ethanol, 5% sodium hydroxide; slightly soluble in water, cold ethanol, cold acetic acid, diluted hydrochloric acid; insoluble ether. The adduct decomposed at temperatures above the melting point to give the original reagents; the addition was also somewhat reversible in cold sodium hydroxide solutions.

Anal. Calcd. for $C_9H_9O_2N$: N, 8.58. Found: N, 8.51.

3,6-Endomethylene-1,2,3,6-tetrahydro-*o*-phthalic Acid.—Two-tenths gram of 3,6-endomethylene-1,2,3,6-tetrahydro-*o*-phthalimide were placed on a steam-bath with 5 ml. of 10% potassium hydroxide and heated for three hours, at the end of which time no ammonia was detectable in the vapors above the flask. Concentrated hydrochloric acid was added in excess, and the mixture was then evaporated to dryness. The residue was then triturated in 20 ml. of ether to remove the maleic acid formed by the alkali-catalyzed reversal of the addition. The remaining organic constituents were taken up in 10 ml. of boiling acetone, and petroleum ether was added to the solution until it became cloudy, whereupon the mixture was left at 0° to crystallize. After one recrystallization from alcohol-ether (1:2) the melting point was observed to be 177°, which was not lowered by 3,6-endomethylene-1,2,3,6-tetrahydro-*o*-phthalic acid from another source.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF COLORADO
BOULDER, COLORADO
RECEIVED NOVEMBER 4, 1948

N,N-Dimethyl-N′-(2-pyridyl)-N′-(2-furfuryl)-ethylenediamine

BY L. P. KYRIDES AND M. F. ZIENTY

In a recent publication Vaughan and Anderson[1] described the preparation of N,N-dimethyl-N′-(2-pyridyl)-N′-(2-furfuryl)-ethylenediamine (I) originally synthesized by Viaud.[2]

These authors reported that (I) is very unstable at temperatures even as low as −80° and that they were unable to prepare its mineral acid salts.[3]

Prior to the disclosure of Vaughan, *et al.*, the monohydrochloride of (I) had been prepared in this Laboratory for pharmacological evaluation. Since our findings do not support the observations reported, we are prompted to record our results.

Furfuryl alcohol was converted to the chloride in 75% yield by a modification of a synthesis described by Kirner,[4] with thionyl chloride in ether solution in the presence of pyridine at −15–20°. Distilled furfuryl chloride[5] was then treated with the lithium salt of N,N-dimethyl-N′-(2-pyridyl)-ethylenediamine in benzene solution at room temperature. After removal of the solvent and unreacted N,N-dimethyl-N′-(2-pyridyl)-ethylenediamine the desired product distilled as a yellow oil, stable at room temperature.

The monohydrochloride was prepared as well as the dihydrogen citrate salt.

The synthesis of (I) is described in detail.

Experimental[6]

N,N-Dimethyl-N′-(2-pyridyl)-N′-(furfuryl)-ethylenediamine.—To a suspension of 8.3 g. (0.36 mole) of lithium amide in 500 cc. of dry benzene was added 59.4 g. (0.36 mole) of N,N-dimethyl-N′-(2-pyridyl)-ethylenediamine,[7,8] and the mixture refluxed for three hours with stirring. The reaction was cooled to 25° and maintained at this temperature while a solution of 42 g. (0.36 mole) of furfuryl chloride in 200 cc. of dry benzene was added dropwise during one hour, then refluxed for one hour. On cooling, the solid material was removed by suction filtration and the solvent distilled under reduced pressure. After a forerun of 17.7 g. (28.7% recovery) of the starting ethylenediamine (b. p. 100–105° (0.4 mm.)), 45.9 g. (52%) of the desired tertiary amine was collected as a light yellow oil, b. p. 117.5–118° (0.2 mm.). The dihydrogen citrate was prepared in 88% yield by treating a methanol solution of 4.9 g. (0.026 mole) anhydrous citric acid with a methanol solution of 10 g. (0.04 mole) of (I) and precipitation with dry ether. Recrystallization of this salt from methanol–ether gave colorless crystals, m. p. 95–97°.[1a]

The monohydrochloride was prepared by treating an ethyl acetate solution of 36.2 g. (0.14 mole) (I) with 5 g. (0.14 mole) dry hydrochloric acid in methanol. On cooling, 37.8 g. (92%) of monohydrochloride was obtained. Recrystallization from ethyl acetate yielded colorless needles, m. p. 117–119°.

