

TABLE I

Phthalazone	Reaction product	REACTION PRODUCTS OBTAINED WITH PHOSPHORUS PENTASULFIDE											
		M.P., <sup>a</sup> °C.	Yield, %	Formula	Carbon, %		Hydrogen, %		Nitrogen, %		Sulfur, %		
					Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	
IIIa	IXa or Xa	174	74	C <sub>8</sub> H <sub>8</sub> N <sub>2</sub> S	59.26	59.21	3.70	3.59	17.28	17.18	19.75	19.56	
IIIb	IXb or Xb	202	78	C <sub>14</sub> H <sub>16</sub> N <sub>2</sub> S	70.59	70.46	4.20	4.00	11.76	11.70	13.44	13.37	
IIIc <sup>b</sup>	XIa	138	81	C <sub>14</sub> H <sub>10</sub> N <sub>2</sub> S	70.59	70.50	4.20	4.12	11.76	11.69	13.44	13.50	
IIIe	XIb	177	67	C <sub>20</sub> H <sub>14</sub> N <sub>2</sub> S	76.43	76.22	4.46	4.39	8.92	8.86	10.19	10.08	
IIIf	XIc	150	73	C <sub>15</sub> H <sub>12</sub> N <sub>2</sub> S	71.43	71.31	4.76	4.59	11.11	10.95	12.70	12.61	
IIIg <sup>c</sup>	IXc or Xc	238	81	C <sub>9</sub> H <sub>8</sub> N <sub>2</sub> S	61.36	61.11	4.55	4.50	15.91	15.68	18.18	18.09	

<sup>a</sup> All melting points are uncorrected. <sup>b</sup> P. C. Mitter and J. N. Sen, *J. Chem. Soc.*, 1145 (1919). <sup>c</sup> F. M. Rowe and A. T. Peters, *ibid.*, 1331 (1933).

*Anal.* Calcd. for C<sub>27</sub>H<sub>22</sub>N<sub>2</sub>O: C, 79.80; H, 5.42; N, 6.89. Found: C, 79.68; H, 5.29; N, 6.67.

(c) **Benzylmagnesium Chloride.**—To a solution of benzylmagnesium chloride (prepared from 0.8 g. of magnesium, 5.5 g. of benzyl chloride and 50 ml. of dry ether) was added a solution of 1.5 g. of IIIe in 40 ml. of benzene. The reaction mixture was worked up in the usual manner. The oily product was solidified after washing with petroleum ether (b.p. 50–60°). Compound VIa was obtained as colorless crystals from benzene; m.p. 182°, yield ca. 0.9 g. VIa is readily soluble in chloroform, difficultly soluble in cold benzene and alcohol, and is insoluble in aqueous sodium hydroxide solution; it gives a green color with sulfuric acid.

*Anal.* Calcd. for C<sub>34</sub>H<sub>28</sub>N<sub>2</sub>: C, 87.93; H, 6.03; N, 6.03. Found: C, 87.68; H, 5.96; N, 5.92.

(d) **Methylmagnesium Iodide.**—To an ethereal solution of methylmagnesium iodide (prepared from 1 g. of magnesium, 7 g. of methyl iodide and 40 ml. of dry ether) was added a solution of 1 g. of IIIe in 30 ml. of dry benzene. The reaction mixture was worked up in the usual manner and the solid was crystallized from alcohol as colorless crystals, m.p. 139°, yield ca. 0.68 g.; VIb is easily soluble in chloroform, difficultly soluble in cold benzene and alcohol, and insoluble in aqueous sodium hydroxide solution; it gives a yellowish-green color with sulfuric acid.

*Anal.* Calcd. for C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>: C, 84.62; H, 6.41; N, 8.97. Found: C, 84.58; H, 6.35; N, 8.67.

**Action of Benzylmagnesium Chloride on IIIf.**—A solution of 1.5 g. of IIIf<sup>2b</sup> in 40 ml. of benzene was treated with benzylmagnesium chloride, as described above. The solid residue, obtained by evaporation of the ether extract, was crystallized from benzene as colorless crystals, m.p. 162°, yield ca. 0.9 g.; VIc is easily soluble in hot chloroform, difficultly soluble in cold ethyl alcohol, and insoluble in aqueous sodium hydroxide solution; it gives a yellow color with sulfuric acid.

