

Determination of the Rate of Debenzoylation of *N*-Benzoyldeoxyadenosine-5' Phosphate.—A solution of the substance in 1 *N* sodium hydroxide was prepared so as to give an optical density reading at 300 $m\mu$ of about 1 in a 1-cm. path cell. The rate was followed by the decrease in the optical density at the above wave length. The half-life was thus found to be 52 hr. at room temperature. In a similar experiment using saturated lithium carbonate (pH 11.3) the half-life was about 100 hr. at room temperature.

Degradation of Cyclic Deoxyadenosine Trinucleotide to Deoxyadenylyl-(3'→5')-deoxyadenosine.—The cyclic trinucleotide (about 200 optical density units at 260 $m\mu$) was dissolved in 1 ml. of 0.1 *N* hydrochloric acid at 50° for 20 min. Concentrated ammonia (0.1 ml.) then was added and the solution kept at 37° for 4 hr. The products were chro-

matographed in solvent C and the band at the origin was cut out and eluted with dilute ammonia. The eluted material (20 optical density units) was digested with 0.04 ml. of the prostatic phosphomonoesterase preparation for 6 hr. The digest was chromatographed in solvent C together with a sample of deoxyadenylyl-(3'→5')-deoxyadenosine prepared from the corresponding dinucleotide by phosphomonoesterase treatment. In addition to the dinucleoside phosphate, spots with R_f values corresponding to those of adenine, adenosine and those traveling slower than deoxyadenosine-5' phosphate were observed. Retreatment of the slow-traveling spots with phosphomonoesterase again gave a similar picture. (The adenine spot arose because of a contaminating enzyme in the phosphomonoesterase preparation which caused the glycosidic cleavage of deoxyadenosine.)

[CONTRIBUTION FROM THE BOUND BROOK LABORATORIES, AMERICAN CYANAMID CO., BOUND BROOK, N. J.]

The 1,2-Dithiolium Cation. A New Pseudoaromatic System. I. Preparation and Properties of 3-Phenyl- and 4-Phenyl-1,2-dithiolium Salts

BY ERWIN KLINGSBERG

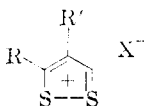
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3-Phenyl- and 4-phenyl-1,2-dithiolium salts (IV and V) are prepared by peracetic acid oxidation of the corresponding phenyl-1,2-dithiole-3-thiones (II and III): the 4-phenyl nitrates *para*; the 3-phenyl, *meta* and *para*. Phenyl-dithiolium salts react with hydrazines to give pyrazoles. Spectral and other properties are discussed.

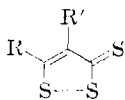
Two recently discovered reactions have given rise to the first known compounds of unequivocal 1,2-dithiolium (I) structure. Leaver and Robertson¹ have shown that hydrogen disulfide condenses with 1,3-diketones to give 3,5-disubstituted dithiolium salts, provided that aryl groups are present. The peracetic acid oxidation of 1,2-dithiole-3-thiones has been used to prepare both aryl derivatives of the system and the parent 1,2-dithiolium cation itself.²



I



IV, R = Ph, R' = H
IVa, X = HSO₄
b, X = I
c, X = ClO₄



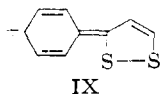
V, R' = Ph, R = H
Va, X = HSO₄
b, X = Br
c, X = I
d, X = SCN
e, X = ClO₄

II, R = Ph, R' = H

III, R' = Ph, R = H

VI, R' = *p*-NO₂C₆H₄, R = H

VIa, X = HSO₄
b, X = Br



IX

VII, R = *m*-NO₂C₆H₄, R' = H
VIIa, X = HSO₄

VIII, R = *p*-NO₂C₆H₄, R' = H
VIIIa, X = Br

When an acetone solution of either isomeric phenyl-1,2-dithiole-3-thione (II, III) is treated with three mole equivalents of peracetic acid, an 85–90% yield of the acid sulfate (IVa, Va) of the corresponding phenyl-1,2-dithiolium salt rapidly crystallizes out of solution. Little can be as-

serted at this time about the mechanism of this reaction in which the extracyclic sulfur is eliminated as sulfate, but analogies may be noted in the formation of thiazoles³ and imidazoles^{4,5} from their 2-mercapto derivatives. Thiopyridones are reported to behave similarly,⁶ although Schmidt and Giesselmann⁷ were unable to effect oxidative desulfuration directly to the pyridine derivative. The success of the present reaction probably depends upon the insolubility of the dithiolium sulfates in acetone, since the dithiolethione system is known to be destroyed by hydrogen peroxide oxidation.⁸

The acid sulfates (IVa, Va) are freely soluble in water to a pale yellow solution, stable in the absence of alkali, which precipitates barium sulfate on addition of barium chloride. The water-insoluble perchlorates, bromides, iodides and thiocyanates separate instantly on addition of the respective anion.

