); **2b**, λ_{max} 500 mμ (log ϵ 4.1 $\times$ 10^4) and λ_{min} 408 mμ (log ϵ 1.3 $\times$ 10^4). These compounds were shown to obey Beer's law over the concentration range employed.

elements of isopropane (C_3H_8). The nmr spectrum showed a doublet at 1.31, a heptet at 3.64, a multiplet at 7.40, and a multiplet at 9.9. These protons were in the ratio 6:1:8:1. The multiplet at 9.9 collapsed to a sharp single peak when decoupled from the aromatic protons at 7.40.

Anal. Calcd for $C_{20}H_{16}S_4$: C, 62.46; H, 4.19; S, 33.35. Found: C, 62.23; H, 4.12; S, 33.59.

B. Pyrolysis of 2,6-Diethylthio-3,5-diphenyl-4-thiothiapyrone (1b).—The above procedure was repeated with similar results although a satisfactory elemental analysis was not obtained. The compound was recrystallized from heptane in orange crystals (mp 200–204°) and exhibited a single spot on tlc in several systems. The nmr spectrum showed a triplet at 1.34, a quartet at 3.05, a multiplet at 7.40, and a multiplet at 9.9. These protons were in the ratio of 3:2:8:1.

Anal. Calcd for $C_{19}H_{14}S_4$: C, 61.57; H, 3.81; S, 34.62; mol wt, 370. Found: C, 60.29; H, 3.75; S, 35.32; mol wt, 367.

Crossover Experimental Involving the Rearrangement of a Mixture of 4-Thiothiapyrones (1d and 1e).—A mixture of 2,6-dibenzylthio-3,5-diphenyl-4-thiothiapyrone (**1d**) and 2,6-di-*p*-nitro-benzylthio-3,5-diphenyl-4-thiothiapyrone (**1e**) was dissolved in bromobenzene and gently refluxed until decomposition products were detected by tlc. Compounds **1d**, **1e**, **2d**, and **2e** were identified by chromatographic comparison with authentic samples in several dissimilar solvent systems. The solvent was removed *in vacuo* and a rough separation of 2- and 4-thiothiapyrones was obtained by treating the residual mixture with hot benzene. The 2-thiothiapyrones were much more soluble than the 4-thio isomers. The components of the mixtures were then separated by ptlc. The crossover product **6** had an R_f value between that of **2d** and **2e** and after recrystallization from benzene it melted with decomposition at approximately 65°.

Nmr analysis of **6** and its precursors showed it to be 4-*p*-nitrobenzylthio-6-benzylthio-3,5-diphenyl-2-thiothiapyrone.[14]

Anal. Calcd for $C_{31}H_{23}NO_2S_4$: C, 65.34; H, 4.07; N, 2.45. Found: C, 65.14; H, 4.20; N, 2.28.

Two other products in the reaction mixture were detected by tlc but were not sufficiently separated for isolation. Their colors and chromatographic behavior indicate that they are the other expected crossover products **7** and **8**.

Registry No.—**1a**, 14172-81-7; **1b**, 14120-38-8; **1c**, 14120-39-9; **1d**, 14120-40-2; **1e**, 14120-41-3; **2b**, 14120-42-4; **2c**, 14120-43-5; **2d**, 14120-44-6; **2e**, 14120-45-7; **5c**, 14120-46-8; **5d**, 14120-47-9; **5e**, 14120-48-0; **6**; 14120-49-1; B (R = *i*-Pr), 14171-81-4; B (R = Et), 14120-50-4.

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[14] The phenyl protons *ortho* to the nitro groups in **1e** appeared as a doublet centered at 8.15 whereas the phenyl protons *ortho* to the nitro groups in **2e** appeared as a pair of doublets centered at 8.08 and 7.91. The protons *ortho* to the nitro group in the crossover product (**6**) appeared as a doublet centered at 7.95. The *p*-nitrobenzyl group in **6** is thus assigned to the 4 position.