*Anal.* Calcd. for C<sub>29</sub>H<sub>26</sub>N<sub>2</sub>: C, 86.31; H, 6.47; N, 6.97. Found: C, 86.25; H, 6.29; N, 6.75.

**Action of Phosphorus Pentasulfide on Phthalazones.**  
*General Procedure.*—To a solution of 1 g. of each of IIIa-b, IIIc-g in 40 ml. of dry benzene, except in the case of IIIa in 40 ml. of dry toluene, was added 1 g. of phosphorus pentasulfide. The reaction mixture was refluxed for 6 hours. It was cooled, filtered off and concentrated. The yellow solid, so obtained, was crystallized from benzene-petroleum ether.

The reaction products, listed in Table I, are easily soluble in hot benzene, but difficultly soluble in cold alcohol and petroleum ether. The products obtained from IIIa-b and IIIg are easily soluble in aqueous sodium hydroxide solution (10%).

GIZA, CAIRO, EGYPT (U.A.R.)

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILL.]

## The Action of Sulfur on Indole

BY WAYNE CARPENTER,<sup>1</sup> M. S. GRANT<sup>2</sup> AND H. R. SNYDER

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The substance earlier obtained by heating indole with sulfur in a sealed tube and formulated as a bis-disulfide (II or III) is much more readily obtained by reaction in dimethylformamide. Its reactions, which are studied for the first time, are more readily interpreted on the basis of the 3,3'-diindolyltetrasulfide structure V.

By heating indole with sulfur in sealed tubes under various conditions, earlier investigators have obtained a number of products. Among the structures which have been proposed for the different compounds isolated are those shown by formulas I, II, III and IV. Formula I was assigned by Raffa<sup>3</sup> to a green substance obtained by heating (190–200°) indole with three equivalents of sulfur for forty-eight hours. From a different mixture (about 0.6 equivalent of sulfur) and under different conditions (150–160°, fifty-two hours), Szperl<sup>4</sup> obtained two other compounds, one of which

he believed to be a bis-disulfide (II or III); the other product, a white, fluorescent, sulfur-free substance (C<sub>16</sub>H<sub>12</sub>N<sub>2</sub>, m.p. 264°) was not assigned a structure. However, it may be identical with a product obtained earlier in a similar reaction by Oddo<sup>5</sup> and shown to be 3,3'-diindolyl (IV, m.p. 286°), which had been prepared still earlier by an unequivocal method by Gabriel, Gerhard and Walter.<sup>6</sup> Still another white crystalline product (m.p. 326°) had been reported by Madelung and Tencer<sup>7</sup> from an equimolar mixture of indole and sulfur heated two hours at 180–190°. None of the compounds appears to have been obtained in good yield.

In the present work it was found that by heating indole and sulfur in dimethylformamide quite good

(1) Part of this work was abstracted from a portion of the Thesis submitted to the Graduate College of the University of Illinois in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1959, by Wayne Carpenter, National Science Foundation Fellow, 1956–1959.

(2) Postdoctorate Research Associate.

(3) L. Raffa, *Gazz. chim. ital.*, **72**, 549 (1942).

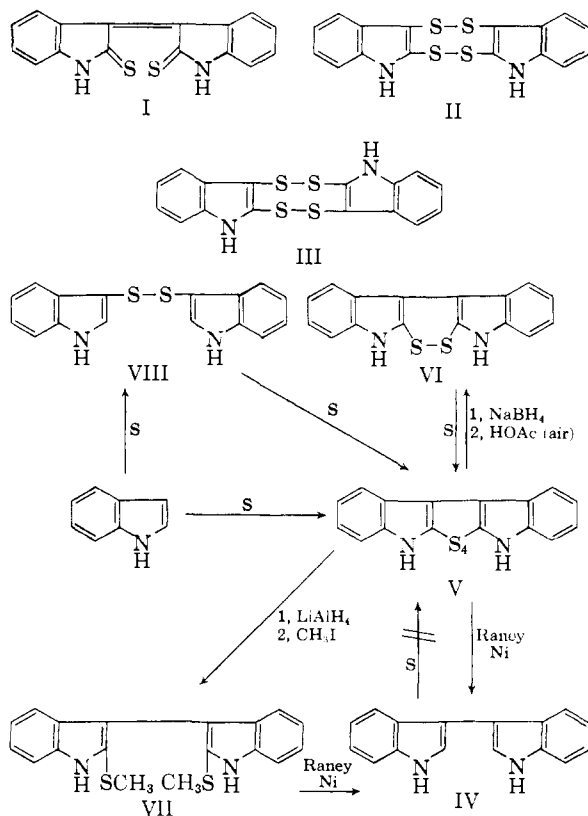
(4) Ludwik Szperl, *Roczniki Chem.*, **18**, 804 (1933).

