hydrochloric acid. The red solid was collected and recrystallized from acetic anhydride to yield 0.8 g. of XVII, m.p. 315°. The material was identical with a sample prepared by method B, as shown by the infrared absorption curve.

Method B.—A solution of 1.5 g. of the ketone I, 0.5 g. of malononitrile, and 35 ml. of acetic anhydride was refluxed for 1 hr. and then chilled. The solid was recrystallized from acetic anhydride to give 0.9 g. of XVII, m.p. 315°.

Anal. Calcd. for $C_{22}H_{11}N_3S$: C, 75.8; H, 3.2; N, 12.0. Found: C, 75.7; H, 3.0; N, 12.1.

1-Carbomethoxycyanomethylene-1*H*-benzo[*b*]pyrido[1,2,3-*m,n*]phenothiazine (XVIII). Method A.—The reaction was carried out as just described in procedure A, but using 5 ml. of methyl cyanoacetate in place of the malononitrile. The yield of product was 0.7 g., m.p. 255°.

Anal. Calcd. for $C_{23}H_{14}N_2O_2S$: C, 72.2; H, 3.7; N, 7.3. Found: C, 71.8; H, 3.9; N, 7.0.

Method B.—The ketone I (1 g.) and 1 ml. of methyl cyanoacetate in 10 ml. of acetic anhydride was refluxed for 3 hr. and, after cooling, the solid was collected and recrystallized from *p*-cymene; yield, 0.8 g., m.p. 256°.

Anal. Found: C, 72.1; H, 3.7; N, 6.8.

1-Chlorobenzo[*b*]pyrido[1,2,3-*m,n*]phenothiazinium Perchlorate (XIX).—A mixture of 2 g. of I and 25 ml. of phosphorus oxychloride was refluxed for 2 hr., cooled to room temperature, and diluted with 100 ml. of ether. The red solid was collected and washed with ether; m.p. 193°. The dichlorophosphite salt in this case was not hygroscopic and proved to be pure, but in the following examples they were hygroscopic.

Anal. Calcd. for $C_{19}H_{11}Cl_3NO_2SP$: C, 50.4; H, 2.4; Cl, 23.1. Found: C, 50.8; H, 2.5; Cl, 23.5.

A sample of the dichlorophosphite salt was added to a mixture of 70% perchloric acid in ethanol. After the mixture had been warmed for a few minutes on the steam bath and chilled in a deep freeze, the solid XIX was collected, m.p. 222°.

Anal. Calcd. for $C_{19}H_{11}Cl_2NO_4S$: Cl, 16.7. Found: Cl, 16.9.

The following compounds were prepared by this procedure.

1-Chlorobenzo[*b*]pyrido[1,2,3-*m,n*]phenoxazinium Perchlorate (XX).—An orange solid was obtained; yield, 65%, m.p. 240°.

Anal. Calcd. for $C_{19}H_{11}Cl_2NO_5$: C, 56.6; H, 2.7; N, 3.5. Found: C, 56.9; H, 3.3; N, 3.7.

3-Chloro[3,2,1-*kl*]phenothiazinium Perchlorate (XXI).—Yield, 70%, m.p. 245°.

Anal. Calcd. for $C_{15}H_9Cl_2NO_4S$: C, 48.8; H, 2.4; N, 3.8. Found: C, 49.0; H, 2.5; N, 3.7.

Compounds VII, VIII, and IX from the Chloro Quaternary Compounds XIX, XX, and XXI.—A mixture of 0.005 mole of the chloro quaternary compound and 0.007 mole of piperidine in 25 ml. of tetrahydrofuran was refluxed for 3 hr. and cooled to room temperature. The yields of XIX, XX, and XXI were 59, 90, and 55%, respectively. The products were identified by melting point and the comparison of their infrared absorption curves with the samples prepared from the methoxy quaternary compounds.

When the reaction time was shortened to 15 min., the yields of XIX, XX, and XXI were 40, 53, and 33% from the chloro quaternary salts and 16, 28, and 11% from the methoxy quaternary salts.

1-(4-Dimethylaminophenyl)benzo[*b*]pyrido[1,2,3-*m,n*]phenothiazinium Perchlorate (XXII).—A mixture of 1 g. of I, 1 ml. of N,N-dimethylaniline, and 7 ml. of phosphorus oxychloride was refluxed for 2 hr., chilled, and diluted with ether. The liquid was decanted from the sticky, purple solid and the solid dissolved in hot acetone. To the solution, 2 ml. of 70% perchloric acid was added, and the solution was then diluted with water, chilled, and the solid collected; yield, 0.8 g., m.p. 250°.