The 1,2-dithiolium cation I, which is isosteric with the tropylium cation, may be regarded as a resonance hybrid of two equivalent sulfonium and two equivalent carbonium ions. The symmetry of the cation V is indicated by n.m.r. spectroscopy. In Va the hetero ring is represented by a single peak, showing the equivalence of its two protons, in the expected ratio of 2:5 against the phenyl protons. In the unsymmetrical isomer IVa, the protons on the hetero ring are represented by two doublets, showing their non-equivalence.

These structures are also in apparent agreement

(3) E. R. Buchman, A. O. Reims and H. Sargent, *J. Org. Chem.*, **6**, 764 (1941).

(4) I. E. Balaban and H. King, *J. Chem. Soc.*, 1858 (1927).

(5) T. O. Norris and R. L. McKee, *J. Am. Chem. Soc.*, **77**, 1033 (1955).

(6) M. Dohrn and P. Diedrich, *Ann.*, **494**, 288 (1932).

(7) U. Schmidt and G. Giesselmann, *Chem. Ber.*, **93**, 1590 (1960).

(8) B. Böttcher and A. Lüttringhaus, *Ann.*, **557**, 89 (1917).

(1) D. Leaver and W. A. H. Robertson, *Proc. Chem. Soc.*, 252 (1960).

(2) E. Klingsberg, *Chemistry & Industry*, 1568 (1960).

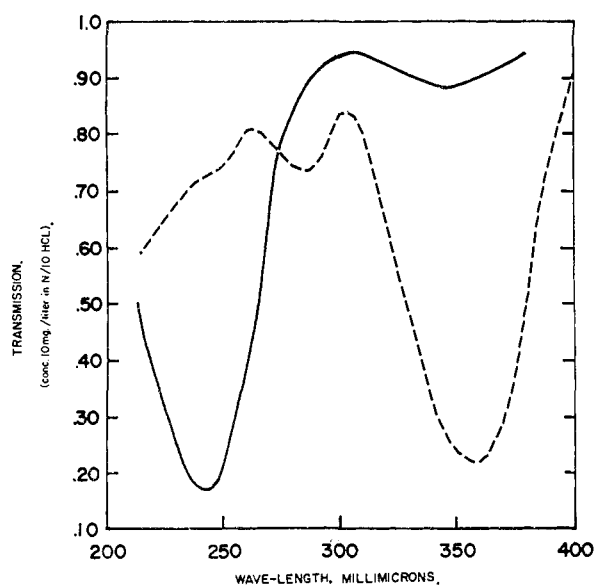


Fig. 1.—Ultraviolet absorption spectra of phenyl-1,2-dithiolium salts: ---, 3-phenyl-1,2-dithiolium hydrogen sulfate (IVa); —, 4-phenyl-1,2-dithiolium hydrogen sulfate (Va).

with the ultraviolet spectra. Inasmuch as the 4-position is incapable of accepting the positive charge in any canonical form, the 3-phenyl derivative has more resonance possibilities (e.g., IX) than the 4-phenyl isomer. As might be expected, this interannular conjugation has a bathochromic effect: the principal absorption peaks of IVa and Va are found at 356 and 242 $m\mu$, respectively. Secondary absorption peaks are shown by IVa at 287 $m\mu$ and by Va at 345 $m\mu$ (Fig. 1).

It is to be expected that the phenyl and dithiolium rings would be the respective sites of electrophilic and nucleophilic attack. The phenyldithiolium salts are, in fact, stable in concentrated sulfuric acid and readily nitrated in this medium. The 4-isomer gives predominant *p*-nitration to VI, while the 3-isomer nitrates *m*- and *p*- to a mixture of VII and VIII. This behavior parallels the nitration of flavylum (phenylpyrylium) salts^{9,10} and confirms the importance of resonance forms such as IX.