(5) B. Oddo and L. Raffa, *Gazz. chim. ital.*, **69**, 562 (1933).

(6) S. Gabriel, W. Gerhard and R. Walter, *Ber.*, **56**, 1024 (1923).

(7) W. Madelung and M. Tencer, *ibid.*, **48**, 949 (1915).

yields (55–60%) of a beautiful yellow crystalline substance, evidently identical with that which Szperl<sup>4</sup> considered to be II or III, are easily obtained. The same product was formed in quinoline, albeit in poor yield, but there was little or no reaction in xylene, cumene or *o*-dichlorobenzene. With the substance now easily available, attempts were made to verify one of the bis-disulfide structures (II or III); however, the results of the study are in better agreement with the diindolyltetrasulfide structure shown in formula V.



Attempts to effect cleavage of a disulfide linkage in the substance formulated as V by the use of bromine, iodine and sulfuryl chloride were fruitless. Treatment with metallic sodium followed by methyl iodide yielded a product (IX) in which the only change appeared to be methylation of the nitrogen atoms. Treatment of V with sodium borohydride in tetrahydrofuran brought about the evolution of hydrogen sulfide and the formation of a water-soluble salt, evidently a mercaptide. However, the yellow product isolated after acidification and exposure to the air appeared to be the pentacyclic disulfide VI. It melted at about 205°, and its infrared spectrum indicated the presence of NH groups and the absence of SH functions. The analysis indicated the loss of two atoms of sulfur as compared to the original compound and suggested that the latter was a tetrasulfide rather than a bis-disulfide. Furthermore, the action of sulfur under the conditions employed with indole reconverted VI to the tetrasulfide V. In another experiment the reduction was effected with lithium aluminum hydride and the mixture which resulted was treated with methyl iodide. The product VII

obtained (C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>S<sub>2</sub>, m.p. 184–186°) was desulfurized by the action of Raney nickel catalyst to 3,3'-diindolyl (IV), identical to a sample prepared by the method of Gabriel, Gerhard and Walter.<sup>6</sup> The same desulfurization product was obtained from the original substance V. It would not be surprising if a substance of the structure II should give 3,3'-diindolyl by desulfurization with the nickel catalyst, since this reagent has been observed previously to bring about the formation of carbon-carbon links.<sup>8,9</sup> However, both the transformation of VI to II by the action of sulfur and the conversion of II to VI by sodium borohydride would be unexpected, and it therefore seems highly probable that V contains the diindolyl system and hence must be a tetrasulfide.

As mentioned above, 3,3'-diindolyl is reported to have been isolated from a reaction of indole with a limited amount of sulfur.<sup>5</sup> An attempt was made to repeat this preparation, but the only product isolated was a sulfur-containing compound which proved to be 3,3'-indolyl disulfide (VIII), identical to a sample prepared by another method.<sup>10</sup> Samples of 3,3'-diindolyl and 3,3'-indolyl disulfide were treated with sulfur in dimethylformamide under the conditions employed in the preparation of V from indole and sulfur. Unexpectedly, V was formed from the disulfide, but not from the diindolyl. Since disulfide is formed from indole and sulfur under relatively mild conditions, it is likely that it is an intermediate in the formation of V, but evidently 3,3'-diindolyl is not an intermediate. It is hoped that the problems that present themselves concerning the mechanism of the formation of V from VIII, but not from IV, and from indole can be investigated further.

### Experimental<sup>11</sup>

**3,3'-Diindolyl-2,2'-tetrasulfide (V).**—A mixture of 11.7 g. of indole, 9.6 g. of sulfur and 50 ml. of dimethylformamide was stirred under nitrogen in an oil-bath maintained at 145° for 3 hours, and then allowed to cool slowly overnight in the oil-bath. The yellow crystals which appeared were removed and thoroughly washed with carbon disulfide. The yield of relatively pure 3,3'-diindolyl-2,2'-tetrasulfide, m.p. 300–305°, was 10.5 g. (59%).

