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]

HAROLD J. TEAGUE AND WILLIAM P. TUCKER

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27607

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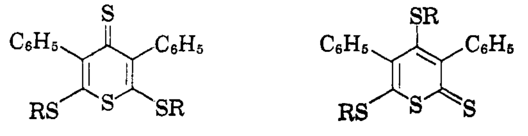
Treatment of either 2,6-dialkylthio-3,5-diphenyl-4-thiothiapyrones (**1**) or the isomeric 4,6-dialkylthio-3,5-diphenyl-2-thiothiapyrones (**2**) with alkyl iodides produces, in high yield, 2,4,6-trialkylthiothiapyrylium salts (**3**). The catalytic effect of these salts on the thermal isomerization 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.



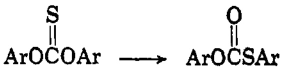
(1)

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

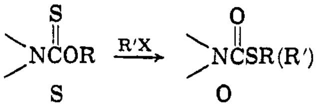
2

Results and Discussion

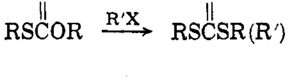
The effect of added alkyl halide on several rearrangements involving thionthiol isomerism has been used to study the character of reactions of this type. For example, the migration of an aryl group from oxygen to sulfur in the rearrangement of diaryl thioncarbonates to diaryl thiolcarbonates (eq 2) is 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.



$$\mathrm{ArO}\overset{\mathrm{S}}{\overset{\|}{\mathrm{C}}}\mathrm{OAr} \longrightarrow \mathrm{ArO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{SAr} \qquad (2)$$



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



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

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.

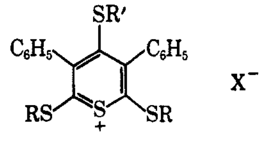
[2] A. Schönberg and W. Asker, *J. Chem. Soc.*, 604 (1946).

[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).

TABLE I

PROPERTIES OF THE 2,4,6-TRIALKYLTHIO-3,5-DIPHENYLTHIAPYRYLIUM SALTS



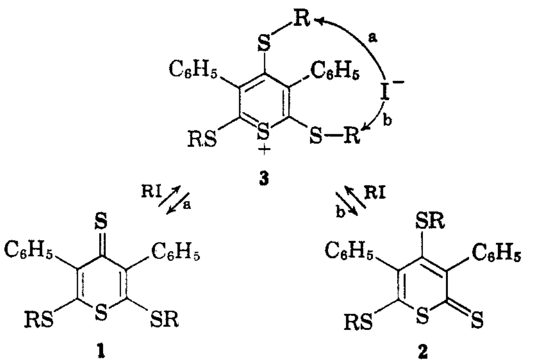
Compd	R	R′	X⁻	Mp dec, °C	Solvent[a]	Formula	Calcd, %			Found, %		
							C	H	S	C	H	S
3a	CH_3	CH_3	I	194–197	1	$C_{20}H_{14}S_4I$	46.7	3.7	24.9	46.6	3.6	24.7
4a	CH_3	CH_3	BF_4	265–268	2	$C_{20}H_{19}S_4BF_4$	50.63	4.04		50.44	3.94	
3b[b]	C_2H_5	C_2H_5	I	161–163	1	$C_{23}H_{25}S_4I$	49.63	4.5	23.04	49.54	4.4	23.12
4b	C_2H_5	C_2H_5	BF_4	199–202	2	$C_{23}G_{25}S_4BF_4$	53.48	4.88		53.33	4.87	
3c	C_2H_5	CH_3	I	180–183	1	$C_{22}H_{23}S_4I$	48.7	4.26	23.7	48.63	4.18	23.8
3c[c]	C_2H_5	CH_3	I	180–184		$C_{22}H_{23}S_4I$	48.7	4.26		48.9	4.3	

[a] Recrystallization solvent: (1) chloroform–hexane; (2) 95% ethanol. [b] This product was formed from either the 2-thio- or 4-thiopyrone and ethyl iodide. [c] This product was produced when **3b** was heated in acetonitrile.

thiocarbamate (eq 3)[5] and xanthate (eq 4)[6] systems. In the last two cases, treatment with a different halide (R′X) leads to a product in which R′ is incorporated, suggesting that these are not true rearrangements but instead represent a special type of displacement reaction.