In the ultraviolet spectra of the nitro compounds, a pronounced flattening of all peaks is observed (Fig. 2). The *m*- and *p*-nitro derivatives of the 3-phenyl cation resemble each other closely; both peaks of the parent cation are shifted hypsochromically, the major peak 15–20 $m\mu$ and the minor peak 25–35 $m\mu$. This effect is possibly explained by the negative inductive and resonance effects of the nitro group, which would be expected, by inhibiting release of electrons from the benzene ring, to reduce the importance of contributing forms like IX. On the other hand, the effect of *p*-nitration on the 4-phenyl cation is much harder to explain. Here the marked flattening of the curve is accompanied by a conspicuous bathochromic shift of 40 $m\mu$

(9) R. L. Shriner and R. B. Moffett, *J. Am. Chem. Soc.*, **66**, 301 (1944).

(10) R. L. Shriner, H. W. Johnston and C. E. Kaslow, *J. Org. Chem.*, **14**, 204 (1949).

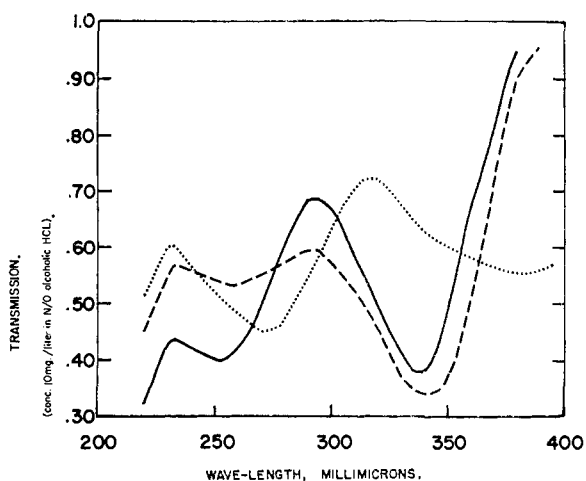
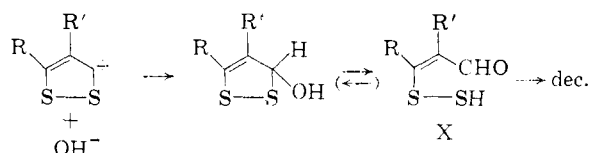


Fig. 2.—Ultraviolet absorption spectra of nitrophenyl-1,2-dithiolium salts: —, 3-(*m*-nitrophenyl)-1,2-dithiolium hydrogen sulfate (VIIa); - - -, 2-(*p*-nitrophenyl)-1,2-dithiolium bromide (VIIIa); ····, 4-(*p*-nitrophenyl)-1,2-dithiolium bromide (VIb).

for the longer wave length maximum and 25 $m\mu$ for the shorter. Simple valence bond theory does not seem to offer any very plausible explanation for this shift.¹¹

The susceptibility of the dithiolium system to nucleophilic attack is shown by its sensitivity to hydroxide ion. Traces of even weak base cause instant decomposition with liberation of sulfur. Presumably the hydroxide ion attacks a positively charged carbon atom with formation of a pseudobasic hemithioacetal followed by ring cleavage to X. Although the ring-opening reaction is formally reversible, monosubstituted disulfides

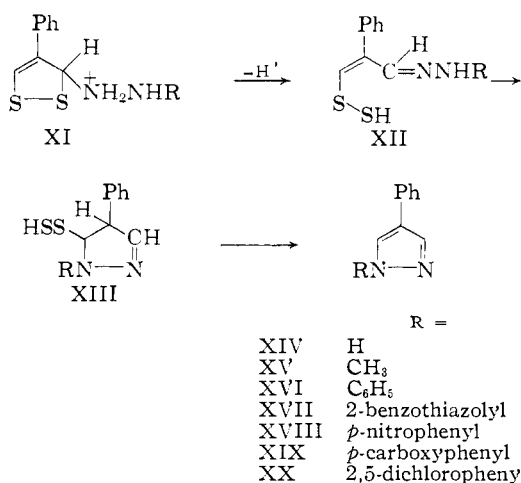


of type X are known to be very sensitive to alkali;¹² consequently, X is destroyed and the decomposition proceeds irreversibly.

