yellow product which separated as plates; yield 28.1 g. (74.8%), m.p. 211–212°.

Anal. Calcd. for $C_{10}H_{11}N_3O_6$: N, 15.61. Found: N, 15.59.

The average yield from fourteen similar runs was 75%.

5-Ethoxy-8-acetylaminoquinoxaline. A solution of 54 g. (0.2 mole) of 1-ethoxy-2,3-dinitro-4-acetamidobenzene in 350 ml. of dimethyl formamide was reduced in a 1-l., one-neck glass reduction flask in the presence of 40 g. of 5% palladium-on-carbon catalyst. The hydrogenation was conducted at room temperature under a hydrogen pressure of 30 pounds per square inch and was complete in 1.5 hr.

In a dry box, the reduction mixture was filtered, under a nitrogen atmosphere, through Filter-Cel into 68.1 g. (0.256 mole) of reagent grade sodium glyoxal bisulfite (Carbide and Carbon) which was dissolved in 1000 ml. of 70° water. This reaction mixture was heated at total reflux for 6 hr. under a nitrogen blanket. The hot reaction mixture was filtered through Filter-Cel and the low-boiling material removed at the water pump. Approximately 250 ml. of brown oil remained. This oil was poured into 3.0 l. of acetone. The bright yellow solid which separated was collected by filtration on a Buchner funnel and washed with three 250-ml. portions of 5° water. The product was crystallized from ethanol; yield 21.3 g. (46.2%) m.p. 186°.

An estimate of the purity of the product was obtained by eluting a sample which had been placed on a strip of 3MM chromatographic paper (S&S) with a mixture of hexane: acetone (3:2). Examination of the paper strip under ultraviolet light indicated the presence of only one component in the analytically pure sample.

Anal. Calcd. for $C_{12}H_{13}N_3O_2$: C, 62.33; H, 5.63; N, 18.18. Found: C, 62.24; H, 5.72; N, 18.15.

5-Ethoxy-8-aminoquinoxaline. An orange mixture of 2 g. (0.0086 mole) of 5-ethoxy-8-acetylaminoquinoxaline and 20 ml. of 2*N* sulfuric acid was heated at 95–98° for 15 min. in a 50-ml. Erlenmeyer flask. The resulting blood red solution was cooled to room temperature and cautiously neutralized, as indicated by moist Alkacid paper, by the addition of solid sodium bicarbonate. When cooled to 0–5°, the bright orange crystals which separated were removed by filtration on a Buchner funnel and washed with two 100-ml. portions of cold water (2–3°). After drying overnight at 50°, the bright orange product weighed 1.48 g. (90.5%) m.p. 85–86°. The melting point remained unchanged by a single crystallization from an ethanol:acetone mixture (3:1) followed by a single crystallization from an ethanol:isopropyl ether mixture (1:1).

Anal. Calcd. for $C_{10}H_{11}N_3O$: C, 63.49; H, 5.82; N, 22.22. Found: C, 63.74; H, 6.28; N, 21.98.

The product appears to undergo a number of the usual reactions of aromatic amines. It can be coupled in the usual fashion with β-naphthol, 1-phenyl-3-methylpyrazolone-5, *p*-cresol, diphenylamine, dimethylaniline and *N*-ethyl-*N*-β-cyanoethyl-*m*-toluidine to form dyes.

5-Ethoxy-8-aminoquinoxaline hydrochloride. An excess of approximately 14% hydrochloric acid was added to a solution of 0.5 g. (0.0027 mole) of 5-ethoxy-8-aminoquinoxaline in 10 ml. of ethanol. The reaction mixture was stirred for 1 hr. at room temperature whereupon anhydrous ethyl ether was added dropwise until the reaction mixture developed a slight opalescence. The cream colored product which separated on cooling to 5° was collected by filtration on a Buchner funnel and washed with two 25-ml. portions of 5° water. After drying overnight at 50°, the product weighed 0.59 g. (90%) m.p. 180–190°. No change in the decomposition range of the product occurred after one crystallization by the dropwise addition of isopropyl ether to a solution of the salt in boiling ethanol and subsequent cooling of the turbid solution. A sharp decomposition point was not obtained in a sealed capillary tube according to the method of Easley and Bahner.[7]

(7) W. K. Easley and C. T. Bahner, *J. Am. Chem. Soc.*, 72, 3803 (1950).