Thiapyrone Chemistry. II.[1a] 2,4,6-Trialkylthiothiapyrylium Salts[1b]

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Treatment of either 2,6-dialkylthio-3,5-diphenyl-4-thiothiapyrones (**1**) or the isomeric 4,6-dialkylthio-3,5-diphenyl-2-thiothiapyrones (**2**) with alkyl iodides produces, in high yield, 2,4,6-trialkylthiothiapyrylium salts (**3**). The catalytic effect of these salts on the thermal isomerization of the parent thiapyrones (**1** and **2**) is examined and discussed. The requirement for a nucleophilic counterion such as iodide in the isomerization reaction is revealed. Other properties of the thiapyrylium salts are reported including an exchange reaction with acetonitrile. Attempts to recrystallize 2,4,6-triethylthio-3,5-diphenylthiapyrylium iodide (**3b**, R = C_2H_5) from acetonitrile produced a new salt, 2,6-diethylthio-4-methylthio-3,5-diphenylthiapyrylium iodide (**3c**), in which the ethyl group at the 4 position of the original salt is replaced by methyl.

The preceeding paper[1a] described the thermal rearrangement of 2,6-dialkylthio-3,5-diphenyl-4-thiothiapyrones (**1**) to the isomeric 4,6-dialkylthio-3,5-diphenyl-2-thiothiapyrones (**2**) (eq 1).[1] It was established that the isomerization of **1** to **2** is reversible and intermolecular. During the course of the previous investigation it was found that alkyl iodides catalyze the rearrangement and allow the isomerization described to be effected at much lower temperatures than in Schönberg's original report.[2] The nature of this catalytic effect and the thiapyrylium salts which serve as intermediates are the subject of the present paper.

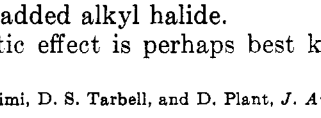

(1)

1a, R = CH_3
b, R = C_2H_5
c, R = $(CH_3)_2CH$
d, R = $C_6H_5CH_2$
e, R = p-$NO_2C_6H_4CH_2$

2

Results and Discussion

The effect of added alkyl halide on several rearrangements involving thionthiol isomerism has been used to study the character of reactions of this type. For example, the migration of an aryl group from oxygen to sulfur in the rearrangement of diaryl thioncarbonates to diaryl thiolcarbonates (eq 2) is not affected by the halides.[3] This rearrangement is known to be intramolecular.[4] However, a number of similar systems are known in which rearrangement is intermolecular and where migration of an alkyl group is facilitated by added alkyl halide.



$$\mathrm{ArO}\overset{\overset{\displaystyle S}{\|}}{\mathrm{C}}\mathrm{OAr} \longrightarrow \mathrm{ArO}\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}\mathrm{SAr} \tag{2}$$

$$\rangle\mathrm{N}\overset{\overset{\displaystyle S}{\|}}{\mathrm{C}}\mathrm{OR} \xrightarrow{R'X} \rangle\mathrm{N}\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}\mathrm{SR(R')} \tag{3}$$

$$\mathrm{RS}\overset{\overset{\displaystyle S}{\|}}{\mathrm{C}}\mathrm{OR} \xrightarrow{R'X} \mathrm{RS}\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}\mathrm{SR(R')} \tag{4}$$

This catalytic effect is perhaps best known in the

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[1] (a) Part I of this series: H. J. Teague and W. P. Tucker, *J. Org. Chem.*, **32**, 3140 (1967). (b) Abstracted from a portion of a thesis submitted by H. J. Teague in partial fulfillment of the requirements for the M. S. degree, May 1967.

[2] A. Schönberg and W. Asker, *J. Chem. Soc.*, 604 (1946).

[3] H. R. Al-Kazimi, D. S. Tarbell, and D. Plant, *J. Am. Chem. Soc.*, **77**, 2479 (1955).

[4] D. H. Powers and D. S. Tarbell, *ibid.*, **78**, 70 (1956).