the 2.55 Å. spacing would not be equal because of the unequal effectiveness of the blocking by interaction of or competition for sites by neighboring formate molecules. As regards the second of the catalytic reactions, the deposition of cobalt on cobalt, it is known[11] that thin deposits of cobalt on copper continue the orientation, structure, and approximate lattice constants of copper. Thus the interpretation of results on the basis of the spacing of the copper crystal would apply equally well to the catalytic deposition of cobalt on the cobalt surface.

We wish to express our appreciation to Dr. Allan T. Gwathmey for his encouragement and constructive criticism.

(11) Cochrane, *Proc. Phys. Soc.* (*London*), **48**, 723 (1936).

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Synthesis and Antifungal Action of 2-Methylmercapto-1,4-naphthoquinone[1,2]

BY JOHN E. LITTLE, THOMAS J. SPROSTON AND MURRAY W. FOOTE

Many methoxyquinones are known to possess marked antibiotic activity. Among these are fumigatin, spinulosin and javanicin. Many others have been tested and found to be remarkably inhibitory to various types of organisms.[3,4,5]

Since naturally occurring 2-methoxy-1,4-naphthoquinone was found to be highly fungistatic against several plant pathogenic fungi,[6] the synthesis of the sulfur analog of this compound was carried out and its fungistatic activity measured.

A simple synthesis in good yield was developed which was based upon mercaptan addition to 1,4-naphthoquinone. The work of Fieser and Turner,[7] involving the addition of mercaptans to 2-methyl-1,4-naphthoquinone, served as a pattern for the synthesis of this new compound.

We have found that the yield can be increased markedly by the well-timed addition of ferric chloride to the reaction mixture. This material probably causes the oxidation step to proceed farther toward completion.[7] It was found that the addition of the ferric chloride increased the yield of crude product (m. p. 183°) from 27 to 56%. When the salt was added at the beginning of the reaction, no product could be obtained. The final pure crystalline product separated from alcohol as yellow needles melting at 186.5–187° (cor.).

The spectrophotometric absorption curve of this compound was obtained. The wave length and intensities of the principal maxima are as follows: 256 mμ (ϵ = 19,700), 298 mμ (ϵ = 7,700) and 407 mμ (ϵ = 3,310). The characteristic naphthoquinone maximum at 330 is evident only as a slight inflection.

The substitution of a sulfur atom for oxygen in the 2-methoxy-1,4-naphthoquinone molecule results in a marked increase in antifungal activity. The $L.D._{50}$ value for this compound as measured against the spores of *Monolinia fructicola*[8] was found to be 1.00 part per million (0.00100 mg. per ml.) as compared to 3.65 parts per million (0.00365 mg. per ml.) for 2-methoxy-1,4-naphthoquinone[6]; an increase in potency of approximately 3.5 fold.[9]

The solubility of 2-methylmercapto-1,4-naphthoquinone determined spectrophotometrically was found to be 7.0 mg. per liter at 26°. The insoluble nature of this material would be of benefit if it were to be used as a plant fungicide.

Experimental

Preparation of 2-Methylmercapto-1,4-naphthoquinone.—16.5 g. of nearly pure naphthoquinone was dissolved in 1000 ml. of absolute alcohol by warming to 40°. The solution was cooled to room temperature and a small quantity of a dark impurity removed by filtration. The solution was then cooled in ice to 15° and 10 g. of ice-cold methyl mercaptan added suddenly while the flask was swirled.

After standing for thirty minutes at room temperature a yellow crystalline precipitate appeared; 15 ml. of 70% $FeCl_3 \cdot 6H_2O$ was now added and a further crystallization observed. After standing for fifteen minutes 22 ml. more of the ferric chloride solution was added and the quantity of precipitate again increased. Further addition of ferric chloride had no effect. The suspension was now cooled to 7°, filtered and dried with petroleum ether on the funnel; 11.9 g. of yellow crystalline material was obtained, m. p. 183°. The yield was 56% of the theoretical. One recrystallization of this material from hot alcohol after treatment with norite and filtration gave 9.16 g., m. p. 186.5–187°. The over-all yield was 45%.

Anal. Calcd. for $C_{11}H_8O_2S$: C, 64.69; H, 3.95; S, 15.70. Found: C, 64.88; H, 4.06; S, 15.93.

Determination of Solubility.—Fifteen milligrams of the finely ground 2-methylmercapto-1,4-naphthoquinone (m. p. 186.5–187°) was stirred in 5 l. of distilled water for thirty-six hours at room temperature. At the end of this time, all of the material had dissolved. The optical density of this solution at the 256 mμ maximum was found to be 0.309. Comparison of this density to that obtained with a saturated solution showed the solubility to be 7.0 mg. per liter.

(1) Printed by permission of Vermont Agricultural Experiment Station; Journal Series No. 1.

(2) We are grateful to the Herman Frasch Foundation for a grant in support of this work.

(3) Geiger, *Arch. Biochem.*, **11**, 23 (1946).

(4) Colwell and McCall, *Science*, **101**, 592 (1945).

(5) Oxford, *Chem. and Ind.*, **161**, 189 (1942).

(6) Little, Sproston and Foote, *J. Biol. Chem.*, **174**, 335 (1948).

(7) Fieser and Turner, THIS JOURNAL, **69**, 2335 (1947).

(8) Committee on Standardization of Fungicidal Tests, *Phytopathology*, **33**, 627 (1943); **37**, 354 (1947).

(9) A more detailed discussion of the fungistatic action of this and other naphthoquinones is in preparation for publication in the near future.

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Configurations of Radicals Derived from *cis*- and *trans*-Isomers

BY FRANK R. MAYO AND KENNETH E. WILZBACH

To obtain evidence concerning the recent proposal of Kistiakowsky,[1] that radicals have a non-

(1) Kistiakowsky, *The Indicator*, **28**, No. 3, 6 (1947), Nichols Medal Address, March 7, 1947.