Anal. Calcd. for $C_{27}H_{21}ClN_2O_4S$: N, 5.6. Found: N, 5.9.

The 1,2-Dithiolium Cation. A New Pseudoaromatic System. III.[1] Conversion of Dithiolium Salts to Quaternary Pyrazolium Salts and Dithiolethiones

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4-Phenyl- and 4-*p*-nitrophenyl-1,2-dithiolium salts react with *N,N'*-disubstituted hydrazines to give *N,N'*-disubstituted pyrazolium salts, and with sulfur to give 1,2-dithiole-3-thiones.

In the first paper in this series[2] we reported the reaction of 1,2-dithiolium salts with hydrazine and monosubstituted hydrazines to give pyrazoles. We have now found that *N,N'*-disubstituted hydrazines react analogously with 4-phenyldithiolium salts at −20 to −40°, giving the *N,N'*-disubstituted pyrazolium salts directly in one step. This reaction, formally a simple extension of the pyrazole synthesis, presents several features of interest: (1) It is a new example of the interconversion of cationoid heteroaromatic systems, recalling the formation of quaternary pyridinium compounds from pyrylium[3] and thiapyrylium[4] salts; (2) It is the first known synthesis of quaternary pyrazolium compounds by a route other than the alkylation of a pyrazole; (3) It is the first synthesis of an *N,N'*-diarylpyrazolium compound by any route.

The corresponding reaction between *sym*-dimethylhydrazine and 4-(*p*-nitrophenyl)-1,2-dithiolium hydrogen sulfate[2] (II) gave the nitrophenylpyrazolium salt (V); this was reduced with hydrazine and palladium catalyst to the amine (VI), which was diazotized and coupled with dimethylaniline to give the azo dye (VII).

Only about half the starting material is converted in this reaction to pyrazolium salt (50–65% yield). The rest is sulfurated to give 1,2-dithiole-3-thione (VIII) by a curious disproportionation reaction in which the breakdown of some of the dithiolium compound provides sulfur for the thiocarbonyl group. This reaction tends to predominate at temperatures above −20°; dithiolethione was in fact the only identifiable product given by 3-phenyldithiolium salts under all conditions that we tried. It is not clear how the hydrazine derivative that is present participates in this reaction. Its participation is not necessary, since even in its absence dithiolium salts in refluxing pyridine solution rapidly disproportionate to dithiolethiones. If an equivalent of sulfur is added, the yield is much higher. This reaction was used to prepare IX, the *p*-nitro derivative of VIII, which seems to be the first known nitro compound in the dithiolethione series. Presumably a nitro group

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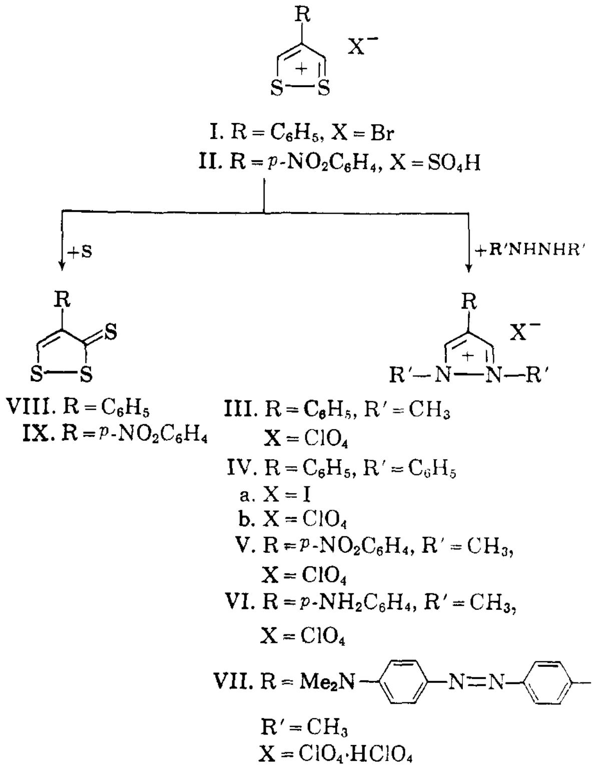
[1] For the previous paper in this series see E. Klingsberg and A. Schreiber, *J. Am. Chem. Soc.*, **84**, 2941 (1962).

[2] E. Klingsberg, *ibid.*, **83**, 2934 (1961).

[3] E. Shaw, in "Pyridine and Its Derivatives," Part Two, E. Klingsberg, ed., Interscience Publishers, Inc., New York, N. Y., 1961, p. 21.