Anal. Calcd. for $C_{10}H_{12}N_3OCl$: Cl, 15.78. Found: Cl, 15.28.

5-Ethoxy-8-p-tolylsulfonamidoquinoxaline. Thirty-three hundredths of a gram (0.027 mole) of *p*-toluenesulfonyl chloride (Eastman, reagent grade) was added to a stirred solution of 0.5 g. (0.0027 mole) of 5-ethoxy-8-aminoquinoxaline in 5 ml. of pyridine. The mixture was stirred and heated at reflux for 30 min. employing a Mag-Mix hotplate. The hot reaction mixture was treated with 1 g. of Nuchar, filtered through Filter-Cel, and cooled to 0–5°. The cream colored product which separated was collected on a Buchner funnel and dried overnight at 50° prior to purification. The product was crystallized from a boiling ethanol:acetone mixture (3:1); yield 0.48 g. (57%) m.p. 132–133°.

Anal. Calcd. for $C_{17}H_{17}N_3SO_3$: N, 12.24; S, 9.32. Found: N, 12.20; S, 9.24.

5-Ethoxy-8-N-acetylsulfanilamidoquinoxaline. This cream colored compound was prepared from (V) essentially as described by Wolfe *et al.*[6] The yield was 90.5%, m.p. 223–229°.

Anal. Calcd. for $C_{18}H_{18}N_4SO_4$: N, 14.51; S, 8.28. Found: N, 14.47; S, 8.20.

5-Ethoxy-8-sulfanilamidoquinoxaline. Alcoholic hydrochloric acid was employed to hydrolyze (VIII) in a similar procedure to that described by Wolfe *et al.*[6] The crude yield was 71%. The pure bright yellow product had an m.p. of 181–182°.

Anal. Calcd. for $C_{16}H_{16}N_4SO_3$: N, 16.28; S, 9.30. Found: N, 16.19; S, 9.09.

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Vinyl Sulfides. VI. Evidence for a Sulfonium Mercaptide Intermediate

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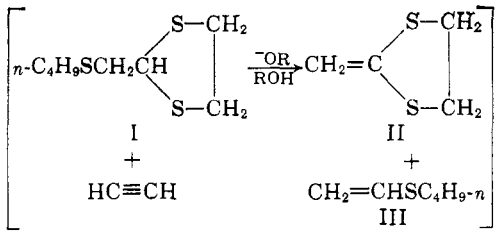
The preparation of ketene mercaptals by the base-catalyzed reaction of *n*-alkylmercaptoacetaldehyde dialkyl mercaptals with acetylene occurs in high yield[1] (Equation 1a). For a continuing study of the properties of ketene mercaptals, the preparation of 2-methylene-1,3-dithiolane (II) was proposed, to be obtained by a similar reaction sequence (Equation 1b). As in the ketene acetal series,[2] the cyclic ketene mercaptal (II) was expected to have considerably better polymerization characteristics than its open chain counterparts. For convenience in product separation *n*-

$$RSCH_2CH(SR)_2 + HC{\equiv}CH \xrightarrow[ROH]{^-OR} CH_2{=}C(SR)_2 + CH_3{=}CHSR \quad (1a)$$

butylmercapto derivatives were employed. The proposed synthesis therefore required the prepara-

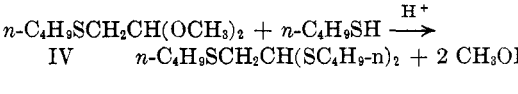
(1) H. J. Schneider, J. J. Bagnell, and G. C. Murdoch, *J. Org. Chem.*, 26, 1987 (1961).