Anal. Calcd. for $C_{14}H_{19}N_3O\cdot HCl$: Cl, 12.61. Found: Cl, 12.80.

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[1] Vaughan and Anderson, THIS JOURNAL, **70**, 2607 (1948). reported m. p. 95–97°.

[2] Viaud, *Technologie Produits Pharmaceutiques*, **2**, 53 (1947).

[3] In a personal communication, Dr. Anderson, after receiving the manuscript of this article, has written us as follows: "We today converted a sample of our stable citrate to the base and then to the hydrochloride in solution. In contrast to our previous experience, the solution remained colorless. Our only explanation is that an impurity in the original base caused its instability to temperature and mineral acids, and in the process of preparing the citrate this impurity was removed. We found also that the 5-bromofurfuryl analog hydrochloride appears to be stable when made from the citrate," and authorizes us to publish this statement as a footnote.

[4] Kirner, THIS JOURNAL, **50**, 1958 (1928).

[5] Gilman and Vernon, *ibid.*, **46**, 2576 (1924), reported furfuryl chloride as extremely unstable.

[6] All melting points are corrected.

[7] Whitmore, Goldsmith and Rytina, THIS JOURNAL, **67**, 393 (1945).

[8] Huttrer, Djerassi, Beears, Mayer and Scholz, *ibid.*, **68**, 1999 (1946).

RESEARCH LABORATORIES OF
SUMNER CHEMICAL COMPANY, INC.
ELKHART, INDIANA
RECEIVED OCTOBER 20, 1948

The Influence of Crystal Face in the Catalytic Deposition of Cobalt on a Single Crystal of Copper[1]

BY HENRY LEIDHEISER, JR., AND RICHARD MEELHEIM

It has previously been shown in two different cases[2,3] that the rate of gaseous, catalytic reactions on the surface of a metal differs with the crystal face exposed at the surface. It has also been shown by Beeck, Smith and Wheeler[4] that the rate of the reaction of hydrogen and ethylene on a nickel film with a (110) orientation parallel to the surface is greater than that on an unoriented film. Results reported herein show that the rate of another type of catalytic reaction, the

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[1] This work was supported by a grant from the Research Corporation.

[2] Reaction of hydrogen and oxygen on copper: Leidheiser and Gwathmey, THIS JOURNAL, **70**, 1200 (1948).

[3] Decomposition of carbon monoxide on nickel: Leidheiser and Gwathmey, *ibid.*, **70**, 1206 (1948).

[4] Beeck, Smith and Wheeler, *Proc. Roy. Soc. (London)*, **A177**, 62 (1940).

chemical deposition from solution of one metal on a crystal of another, differs with the face exposed at the surface. An explanation for the results is proposed on the basis of interatomic distances.

In the study of catalytic reactions with the aid of large single crystals, there are two general methods by which the rates of reaction on the different faces may be determined. When the products of the reaction are continually removed from the catalyst surface, it is necessary to expose only one face at a time. The rate of formation of the product is then determined by analysis of the exit gases or liquids. A second method consists of using a monocrystalline sphere[5] containing all crystal faces, and choosing a reaction which leaves a deposit on the surface, from which conclusions may be drawn concerning the comparative activity of the various faces. Both methods have their advantages and disadvantages but the latter method possesses the unique advantage of exposing all crystal faces simultaneously.