Like other bases, hydrazine decomposes dithiolium salts in aqueous solution. In the absence of water, however, the reaction takes an entirely different course and gives pyrazoles. Thus 4-phenyldithiolium salts react rapidly and exothermally with 85% hydrazine hydrate at room temperature to give a quantitative yield of 4-phenylpyrazole (XIV). Under these conditions hydroxyl ion attack is minimized. The initial product (XI) of the reaction with a hydrazine can give XII on ring opening. Instead of decomposition, this is now capable of recyclization to XIII, a precursor of a 4-phenylpyrazole. While the outlines of the process seem clear, it is not possible to assert much

(11) Even such familiar nitro compounds as the nitrophenols and nitroanilines show unexplained anomalies in their ultraviolet absorption spectra: G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 294.

(12) H. Böhm, in Houben-Weyl, "Methoden der Organischen Chemie," 4th ed., Vol. 1X, Stuttgart, 1955, p. 54.



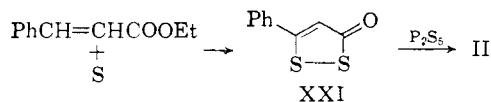
more in detail at this point when the fate of the eliminated sulfur is not known. Elemental sulfur has not been observed in these reactions.

Methylhydrazine and phenylhydrazine react analogously with Va. Hydrazine and IVa give 3-phenylpyrazole.

For reaction with higher-melting hydrazines, pyridine proved to be an excellent solvent. In it, 4-phenyldithiolium bromide reacted smoothly with 2-hydrazinobenzothiazole, *p*-nitrophenylhydrazine, *p*-hydrazinobenzoic acid and 2,5-dichlorophenylhydrazine to give 80–100% yields of the corresponding 1-aryl-4-phenylpyrazoles (XVII, XVIII, XIX and XX, respectively).

3-Phenyldithiolium salts and substituted hydrazines give mixtures as might be expected. Pure products can be isolated, but the reaction looks unpromising from the practical standpoint.

Preparation of Dithiolethiones.—The 4-phenyl-1,2-dithiole-3-thione (III) used in this investigation was prepared from α -methylstyrene and sulfur by the method of Fields,¹³ using refluxing mesitylene (b.p. 165°) as solvent instead of *t*-butylbenzene at 156°. The 5-phenyl isomer II was prepared from 5-phenyl-1,2-dithiole-3-one (XXI). The reaction of sulfur and ethyl cinnamate to give XXI has long been known,¹⁴ but yields and procedural details apparently never have been reported.¹⁵ We have found that 60–65% yields of XXI readily are obtained simply by boiling sulfur and ethyl cinnamate in an open flask for an hour. For the conversion of XXI to II, phosphorus pentasulfide in pyridine gives yields above 90%



and is much preferable to the inconvenient carbon disulfide method recently recommended by Böttcher and Bauer.¹⁶ It is thus possible to prepare II conveniently on any desired scale in two steps from ethyl cinnamate.¹⁷

(13) E. K. Fields, *J. Am. Chem. Soc.*, **77**, 4255 (1955).

(14) E. Baumann and F. Fromm, *Ber.*, **30**, 110 (1897).

(15) A. Lüttringhaus, H. B. König and B. Böttcher, *Ann.*, **560**, 201 (1948).

(16) B. Böttcher and F. Bauer, *ibid.*, **568**, 227 (1950).

(17) In a recent study of various methods of preparing dithiolethiones ("trithiones"), U. Schmidt, A. Lüttringhaus and H. Trufzger

Experimental

Melting points are corrected; the behavior of dithiolium salts sometimes is affected by the rate of heating.

3-Phenyl-1,2-dithiolium Hydrogen Sulfate (IVa).—Twelve grams (0.057 mole) of 5-phenyl-1,2-dithiole-3-thione was dissolved in 400 ml. of acetone with gentle warming. The solution then was stirred in an ice-bath while 32 g. (0.17 mole) of 40% peracetic acid was added during 15 minutes. (In order to prevent crystallization of starting material, the addition of the peracetic acid was begun before the acetone solution was thoroughly chilled.) The product, which separated copiously during the addition, was stirred 10 minutes longer in the ice-bath, filtered, and washed with a little cold acetone; yield 14.2 g. (90%) of pale yellow solid, m.p. 205–207° dec. It crystallized as yellow needles from ethanol (50 ml./g.) in a 65–70% recovery, with unchanged m.p.