The rearrangement shown in eq 1 is also catalyzed by alkyl halides. Whereas the uncatalyzed rearrangement of **1b** to **2b** requires temperatures of approximately 200°, the isomerization takes place at 80–100° in the presence of small amounts of alkyl iodide.[1a] A plausible mechanism for the catalyzed rearrangement is shown in Scheme I. According to this mechanism, thiapyrones **1** and **2** should produce the same 2,4,6-trialkylthio-3,5-diphenylthiapyrylium iodide (**3**). The nucleophilic iodide ion could then displace the alkyl group at the 4 position to give **1** (path a) or at the 2 or 6 position to give **2** (path b).

SCHEME I

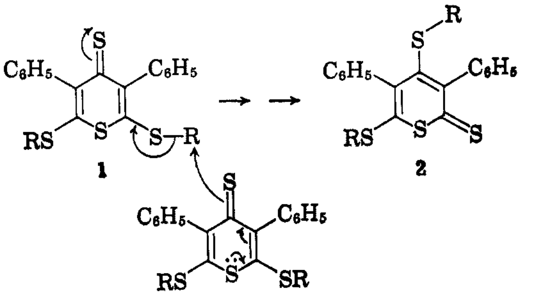


The response of the rearrangement to this catalysis led us to investigate the proposed intermediate ionic species **3**. Treatment of **1b** ($R = C_2H_5$) with excess ethyl iodide resulted in the immediate formation of 2,4,6-triethylthio-3,5-diphenylthiapyrylium iodide (**3b**, $R = C_2H_5$) in nearly quantitative yield. Other salts of this series were prepared similarly and their properties are given in Table I.[7]

The 2-thiothiapyrones (**2**) when treated with excess alkyl iodide produced the same thiapyrylium salts as **1** (see Scheme I). However, this reaction appeared to be much slower than the alkylation of **1**. The iodide salts (**3**) were effective in catalyzing the rearrangement of **1** to **2**.

The pathway for the rearrangement of **1** to **2** (eq 1) catalyzed by alkyl iodide was thought at first to be similar to that proposed for the noncatalyzed reaction which occurs at much higher temperatures (Scheme II).[1a] Formation of the intermediate thiopyrylium ion was believed to be followed by displacement of alkyl at either the 2 or 4 position by a thiapyrone molecule (Scheme III). It now appears, however, that iodide ion, not pyrone molecule, is the displacing species. The importance of iodide was demonstrated by the failure of the analogous fluoroborate salts (**4**) to catalyze the rearrangement. Furthermore, it was found that heating iodide **3a** or **b** in solution at 100° resulted in the loss of alkyl iodide and the production of a mixture of **1** and **2**. This resembles the well-known equilibrium which exists between a trialkylsulfonium salt and its constituent dialkyl sulfide and alkyl halide.[8] The thiapyrylium fluoroborates were stable under conditions by which the iodides decomposed.

SCHEME II



Attempted recrystallization of **3b** ($R = C_2H_5$) from

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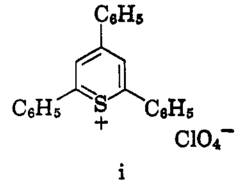
[5] (a) H. L. Wheeler and B. Barnes, *Am. Chem. Soc. J.*, **24**, 60 (1900); (b) H. L. Wheeler and G. K. Austin, *ibid.*, 424 (1900).

[6] E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. 4, Chemical Publishing Co., Inc., New York, 1962, p 168.