[4] R. Wizinger and P. Ulrich, *Helv. Chim. Acta*, **39**, 207 (1956).



I. R = C_6H_5, X = Br
II. R = p-$NO_2C_6H_4$, X = SO_4H

VIII. R = C_6H_5
IX. R = p-$NO_2C_6H_4$

III. R = C_6H_5, R' = CH_3
X = ClO_4
IV. R = C_6H_5, R' = C_6H_5
a. X = I
b. X = ClO_4
V. R = p-$NO_2C_6H_4$, R' = CH_3,
X = ClO_4
VI. R = p-$NH_2C_6H_4$, R' = CH_3,
X = ClO_4
VII. R = $Me_2N-C_6H_4-N{=}N-C_6H_4-$
R' = CH_3
X = $ClO_4 \cdot HClO_4$

could not survive the severe conditions used heretofore in the synthesis of aryldithiolethiones.[2]

The sulfuration of dithiolium salts in pyridine solution proceeds even at room temperature; with the exception of the recently discovered Asinger reaction of aliphatic ketones,[5] the direct bonding of carbon by elemental sulfur under such mild conditions is perhaps without parallel in organic chemistry.

Experimental[6]

1,2-Dimethyl-4-phenylpyrazolium Perchlorate (III).—*sym*-Dimethylhydrazine dihydrochloride (3.2 g.; 0.024 mole) was stirred at −30 to −40° in 30 ml. of pyridine and 15 ml. of acetone while 5.0 g. (0.019 mole) of 4-phenyl-1,2-dithiolium bromide (I) was added during 45 min. The mixture was stirred 6.5 hr. longer at −30° and over the weekend at room temperature, lightly stoppered. The yellow product was filtered, washed with a little pyridine, dried, dissolved in water, and treated with 70% perchloric acid. The heavy white precipitate was filtered and washed with a little water; yield, 3.3 g. (62%), m.p. 177.5–180°. It crystallized as white needles from ethanol, m.p. 181–183°.

Anal. Calcd. for $C_{11}H_{13}ClN_2O_4$: C, 48.5; H, 4.8; Cl, 13.0; N, 10.3. Found: C, 48.7; H, 4.8; Cl, 13.3; N, 10.3.

1,2,4-Triphenylpyrazolium Iodide (IVa).—A solution of 9.2 g. (0.050 mole) of hydrazobenzene in 100 ml. of pyridine and 50 ml. of ethanol was stirred at −15 to −20° while 10.0 g. (0.0386 mole) of 4-phenyl-1,2-dithiolium bromide was added during 1 hr. The very viscous resulting mixture was stirred 2.5 hr. longer at −20° and then over the weekend at room temperature. The reaction mixture was treated with dilute hydrochloric acid and filtered, giving 5.0 g. of crude 4-phenyl-1,2-dithiole-3-thione. Addition of hydriodic acid to the filtrate gave 9.7 g. (60%) of 1,2,4-triphenylpyrazolium iodide, m.p. 277–282° dec. Crystallization from ethanol raised the m.p. to 288.5–290°.

Anal. Calcd. for $C_{21}H_{17}IN_2$: C, 59.5; H, 4.0; I, 29.9; N, 6.6. Found: C, 59.1; H, 4.1; I, 29.5; N, 6.5.

The perchlorate (IVb) was prepared from the iodide in hot ethanol solution and crystallized from ethanol, m.p. 304–305.5° dec.

Anal. Calcd. for $C_{21}H_{17}ClN_2O_4$: C, 63.6; H, 4.3; Cl, 8.9; N, 7.1. Found: C, 63.9; H, 4.6; Cl, 9.2; N, 7.3.

1,2-Dimethyl-4-(*p*-nitrophenyl)pyrazolium Perchlorate (V).—A solution of 0.94 g. (7.0 mmoles) of *sym*-dimethylhydrazine dihydrochloride in 5 ml. of pyridine and 3 ml. of ethanol was stirred at −79° while 1.60 g. (5.0 mmoles) of 4-(*p*-nitrophenyl)-1,2-dithiolium hydrogen sulfate (II) was added during 45 min. The resulting yellow suspension was stirred 3.5 hr. longer at −79° and then overnight at room temperature. The solid was filtered, washed with a little pyridine, dissolved in 15–20 ml. of water, freed of insoluble matter by filtration, and treated with 0.5 ml. of 70% perchloric acid. The heavy yellow precipitate was chilled, filtered, and washed with a little cold water; yield, 0.82 g. (52%), m.p. 168.5–170.5°. Crystallization from ethanol raised the m.p. to 172.5–174.5°.