Anal. Calcd. for C₉H₉O₄S₃: C, 39.1; H, 2.9; S, 34.8. Found: C, 39.4; H, 2.9; S, 34.9.

In 0.1 N HCl this showed absorption maxima at 356 (ϵ 19,000) and 287 m μ (ϵ 3,800). When an aqueous solution was treated with barium chloride, the theoretical quantity of barium sulfate precipitated. Several water-insoluble 3-phenyl-1,2-dithiolium salts were prepared readily:

Iodide (IVb), bright orange, m.p. 164–167° dec. (ethanol). *Anal.* Calcd. for C₉H₇IS₂: C, 35.3; H, 2.3; I, 41.5; S, 20.9. Found: C, 35.3; H, 2.1; I, 41.3; S, 20.9.

Perchlorate (IVc), buff, m.p. 180–182.5° (methanol). *Anal.* Calcd. for C₉H₇ClO₄S₂: C, 38.8; H, 2.5; Cl, 12.7; S, 23.0. Found: C, 38.8; H, 2.8; Cl, 12.8; S, 22.6.

4-Phenyl-1,2-dithiolium hydrogen sulfate (Va) was prepared similarly in 85% yield from 4-phenyl-1,2-dithiole-3-thione¹⁸ using 250 ml. of acetone. It decomposed at 230–232°, and crystallized from ethanol as yellow needles, dec. 236.5–237°. Like IVa, it was soluble in water and dil. HCl and gave a quantitative precipitate of barium sulfate when treated with barium chloride. In 0.1 N HCl it showed absorption maxima at 242 (ϵ 21,500) and 345 m μ (ϵ 1,400).

Anal. Calcd. for C₉H₉O₄S₂: C, 39.1; H, 2.9; S, 34.8. Found: C, 39.1; H, 3.1; S, 35.0.

These various water-insoluble salts were prepared: Bromide (Vb), yellow needles, dec. 237–240° (ethanol). *Anal.* Calcd. for C₉H₇BrS₂: C, 41.7; H, 2.7; Br, 30.9; S, 24.7. Found: C, 41.6; H, 2.8; Br, 31.1 (by direct titration with silver nitrate in aqueous ethanol); S, 24.9.

Iodide (Vc), orange, dec. 199–201° (ethanol). *Anal.* Calcd. for C₉H₇IS₂: C, 35.3; H, 2.3; I, 41.5; S, 20.9. Found: C, 35.4; H, 2.4; I, 41.5; S, 21.3.

Thiocyanate (Vd), yellow-brown, dec. 139–140° (ethanol). *Anal.* Calcd. for C₁₀H₇NS₃: C, 50.6; H, 3.0; N, 5.9; S, 40.5. Found: C, 50.4; H, 3.1; N, 5.9; S, 40.7.

Perchlorate (Ve), pale yellow needles, m.p. 210–212° dec. (ethanol). *Anal.* Calcd. for C₉H₇ClO₄S₂: C, 38.8; H, 2.5; Cl, 12.7; S, 23.0. Found: C, 38.9; H, 2.5; Cl, 12.6; S, 22.8.

4-(*p*-Nitrophenyl)-1,2-dithiolium Hydrogen Sulfate (VIa).—A solution of 6.5 g. (0.0236 mole) of 4-phenyl-1,2-dithiolium hydrogen sulfate in 20 ml. of concd. H₂SO₄ was stirred at 0–5° while a solution of 1.60 ml. (0.026 mole) of concd. HNO₃ in 2.0 ml. of concd. H₂SO₄ was added during 1 hour. The solution was stirred an hour longer at 0–5° and another hour at room temperature, and then poured into 50 g. of ice. The product was chilled, filtered, washed with a little cold dil. H₂SO₄, and dried on a porous plate; yield 5.0 g. (66%), dec. 214–220°. Crystallization from methanol gave yellow needles, m.p. 220–222° dec.

Anal. Calcd. for C₉H₇NO₆S₂: C, 33.7; H, 2.2; N, 4.4; S, 29.9. Found: C, 33.7; H, 2.2; N, 4.4; S, 30.2.

Oxidation with potassium dichromate in sulfuric acid gave *p*-nitrobenzoic acid.