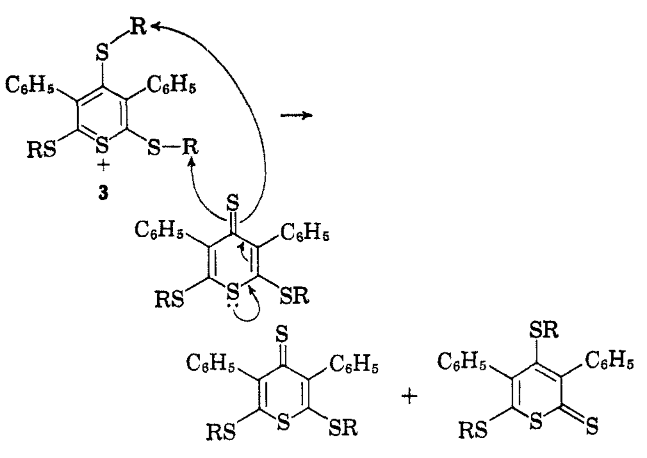
[7] Thiapyrylium salts such as 2,4,6-triphenylthiopyrylium perchlorate (i) have been previously prepared [*cf.*, R. Wizinger and P. Ulrich, *Helv. Chim. Acta*, **39**, 207 (1956)], but those in Table I are the first of this type to be reported.



i

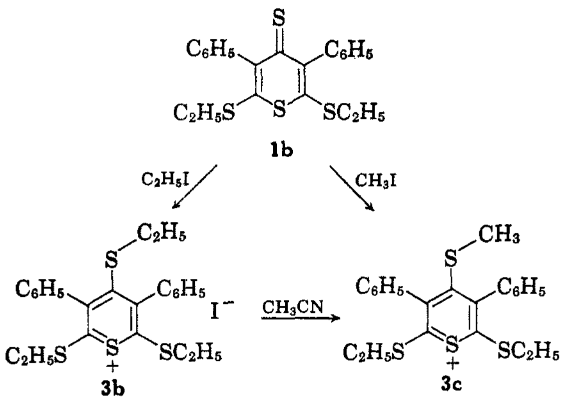
[8] Reference 6, Vol. 2, 1960, p 72.

SCHEME III



acetonitrile revealed an unusual exchange reaction. After several minutes in refluxing acetonitrile, **3b** was converted to 2,6-diethylthio-4-methylthio-3,5-diphenylthiapyrylium iodide (**3c**) (Scheme IV). Compound **3c** was identified by analysis, nuclear magnetic resonance (nmr) spectroscopy, and comparison with an authentic sample prepared by treatment of thiapyrone **1b** ($R = C_2H_5$) with excess methyl iodide. So far, attempts to establish the pathway by which this exchange occurs have not been successful. It seems reasonable to expect that an alkyl group is transferred from **3b** to the solvent to form an azocarbonium ion (eq 5).[9] How the transfer back to **1b** is accomplished is not clear. Iodide ion again plays an important role since the corresponding fluoroborate salt **4b** does not undergo this exchange with acetonitrile. The ethyl isonitrile (eq 5) has not been detected nor do we believe it to be one of the reaction products.

SCHEME IV



$$\mathbf{3b} + CH_3CN \longrightarrow \mathbf{1b} + [CH_3C{\equiv}NC_2H_5]^+I^- \longrightarrow \mathbf{3c} + [C_2H_5N{\equiv}C] \qquad (5)$$

Experimental Section[11]

2,4,6-Trialkylthio-3,5-diphenylthiapyrylium Iodides (3). A. From 4-Thiothiapyrones.—A solution of 4-thiothiapyrone in methyl or ethyl iodide was allowed to stand at room temperature overnight. The red-brown needles which formed were collected, dried, and then recrystallized from an appropriate solvent. Yields in all cases were nearly quantitative.

B. From 2-Thiothiapyrones.—In the manner described above, the 2-thiothiapyrones were also alkylated by allowing them to stand at room temperature in methyl or ethyliodide. In these cases, however, approximately 2 days were required for complete reaction.