(2) S. M. McElvain, *Chem. Rev.*, 45, 486 (1949).

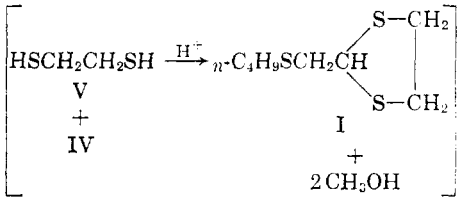


(1b)

tion of 2-*n*-butylmercaptomethyldithiolane-1,3 (I). The route selected for preparation of I involved the acid-catalyzed reaction of *n*-butylmercaptoacetaldehyde dimethylacetal[3] (IV) with 1,2-ethanedithiol (V) (Equation 2b). *n*-Butylmercaptoacetaldehyde di-*n*-butylmercaptal (VI) has been prepared in high yield by acid-catalyzed reaction of IV with *n*-butyl mercaptan[3] (Equation 2a). Reaction

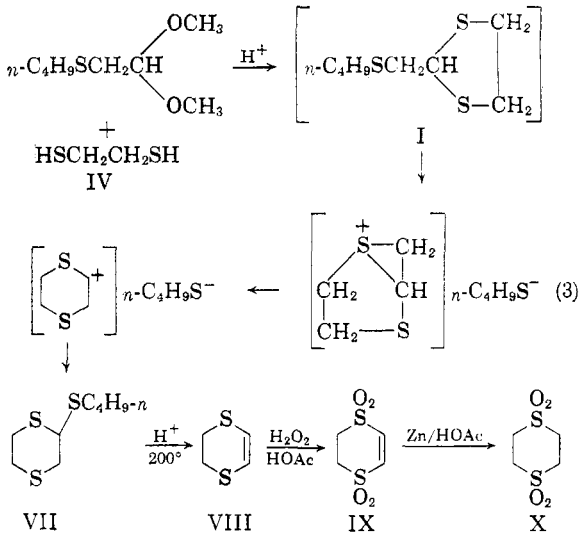


(2a)



(2b)

of stoichiometric amounts of IV and V proceeded in high yield to a single product with analyses expected for I. However, reaction of presumed I with acetylene failed to produce any of the desired II or any by-product *n*-butyl vinyl sulfide (III). Furthermore, distillation of presumed I from *p*-toluenesulfonic acid gave dithiene (VIII) which was identified by oxidation to the tetroxide (IX) and comparison with an authentic sample prepared by the reaction of chlorodimethylacetal with V.[4] The data suggest that the reaction of IV and V leads to formation of 2-(*n*-butylmercapto)dithiane-1,4 (VII), and is best described by assuming cyclic sulfonium mercaptide intermediates (equation 3), similar to the well known sulfonium halides.[4,5,6] Whether the reaction involves intermediate formation of VIII by elimination of mercaptide was not ascertained. The acid-catalyzed addition of mercaptans to 1,2-bis(alkylmercapto)ethylenes has been reported.[7] Parham[8] has suggested an alternate mechanism which does not involve formal charge separation.



(3)

EXPERIMENTAL

Reaction of n-butylmercaptoacetaldehyde dimethylacetal (IV) *with 1,2-ethane-dithiol* (V). Ethanedithiol (47 g., 0.5 mole), *n*-butylmercaptoacetaldehyde dimethylacetal (89 g., 0.5 mole) and *p*-toluenesulfonic acid (1 g.) were mixed at room temperature. The reaction mixture warmed noticeably, and upon standing overnight developed two phases.

The entire reaction mixture was washed with aqueous sodium hydroxide (10%) until the strong odor of V was absent. The oil layer was flash-distilled to give a water-white distillate (86 g., b.r. 50–132°/0.5 mm., pot temperature <210°) and a residue of 22 g. which was not examined further.

Redistillation of the product through a modified Claisen gave VII (84 g., 0.40 mole, 82% yield) as colorless oil, b.p. 110°/0.5 mm., n_{25}^{25}, 1.5673, d_{25}^{25}, 1.1292.