The infrared spectrum of this material had a carbonyl band at 1650 cm.<sup>-1</sup>, which was attributed to admixture with dimethylformamide, presumably as solvate. Several recrystallizations from acetone removed the impurity, as evidenced by the absence of the 1650 cm.<sup>-1</sup> band. The pure material melted at 305°.

*Anal.* Calcd. for C<sub>16</sub>H<sub>10</sub>N<sub>2</sub>S<sub>4</sub>: N, 7.82; S, 35.64. Found: N, 7.61; S, 35.40.

**2,2'-Dithiomethyl-3,3'-diindolyl (VII).**—Nine-tenths of a gram of lithium aluminum hydride was added cautiously to a solution of 1.22 g. of 3,3'-diindolyl-2,2'-tetrasulfide (V) in 100 ml. of anhydrous tetrahydrofuran. A gas was evolved. After the reaction mixture had been stirred at room temperature for 10 minutes, it was diluted with 200 ml. of ether and then 100 ml. of water was carefully added and the suspension was filtered. The aqueous layer was stirred with 10

(8) A. Grigorovskii and V. Federov, *J. Applied Chem. (U.S.S.R.)*, **21**, 529 (1948); *C. A.*, **43**, 646 (1949).

(9) H. Hauptmann, W. Walter and C. Marino, *THIS JOURNAL*, **80**, 5833 (1958).

(10) M. S. Grant and H. R. Snyder, *ibid.*, **82**, 2742 (1960).

(11) All melting points are uncorrected. Microanalyses were performed by Mr. J. Nemeth, Mrs. Maria Stingl, Miss Claire Higham, Miss Jane Liu and by the Clark Microanalytical Laboratory, Urbana, Ill. The infrared spectra were determined by Mr. James Brader, Mr. Paul E. McMahon, Miss Mary DeMott and Miss Charlene Leubke.

ml. of methyl iodide for 48 hours at 25°. The mixture was then extracted with ether (2 × 50 ml.). The ether extracts were washed with water, dried over magnesium sulfate, filtered and then evaporated under vacuum to give 0.466 g. of clear oil which slowly solidified. After four recrystallizations from ethanol-water, light yellow crystals, m.p. 184–186°, were obtained. These were dried for 24 hours at 25° (0.2 mm.), over phosphorus pentoxide.

*Anal.* Calcd. for  $C_{18}H_{16}N_2S_2$ : C, 66.63; H, 4.97; N, 8.64. Found: C, 66.59; H, 4.95; N, 8.42.

**3,3'-Diindolyl (IV).**—One hundred grams of water-wet Raney nickel (W-2) was activated by washing with 300 ml. of 95% ethanol. The nickel, 3.18 g. of 3,3'-diindolyl-2,2'-tetrasulfide (V) and 200 ml. of 95% ethanol were heated under reflux for 5.5 hours. The mixture was filtered while hot. The filter cake was washed with dimethylformamide (3 × 50 ml.). The filtrate and washings were combined and diluted with enough water to completely precipitate the organic material, which was subsequently removed by filtration and then desiccated over phosphorus pentoxide. The yield of crude 3,3'-diindolyl, a white solid, m.p. 250–285°, was 0.826 g. (40%). This material was recrystallized once from ethyl acetate and once from toluene, and then dried for 20 hours at 25° (0.2 mm.), m.p. 284–286°.

*Anal.* Calcd. for  $C_{16}H_{12}N_2$ : C, 82.73; H, 5.21; N, 12.06. Found: C, 82.93; H, 5.35; N, 11.85.

An authentic sample of 3,3'-diindolyl, m.p. 286–287°, was synthesized according to the method of Gabriel, Gerhard and Walter.<sup>6</sup> The mixed m.p. of this sample with IV was 285–286°. The infrared spectra of the two samples were identical.

Diindolyl is highly fluorescent, exhibiting blue to blue-green fluorescence under ultraviolet light both as a solid and in solution. Its characteristic fluorescence has been reported previously by Oddo<sup>8</sup> and by Gabriel.<sup>6</sup> They recorded its melting point as 285–287°.