The yellow-orange bromide VIb, crystallized from methanol, melted 237–238° dec. In 0.1 N alcoholic HCl the bromide showed absorption maxima at 267 (ϵ 10,400) and 385 m μ (ϵ 7,960).

obtained a 43% yield of II from ethyl benzoylacetate, sulfur and P₂S₅ in an autoclave reaction; *Ann.*, **631**, 129 (1960). Results are equally good, and the need for an autoclave obviated, if the reaction is run in refluxing pyridine, known as the solvent of choice for use with P₂S₅ (cf. A. Schöberl and A. Wagner, in Houben-Weyl, "Methoden der Organischen Chemie," 4th ed., Vol. IX, Stuttgart, 1955, p. 764). However the two-step synthesis from ethyl cinnamate is preferable.

Anal. Calcd. for $C_9H_6BrNO_2S_2$: C, 35.5; H, 2.0; N, 4.6. Found: C, 35.7; H, 1.9; N, 4.8.

Nitration of 3-Phenyl-1,2-dithiolium Hydrogen Sulfate.—A solution of 10.0 g. (0.0362 mole) of 3-phenyl-1,2-dithiolium hydrogen sulfate in 20 ml. of concd. H_2SO_4 was stirred at 0–5° while a solution of 2.6 ml. (0.042 mole) of concd. HNO_3 in 3.0 ml. of concd. H_2SO_4 was added during 2 hours. The solution was stirred an hour longer at 5° and another hour at room temperature, and then poured into 100 g. of ice. The resulting yellow solution rapidly deposited a yellow solid, which was filtered at about –15° through a fritted funnel, sucked as dry as possible, washed with a few ml. of very cold methanol, and dried; yield, 7.5 g. of tan product containing *m*- and *p*-nitro derivatives. Crystallization from methanol gave 3-(*m*-nitrophenyl)-1,2-dithiolium hydrogen sulfate (VIIa), m.p. 187–188.5°, oxidized by potassium dichromate to *m*-nitrobenzoic acid. In 0.1 *N* alcoholic HCl it showed absorption maxima at 337 (ϵ 13,300) and 250 $m\mu$ (ϵ 12,700).

Anal. Calcd. for $C_9H_7NO_6S_2$: C, 33.7; H, 2.2; N, 4.4; S, 29.9. Found: C, 34.0; H, 2.1; N, 4.2; S, 30.0.

To the filtrate from the nitration (120 ml. in volume) was added 2.7 ml. (0.024 mole) of 48% HBr. Thorough chilling and filtration, followed by washing with a little very cold methanol, gave 2.9 g. (0.0095 mole, 26%) of 3-(*p*-nitrophenyl)-1,2-dithiolium bromide (VIIIa), dec. 220–222° (inserted into bath at 200°). It was purified by crystallization from methanol, without significant change in m.p. Potassium dichromate oxidation gave *p*-nitrobenzoic acid. In 0.1 *N* alcoholic HCl it showed absorption maxima at 340 (ϵ 14,200) and 260 $m\mu$ (ϵ 8,400).

Anal. Calcd. for $C_9H_6BrNO_2S_2$: C, 35.5; H, 2.0; N, 4.6. Found: C, 35.8; H, 2.1; N, 4.6.

4-Phenylpyrazole (XIV).—4-Phenyl-1,2-dithiolium bromide (0.50 g., 1.9 mmoles) was ground into 5 ml. of 85% hydrazine hydrate in a test-tube, stirred for 20 minutes, diluted, and filtered, yielding 0.28 g. (100%) of 4-phenylpyrazole, m.p. 234–235°. Crystallization from ethanol raised the m.p. to 236–237°. Identification was confirmed by elemental analysis and formation of a chloroplatinate,¹⁹ dec. 281–282°. The other 4-phenyl-1,2-dithiolium salts behaved similarly. Methylhydrazine gave 1-methyl-4-phenylpyrazole (XV), m.p. 101–103°. Phenylhydrazine and 4-phenyl-1,2-dithiolium hydrogen sulfate in refluxing ethanol gave 1,4-diphenylpyrazole (XVI), m.p. 92–94.5°. Hydrazine hydrate and 3-phenyl-1,2-dithiolium hydrogen sulfate reacted in ethanol at room temperature to give 3-phenylpyrazole,²² m.p. 72–76°.