(3) W. E. Parham, H. Wynberg, and F. L. Ramp, *J. Am. Chem. Soc.*, **75**, 2065 (1953).

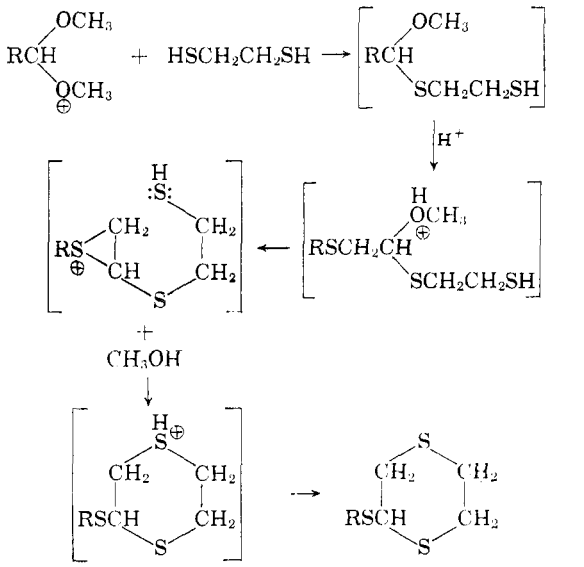
(4) W. E. Parham, J. Heberling, and H. Wynberg, *J. Am. Chem. Soc.*, **77**, 1169 (1955).

(5) R. C. Fuson *et al.*, *J. Org. Chem.*, **11**, 475 (1946); *J. Am. Chem. Soc.*, **71**, 1582 (1949).

(6) C. S. Marvel and E. D. Weil, *J. Am. Chem. Soc.*, **76**, 61 (1954).

(7) H. C. Volger and J. F. Arens, *Rec. Trav. Chim.*, **76**, 853 (1957).

(8) W. E. Parham, in a private communication, suggests the following mechanism:



In 1954, Parham and co-workers, in unpublished observations, noted the formation of a single trisulfide by the acid-catalyzed reaction of benzylmercaptoacetaldehyde dimethylacetal and ethanedithiol. A trisulfide with essentially the same physical properties was obtained by the reaction of 2-ethoxy-1,4-dithiane with benzyl mercaptan. However, the trisulfones obtained from the similar trisulfides were not identical and the study was not pursued.

Anal. Calcd. for $C_8H_{16}S_3$: C, 46.11, H, 7.74, S, 45.15, M_D 60.94. Found: C, 46.18, H, 7.67, S, 45.96, M_D 60.47.

Identification of 2-n-butylmercaptodithiane-1,4 (VII). A mixture of VII (58 g., 0.28 mole) and *p*-toluenesulfonic acid (1 g.) was heated slowly, with stirring, in a flask fitted with a distillation column. Temperature and pressure were regulated to remove from the distillation flask any material with boiling point lower than the starting material. Decomposition began at 170° and heating was continued for 1 hr., with a maximum pot temperature of 205°. A small amount of VII was distilled to sweep lower boiling materials from the reaction flask. The distillate and trapped (−70°) products were diluted with ethyl ether and were washed quickly with 10% sodium hydroxide.

Distillation of the organic layer gave VIII (11 g., 0.08 mole, 30% yield), identical with authentic VIII obtained by reaction of V with chlorodimethylacetal.[3]

A sample (1.8 g.) of VIII, obtained by acid-catalyzed decomposition of VII, was oxidized with peracetic acid at 0–5° to give 1,4-dithiene tetroxide (IX, 2.5 g.). IX was insoluble in organic solvents. A portion (0.5 g.) was recrystallized from concentrated nitric acid to give a white powder (0.3 g.), m.p. >280°.

Anal. Calcd. for $C_4H_6S_2O_4$: C, 26.36, H, 3.32, S, 35.19. Found: C, 26.36, H, 3.47, S, 34.97.