Anal. Calcd. for $C_{11}H_{12}ClN_3O_6$: C, 41.6; H, 3.8; Cl, 11.2; N, 13.2. Found: C, 41.3; H, 3.6; Cl, 11.2; N, 13.4.

1,2-Dimethyl-4-(*p*-aminopheny)pyrazolium Perchlorate (VI).—To a stirred suspension of 1.50 g. (4.74 mmoles) of 1,2-dimethyl-4-(*p*-nitrophenyl)pyrazolium perchlorate and 0.15 g. of 10% palladium–charcoal catalyst in 8 ml. of ethanol was added, during 1.5 hr. at room temperature, a solution of 1.0 ml. of 100% hydrazine hydrate in 2.0 ml. of ethanol. The flask was stoppered lightly and the suspension stirred overnight. The suspended solids were then filtered, heated to the boil in 35 ml. of water, and filtered. The yellow product crystallized on cooling; yield, 1.10 g. (81%), m.p. 213–214.5°. Crystallization from dilute ethanol raised the m.p. to 221.5–222°.

Anal. Calcd. for $C_{11}H_{14}ClN_3O_4$: C, 46.0; H, 4.9; Cl, 12.3; N, 14.6. Found: C, 46.3; H, 5.0; Cl, 12.4; N, 14.8.

1,2-Dimethyl-4-(*p*-dimethylaminophenylazophenyl)pyrazolium Perchlorate Hydroperchlorate (VII).—A mixture of 0.50 g. (1.7 mmoles) of 1,2-dimethyl-(4-*p*-aminophenyl)pyrazolium perchlorate, 1.5 ml. of concentrated hydrochloric acid, and 15 ml. of water was stirred in an ice bath and diazotized in the usual manner by the addition of 0.2 g. (1.7 mmoles) of sodium nitrite dissolved in 4–5 ml. of water. After the addition of 0.21 g. (0.22 ml.; 1.7 mmoles) of dimethylaniline, the mixture was buffered (congo red paper) with sodium acetate solution and stirred 4 hr. in the ice bath and overnight at room temperature. The addition of 0.5 ml. of 70% perchloric acid gave a deep purple precipitate of dye, which was filtered, washed with a little cold water, and dried; yield 0.75 g. (83%), m.p. 211–215° dec. Crystallization from nitromethane raised the decomposition temperature to 217–217.5°.

Anal. Calcd. for $C_{19}H_{23}Cl_2N_5O_8$: C, 43.8; H, 4.4; Cl, 13.8; N, 13.5. Found: C, 43.7; H, 4.7; Cl, 13.7; N, 13.8.

Reaction of 4-Phenyl-1,2-dithiolium Bromide with Sulfur.—A solution of 1.30 g. (5.0 mmoles) of 4-phenyl-1,2-dithiolium bromide (I) and 0.20 g. (6.3 mg.-atoms) of sulfur in 40 ml. of pyridine was refluxed 0.5 hr., rapidly acquiring a deep red color. Cooling, dilution with hydrochloric acid and filtration gave 0.95 g. (91%) of 4-phenyl-1,2-dithiole-3-thione (VIII), m.p. 102–110°. Crystallization from methylcyclohexane raised the m.p. to 121.5–123°. Identification was confirmed by mixed melting point and infrared comparison.

When the sulfur was omitted, the yield of crude product, m.p. 114–118°, was 0.50 g. 3-Phenyl-1,2-dithiolium hydrogen sulfate and sulfur reacted in refluxing pyridine to give 5-phenyl-1,2-dithiole-3-thione.

4-(*p*-Nitrophenyl)-1,2-dithiole-3-thione (IX).—4-(*p*-Nitrophenyl)-1,2-dithiolium hydrogen sulfate[2] (1.00 g.; 3.1 mmoles) and sulfur (0.10 g.; 3.1 mg.-atoms) were warmed in 5 ml. of pyridine on the steam bath for 15 min., giving a deep red solution, which was then cooled and diluted. The yield of yellow solid, m.p. 160–167°, was 0.77 g. (97%). Crystallization from xylene or chloroform raised the m.p. to 176–178°.

Anal. Calcd. for $C_9H_5NO_2S_3$: C, 42.5; H, 2.0; N, 5.5; S, 37.6. Found: C, 42.4; H, 2.0; N, 5.4; S, 38.1.

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(5) R. Wegler, E. Kühle, and W. Schäfer, *Angew. Chem.*, **70**, 351 (1958).

(6) Melting points are corrected.