**3,3'-Diindolyl-2,2'-disulfide (VI).**—A solution of 3.12 g. of 3,3'-diindolyl-2,2'-tetrasulfide in 30 ml. of tetrahydrofuran was slowly added to a solution of 1.0 g. of sodium borohydride in 65 ml. of tetrahydrofuran. Vigorous evolution of a gas containing hydrogen sulfide occurred during the addition and a yellow solid precipitated. The reaction mixture was stirred for five hours at room temperature. The addition of 200 ml. of water resulted in complete solution of the yellow precipitate. Ten milliliters of acetic acid was then added followed by 200 ml. of ether, to dissolve the precipitate. The ether layer was then separated, dried over anhydrous sodium sulfate and filtered. Petroleum ether was added to precipitate the organic material, which was removed by filtration and dried under vacuum. The crude material weighed 1.63 g. and melted at 180–200° (dec.) after one recrystallization from chloroform it melted at 205–208°.

*Anal.* Calcd. for  $C_{16}H_{10}N_2S_2$ : C, 65.27; H, 3.42; N, 9.52. Found: C, 65.41; H, 3.67; N, 9.45.

**3,3'-Indolyl Disulfide (VIII).**—A mixture of 1.6 g. of sulfur and 11.7 g. of indole was heated under nitrogen at 124° for 48 hours, during which time it was occasionally necessary to return the indole which had sublimed to the upper portions of the flask. At the end of 48 hours 100 ml. of methylcyclohexane was stirred into the hot mixture. The methylcyclohexane layer was decanted and the lower, brown layer was washed with three 100-ml. portions of hot petroleum ether (high boiling). The brown viscous residue was freed of all solvents by heating it under vacuum on the steam-bath. The residue, 4.50 g., was dissolved in about 35 ml. of hot toluene and then filtered. The toluene solution was allowed to cool overnight in the refrigerator. Small brown globules appeared, which were removed, m.p. 215–225° (0.30 g.). A second crop of material (0.524 g.) was obtained by adding 10 ml. of *n*-pentane to the toluene solution and allowing it to stand overnight. A third crop, obtained in like manner, weighed 0.124 g. All three crops of brown solid were recrystallized separately from ethanol-water to give tan needles. All three fractions were shown to be identical by mixed melting point determinations. The purest sample obtained melted at 217–222° and did not depress the melting point of a sample of 3,3'-indolyl disulfide which was prepared from 3-thiocyanindole.<sup>10</sup> The infrared spectra of the two samples of 3,3'-diindolyl disulfide are identical.

**Desulfurization of 2,2'-Dithiomethyl-3,3'-diindolyl (VII).**—A mixture of 0.226 g. of VII, 10 g. of water-wet, W-2 Raney nickel (activated by washing with ethanol) and 50 ml. of absolute ethanol was heated under reflux for 4 hours. The mixture was filtered while hot and the filter cake was washed liberally with dimethylformamide. The filtrate and washings were combined and diluted with water. The white, flocculent precipitate which formed was removed by filtration and dried; wt. of the crude 3,3'-diindolyl, 0.118 g., m.p. 264–273°. After one recrystallization from ethanol-water the material melted at 280–284° and did not depress the melting point of a sample of 3,3'-diindolyl prepared by desulfurization of V.

**Reaction of 3,3'-Diindolyl-2,2'-disulfide (VI) with Sulfur.**—A mixture of 1.35 g. of VI and 0.5 g. of sulfur was stirred in 15 ml. of dimethylformamide at 145° under nitrogen for 4 hr. The mixture was allowed to cool overnight. The crystalline mass was filtered off and washed with carbon disulfide giving 1.07 g. (64%) of product, m.p. 303–305°. Recrystallization twice from acetone gave a product of m.p. and mixed m.p. with V 305°. The infrared spectrum of this compound is identical with that of V.

*Anal.* Calcd. for  $C_{16}H_{10}N_2S_4$ : C, 53.64; H, 2.81; N, 7.82. Found: C, 53.90; H, 2.77; N, 7.90.

**Reaction of 3,3'-Indolyl Disulfide (VIII) with Sulfur.**—A solution of 2.78 g. of VIII in 50 ml. of dimethylformamide was heated to 120°. One gram of sulfur was then added. Vigorous evolution of hydrogen sulfide occurred and the solution became quite dark. The reaction mixture was then heated at 130° for 75 minutes and then allowed to cool. The yellow crystals which formed overnight were removed by filtration, washed with carbon disulfide and then dried; wt. 1.18 g., m.p. 296–301°. The material was purified by extracting it with methylcyclohexane in a Soxhlet extractor for 24 hours. The product, being nearly insoluble in non-polar solvents, was slowly dissolved by the hot methylcyclohexane and was reprecipitated in the boiling flask of the extractor. The material thus purified was quite pure and was shown to be 3,3'-diindolyl-2,2'-tetrasulfide from its infrared spectrum and melting point of 305°.