The sulfone (IX, 0.5 g.) was refluxed with zinc dust in acetic acid for 1 hr. to produce 1,4-dithiane tetroxide (X, 0.3 g.), which was washed with ethanol and dried, m.p. >280°.

Anal. Calcd. for $C_4H_8S_2O_4$: C, 26.08, H, 4.38, S, 34.81. Found: C, 26.01, H, 4.32, S, 34.77.

Infrared spectra of IX and X were identical with those of samples prepared in a similar way from authentic[3] VIII.

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The Nature of the Alkyl Groups in Nidulin

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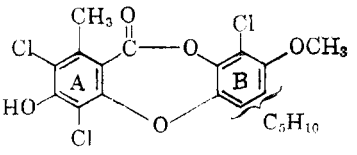
In 1954, Dean, Roberts, and Robertson, after extensive chemical investigation, proposed structure (I) for nidulin, the principal metabolic product of the mold *Aspergillus nidulans*.[1]



I

The 60-Mc NMR spectra of nidulin, *O*-methylisonidulin, and the product of the successful hydrogenation of nidulin, dihydronidulin,[2] are reproduced in Fig. 1.

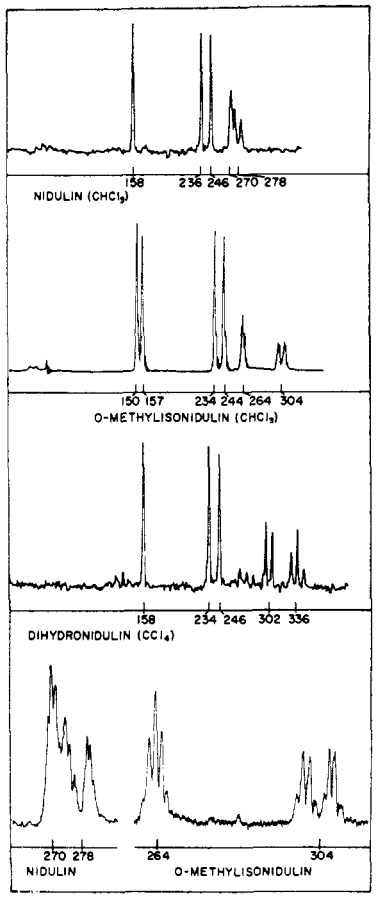


Figure 1

The secondary splittings of the vinyl methyl doublet-of-quartets signal (at 278 c.p.s. in nidulin and 304 c.p.s. in *O*-methylisonidulin) were found to be 1.11 ± .04 c.p.s. for nidulin and 1.52 ± .05 c.p.s. for *O*-methylisonidulin. The major splittings of these signals were essentially identical: 6.76 ± .08 c.p.s. for *O*-methylisonidulin and 6.77 ± .08 c.p.s. for nidulin. These results may be seen qualitatively in a slow sweep of the vinyl region of each spectrum in Fig. 1.

As a consequence of the detailed analysis of the NMR spectra of nidulin, *O*-methylisonidulin, and dihydronidulin, the nature of the five remaining carbons can be determined.

The appearance of two unsplit methyl peaks in the aromatic methyl (*ca.* 250 c.p.s.) region of the spectra of each of these compounds can have but one interpretation: that in nidulin there are two aromatic methyl groups. The previous authors have demonstrated the existence of one such methyl group attached to the A-ring.[1] Since it is known to be the only methyl group on the A-ring, the other aromatic methyl group must be attached to the B-ring. Hence, the previously undetermined five-carbon residue consists of a methyl group and a C_4H_7 fragment.

The presence of a double bond in the C_4H_7 fragment is substantiated by a quartet-of-quartets signal, proportional to a single proton in area, in the vinyl hydrogen portion of the spectrum. Although the fine structure of this signal can be observed only on slow, high-gain sweeps, its position

(1) F. M. Dean, J. C. Roberts, and A. Robertson, *J. Chem. Soc.*, **1954**, 1432–9.

(2) D. S. Noyce, personal communication.