Monocrystalline spheres of copper, $^{5}/_{8}$ in. in diameter with a shaft $^{3}/_{16}$ in. in diameter, were mechanically and electrolytically polished by the method previously described.[6] They were immersed in potassium formate solutions of a cobalt salt at 180–250° and cobalt was catalytically[7] deposited on the surface. From the known reaction of other metallic salts in potassium formate solution,[8] the reaction was considered to be: $CoCl_2 + HCOOK \rightarrow Co + CO_2 + HCl + KCl$. The greatly different catalytic activities of the various faces were indicated by a pattern on the surface. The same pattern was observed over a large concentration range with cobalt chloride, cobalt carbonate, and cobalt sulfate solutions. The relative catalytic activities of the faces of copper in order of decreasing activity were as follows: (210), (310), (321), and (320); (311) and (211); (100); (331) and (221); (110); and (111). Faces whose indices were all different, such as (210), (310), etc., were far more active than any of the others. At 240° with a concentration of cobalt chloride hexahydrate of 1 g. per 100 g. of potassium formate, a cobalt deposit was observed on the (210) face in less than 30 seconds whereas the (111) face remained free of a visible deposit of cobalt for ten minutes.

There were two separate steps which took place in this catalytic reaction. First cobalt deposited catalytically on certain faces of the copper sphere. Then cobalt deposited catalytically on the cobalt deposits. From the pattern formed it was concluded that the rates of both of these reactions differed with the crystal face exposed at the surface.

Evidence was obtained in these experiments which suggests that the formate molecule was largely responsible for the relative rates of catalytic reaction on the different faces of a copper crystal in potassium formate solution. This evidence is summarized in the following statements. (1) The reaction pattern was independent of the anion of the metallic salt present in the solution. (2) An entirely different pattern was obtained when cobalt was chemically deposited on copper from a hypophosphite solution by the method of Brenner and Riddell.[9] (3) A third and different pattern was obtained when cobalt was electrodeposited on a copper crystal from several aqueous baths. Attempts were made to electrodeposit cobalt from formic acid solutions and from aqueous solutions containing formate, but secondary electrochemical reactions predominated. The essential process in all of these experiments was the reduction of cobalt ions in solution to cobalt at the surface of a monocrystalline sphere of copper. However, in each case the chemical environments were different. (4) Nickel salts in potassium formate yielded exactly the same pattern as cobalt salts. It should be pointed out that the chemical properties and interatomic spacings of nickel are similar to those of cobalt.

Additional indirect evidence for the influence of potassium formate on the reaction pattern is found in the comparative spacings of the formate radical and the copper–copper distance. At room temperature the spacing between oxygen atoms in the formate molecule is 2.24 Å.[10] and the distance of closest approach of copper atoms is 2.55 Å. The next shortest copper–copper spacing is 3.60 Å. No data are available for the formate molecule at the temperatures used in this study, but it would be expected that the qualitative relationship of these two important spacings would still hold. When the results are examined, it is observed that only those faces which do not have a 2.55 Å. copper–copper spacing parallel to the surface—thus faces with indices (xyz)—are the most active ones in the catalytic deposition of cobalt. In addition faces with the greatest number of 2.55 Å. spacings parallel to the surface are the least active. Thus it is proposed that the formate molecule or ion is adsorbed most strongly on the 2.55 Å. copper–copper spacing and partially blocks the surface for reaction. The activity of all faces containing

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(5) In the case of the face-centered cubic metal copper, each face occurs on the sphere a minimum of six times. Thus when the various crystal faces react differently, a pattern, due to the repetition of results in each octant on the surface, occurs during reaction and the faces may be identified from the symmetry of this pattern.

(6) Gwathmey and Benton, *J. Phys. Chem.*, **44**, 35 (1940).

(7) The copper crystal is considered to be a catalyst in this study because it accelerated the rate of the reaction. It is appreciated that there might be objections to considering this reaction as a catalytic process according to the accepted definition in that the copper surface was visibly altered as the cobalt deposited. In the opinion of the authors, the same factors which make a substance a catalyst in the conventional sense were operative in the reaction described here.

(8) Gurevich and Pokrovskii, *Ukrainskii Khem. Zhurnal*, **2**, 414 (1926); *Chem. Abst.*, **22**, 1714 (1928).

(9) Brenner and Riddell, *J. Research Natl. Bur. Standards*, **39**, 385 (1947).

(10) L. Pauling, "Nature of the Chemical Bond," second edition Cornell University Press, Ithaca, New York, 1945, p. 203.

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.

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

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RECEIVED NOVEMBER 8, 1948

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.

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(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.

RECEIVED AUGUST 14, 1948

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-

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