**N,N'-Dimethyl-3,3'-diindolyl-2,2'-tetrasulfide (IX).**—A solution of 9.2 g. of 3,3'-diindolyl-2,2'-tetrasulfide in 200 ml. of dry tetrahydrofuran was stirred vigorously while 2.4 g. of sodium was added in small chunks. The mixture was stirred 5 hours at room temperature and then about 35 g. of methyl iodide was added and the stirring was discontinued. Ligroin (200 ml.) was added to the reaction mixture after it had stood overnight. The inorganic solids which precipitated were removed by filtration and the filtrate was evaporated under vacuum on the steam-bath to a tarry solid. This was triturated with ether. The crystals which formed were removed by filtration and recrystallized from ethyl acetate. The yellow, crystalline material weighed 1.9 g. and melted with decomposition at 252–254°. Its infrared spectrum is very similar to that of V except that there is no N-H band in the 3000–3600  $cm^{-1}$  region.

*Anal.* Calcd. for  $C_{18}H_{14}N_2S_4$ : C, 55.92; H, 3.65; N, 7.24. Found: C, 56.34; H, 3.81; N, 7.16.

**Attempted Desulfurization of V with Mercury.**—A mixture of 0.75 g. of V, 2.0 g. of mercury and 50 ml. of anhydrous tetrahydrofuran was vigorously stirred for 5 days at room temperature. A small amount of mercuric sulfide was formed, which was removed with the excess mercury by filtration. The filtrate was evaporated to a brown residue, which was extracted with methylcyclohexane in a Soxhlet extractor for several hours. The yellow crystalline substance which separated from the methylcyclohexane weighed 0.69 g. and was shown by mixed melting point to be identical to the starting material V.

**Attempted Sulfurization of 3,3'-Diindolyl.**—3,3'-Diindolyl (0.64 g.), sulfur (0.5 g.) and 10 ml. of dimethylformamide were stirred under nitrogen atmosphere for 4.5 hr. at 137°. The dark red reaction mixture was poured into 200 ml. of water containing about 20 g. of sodium chloride. The brown precipitate which formed was removed, washed with carbon disulfide and then dissolved in 30 ml. of boiling acetone. The acetone solution was treated with Darco and filtered. Water was then added to the filtrate until crystals began to appear. Slow crystallization in the refrigerator afforded 0.14 g. of light brown crystals, m.p. 272–276°. A second crop of crystals, m.p. 240–270°, was obtained by concentrating the mother liquor. Neither fraction of crystals displayed

fluorescence. However, the fluorescence was restored by chromatographing the material on alumina and then recrystallizing from toluene. The infrared spectra of both the

fluorescent and non-fluorescent materials were nearly identical to that of 3,3'-diindolyl. No 3,3'-diindolyl-2,2'-tetrasulfide was obtained from the chromatography.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILL.]

## Thiocyanation of Indole. Some Reactions of 3-Thiocyanindole

BY M. S. GRANT<sup>1</sup> AND H. R. SNYDER

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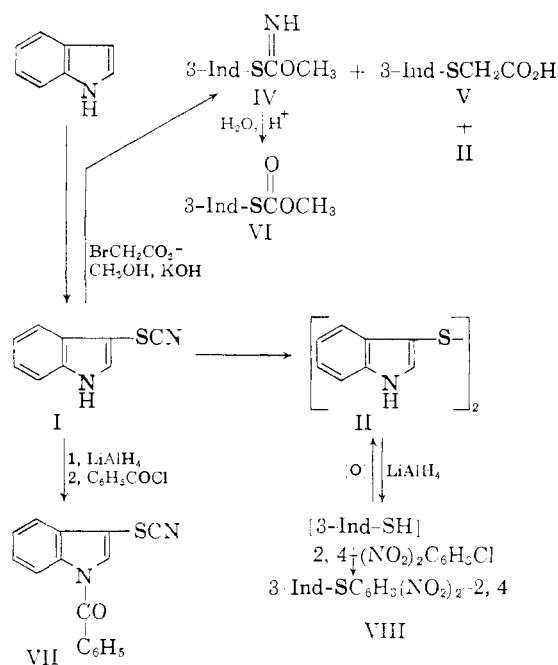
Thiocyanation of indole produces 3-thiocyanindole in good yield. Under the influence of bases and under a variety of conditions the thiocyanate compound is converted to 3,3'-indolyl disulfide, and attempts to isolate 3-mercaptoindole as an intermediate, either as such or as the S-carboxymethyl derivative, have met with little success. Neither could the mercaptan be isolated after lithium aluminum hydride reduction of the thiocyanate, but its 2,4-dinitrophenyl derivative was obtained by a similar reduction of the disulfide and treatment of the reduction mixture with 2,4-dinitrochlorobenzene. The nucleus of 3-thiocyanindole is strongly deactivated, but the indolic nitrogen atom is attacked by some reagents.