The properties of these ions are given in Table I. The nmr spectra are consistant with the proposed structures.

2,4,6-Trialkylthio-3,5-diphenylthiapyrylium Fluoroborates (4).—A solution of 1.0 g (2.7 mmoles) of 4-thiothiapyrone (**1a**) in 20 ml of methylene chloride was treated with excess trimethyloxonium fluoroborate.[12] The solution immediately changed in color from green to orange and was stirred at room temperature for 1 hr. After removal of the solvent, the residue was washed with water and recrystallized from 95% ethanol. The bright orange product was obtained in 74% yield.

In a similar manner, the ethyl 4-thiothiapyrone (**1b**) was alkylated with triethyloxonium fluoroborate.[12] A nearly quantitative yield of the triethyl salt was produced.

The properties of these ions are included in Table I. Their nmr spectra are consistent with the proposed structures and nearly identical with the spectra of the analogous iodide salts.

Thermal Decomposition of 2,4,6-Trialkylthio-3,5-diphenylthiapyrylium Iodides (3).—After heating thiapyrylium iodide **3a** or **b** in solution at 80–100° for approximately 10 min the loss of alkyl iodide was detected and a mixture of the corresponding 4-thio- and 2-thiothiapyrones (**1** and **2**) was produced. Many hours of heating were necessary to completely discharge the alkyl iodide. Bromobenzene was the solvent commonly used for this reaction but similar results were obtained in other solvents.

The fluoroborate salts (**4a** and **b**) were stable under these conditions even at the boiling temperature of bromobenzene (157°).

Isomerization of 2,6-Diethylthio-3,5-diphenyl-4-thiothiapyrone (1b). A. Catalyzed by Thiapyrylium Iodide (3b).—A benzene solution of **1b** containing a catalytic amount of the iodide salt **3b** was refluxed and the progress of the rearrangement monitored by thin layer chromatography. The presence of isomeric **2b** was detected after approximately 30 min. After a 2 hr reflux period, no further change in the ratio of **1b** to **2b** was observed.

B. Attempted Catalysis by Thiapyrylium Fluoroborate (4b).—When the above experiment was repeated using the fluoroborate salt **4b** as catalyst no rearrangement was detected either in refluxing benzene or in several other solvents including toluene and bromobenzene.

Alkyl Exchange between Triethylthiothiapyrylium Iodide and Acetonitrile.—Attempted recrystallization of **3b** from acetonitrile gave, after several minutes reflux, a new product, isolated and characterized as 2,6-diethylthio-4-methylthio-3,5-diphenylthiapyrylium iodide (**3c**). Identification included elemental analysis and comparison of its melting point, mixture melting point, and nmr spectrum with those of an authentic sample.

Refluxing the corresponding fluoroborate salt (**4b**) with acetonitrile for 1 hr did not cause a similar alkyl exchange to take place. The original salt was recovered unchanged.

Registry No.—**3a**, 14172-78-2; **3b**, 14172-79-3; **3c**, 14172-80-6; **4a**, 14239-37-3; **4b**, 14264-65-4.

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[9] Alkylation by an azocarbonium ion has not been previously observed although the ions are not unknown. Ramsey and Taft[10] reported alkylation of acetonitrile by trimethoxymethyl fluoroborate. We found that treatment of acetonitrile with trimethyloxonium fluoroborate gave a solution whose nmr spectrum was not inconsistent with that expected for the azocarbonium ion shown in eq 5. This solution, however, does not contain iodide ion, and with **1b** does not give a stable thiapyrylium salt.

[10] B. G. Ramsey and R. W. Taft, *J. Am. Chem. Soc.*, **88**, 3058 (1966).

[11] The preparation and properties of the thiapyrones required for this investigation are described in the preceding paper.[1a]

[12] H. Meerwein, G. Hinz, P. Hofmann, E. Kroning, and E. Pfeil, *J. Prakt. Chem.*, **147**, 257 (1937).