1-(2-Benzothiazolyl)-4-phenylpyrazole (XVII).—A solution of 1.00 g. (3.9 mmoles) of 4-phenyl-1,2-dithiolium bro-

mide and 0.80 g. (4.8 mmoles) of 2-hydrazinobenzothiazole in 35 ml. of pyridine was warmed for an hour on the steam-bath, refluxed for an hour, and then diluted with cold HCl. Filtration gave 1.10 g. (quantitative yield) of yellow product, m.p. 137–141°. Crystallization from ethanol and then from methylcyclohexane gave a white product, m.p. 146.5–148°.

Anal. Calcd. for $C_{16}H_{11}N_3S$: C, 69.4; H, 4.0; N, 15.2; S, 11.5. Found: C, 69.3; H, 4.2; N, 15.1; S, 11.9.

Under the same conditions *p*-nitrophenylhydrazine gave 1-(*p*-nitrophenyl)-4-phenylpyrazole (XVIII), crystallizing from methylcyclohexane as a yellow solid, m.p. 193–194°.

Anal. Calcd. for $C_{15}H_{11}N_3O_2$: C, 67.9; H, 4.1; N, 15.8. Found: C, 68.3; H, 4.2; N, 15.7.

p-Hydrazinobenzoic acid gave 1-(*p*-carboxyphenyl)-4-phenylpyrazole (XIX), crystallizing from xylene as a glistening white solid, m.p. 268.5–269°.

Anal. Calcd. for $C_{16}H_{12}N_2O_2$: C, 72.8; H, 4.5; N, 10.6. Found: C, 72.6; H, 4.6; N, 10.9.

2,5-Dichlorophenylhydrazine gave 1-(2,5-dichlorophenyl)-4-phenylpyrazole (XX), crystallizing from hexane as a yellow solid, m.p. 93.5–95.5°.

Anal. Calcd. for $C_{15}H_{10}Cl_2N_2$: C, 62.2; H, 3.5; Cl, 24.6; N, 9.7. Found: C, 62.3; H, 3.3; Cl, 24.6; N, 9.7.

5-Phenyl-1,2-dithiole-3-one¹⁴ (XXI).—Three hundred ml. (315 g., 1.8 moles) of ethyl cinnamate was heated to the boil in a 2-liter wide-mouth erlenmeyer flask and 90 g. (2.8g. atoms) of sulfur added. The sulfur dissolved readily and the mixture then was boiled gently for 1 hour, cooled, diluted with 125 ml. of ethanol, chilled thoroughly, and filtered. The yield of tan product, m.p. 102–112°, was 170 g. (63% based on sulfur). Crystallization from 300 ml. of pyridine gave 116 g. of flesh-colored product that was used in the reaction with P_2S_5 . It may also be crystallized from ethanol or acetic acid, but usually shows a wide melting range. Crystallization from methylcyclohexane gave a tan product, m.p. 114–117°, with a satisfactory analysis.

Anal. Calcd. for $C_9H_6OS_2$: C, 55.6; H, 3.1; S, 33.0. Found: C, 55.7; H, 2.9; S, 33.2.

5-Phenyl-1,2-dithiole-3-thione (II).—A solution of 20.0 g. (0.103 mole) of 5-phenyl-1,2-dithiole-3-one and 30.0 g. (0.135 mole) of phosphorus pentasulfide in 200 ml. of pyridine was refluxed for 4 hours, cooled partially, diluted carefully (exotherm!) with 150 ml. of water, chilled, and filtered. The yield of brown product, m.p. 116–119°, was 19.9 g. (92%). Crystallization from 150 ml. of butyl acetate gave 17.5 g. of brown needles, m.p. 125–127°.

Acknowledgments.—The author is greatly indebted to Miss Ann M. Schreiber for experimental assistance, to John Lancaster for n.m.r. data, to Anthony Ferri and Miss Vera Jordan for ultraviolet absorption data, and to the late O. E. Sundberg and his staff for microanalyses.

(18) H. Rupe and A. Huber, *Helv. Chim. Acta*, **10**, 846 (1927).

(19) E. Buchner and H. Dessauer, *Ber.*, **26**, 261 (1893); cf. L. Knorr, *ibid.*, **28**, 688 (1895).

(20) K. v. Auwers and E. Cauer, *J. prakt. Chem.*, **126**, 192 (1930).

(21) H. Rupe and E. Knup, *Helv. Chim. Acta*, **10**, 299 (1927).

(22) K. v. Auwers and W. Schmidt, *Ber.*, **58**, 528 (1928).