3-Thiocyanindole has been of interest to us as a possible source, through the procedure developed by Matteson<sup>2</sup> for thieno[3,2-*b*]pyrrole, of the known 4H-thieno[3,2-*b*]indole.<sup>3</sup> Matteson<sup>4</sup> found indole to be thiocyanated by the action of cupric thiocyanate to give a monothiocyanate of undetermined structure in 59% yield, along with a small amount of a high melting impurity that was not removed by sublimation. It is now shown that the major product is 3-thiocyanindole (I), and the high-melting by-product probably was 3,3'-indolyl disulfide (II). The conversion of the former to the latter proceeds with remarkable facility; even attempts to chromatograph I on basic alumina caused the transformation to occur. The disulfide II recently has been prepared directly from indole and sulfur.<sup>5</sup>

In the present work thiocyanogen was generated from potassium thiocyanate and bromine in methanol at  $-60^{\circ}$ , and this solution was treated with indole in methanol at  $-70^{\circ}$  for one hour before being allowed to warm to room temperature. This procedure led to 3-thiocyanindole in 89% yield. That substitution occurred in the pyrrole nucleus was shown by the infrared spectra of several of the derivatives of I, which revealed the characteristic absorption of an *o*-disubstituted benzene ring. That attack occurred in the 3-position was shown by the thiocyanation of indole-2-carboxylic acid and conversion of the product III to the same disulfide II as was obtained from I.

Attempts to alkylate the sulfur atom of I by treatment with bromoacetate and base gave mainly the disulfide II, together with some S-3-indolyl-O-methyl thioimidocarbonate (IV) and very small amounts of the originally expected S-3-indolylthioacetic acid (V), isolated as the ammonium salt. Very mild hydrolysis of the thioimidocarbonate (IV) converted it to the thiocarbonate (VI).

Since aromatic thiocyanates can be converted to thiophenols by reduction with lithium aluminum hydride,<sup>6</sup> the action of this reagent on I was studied.



After the reduction, benzoyl chloride was added, but the only product isolated was N-benzoyl-3-thiocyanindole (VII, 35%). Evidently reduction was incomplete, and I is more readily benzoylated than its reduction products. When the reduction mixture was treated with bromoacetate the main product was the disulfide, with a trace of the expected thioacetic acid derivative V, isolated as the ammonium salt. Similar reductions were run on the disulfide II, but only the disulfide was obtained from efforts to isolate the mercaptan. Probably the mercaptan was formed, but was reoxidized during the isolation, for addition of 2,4-dinitrochlorobenzene to a similar reaction mixture led to the expected thioether (VIII, 37%).

Oddo and Mingoia<sup>7</sup> describe a compound obtained from the successive treatment of indole-magnesium bromide with sulfur and benzoyl chloride as the benzoyl derivative of 3-mercaptoindole, and they hydrolyzed the ester to a substance, regarded as 3-mercaptoindole or the tautomeric thio-

(1) Postdoctoral Research Associate.

(2) D. S. Matteson and H. R. Snyder, *J. Org. Chem.*, **22**, 1500 (1957).

(3) P. A. S. Smith and J. H. Boyer, *THIS JOURNAL*, **73**, 2626 (1951).

(4) D. S. Matteson, Thesis, Doctor of Philosophy, University of Illinois, 1957.

(5) W. Carpenter, M. S. Grant and H. R. Snyder, *THIS JOURNAL*, **82**, 2739 (1960).

(6) J. Strating and H. J. Backer, *Rec. trav. chim.*, **69**, 638 (1950).

(7) B. Oddo and Q. Mingoia, *Gazz. chim. ital.*, **62**, 299 (1932).