orate at room temperature. A small amount of oil remained and, after purification, 0.86 g. of trinitrostyrene was recovered. Heating a solution of 1 g. of trinitrostyrene in 10 cc. of benzene with 0.3% benzoyl peroxide under reflux for two days produced darkening but no polymer.

(c) **Emulsion.**—The following trinitrostyrene–styrene emulsions in water were heated in a bath at 50° which was equipped for rotating the mixtures (figures are per cent. of trinitrostyrene based on total monomer composition): 100, 20, 0.4, 0%. Ammonium persulfate activated with sodium bisulfite was used as initiator, and the time was twenty hours. In the first two cases, no polymer was obtained, and the trinitrostyrene was recovered. With 0.4% of the trinitro compound, a yield of 20% of polymer was obtained. The styrene, under the same conditions, polymerized almost quantitatively.

(d) **Emulsion with Isoprene.**—When mixtures of styrene, trinitrostyrene and isoprene were heated at 50° for twenty-three hours in emulsion with the persulfate–bisulfite combination, the trinitrostyrene was recovered unchanged. The same result was obtained when the styrene was omitted; under the same conditions, styrene and isoprene (80:20) gave a good yield of polymer.

(e) **Solution with Maleic Anhydride.**—When maleic anhydride was heated in benzene solution with trinitrostyrene (with and without styrene) and with benzoyl peroxide as the initiator, no polymer was obtained. Under the same conditions, the styrene/maleic anhydride heteropolymer began to precipitate in fifteen minutes.

Summary

2,4,6-Trinitrostyrene has been prepared, but efforts to polymerize it under various conditions and to copolymerize it with isoprene, maleic anhydride, or styrene have failed. It acts as an inhibitor of styrene polymerization.

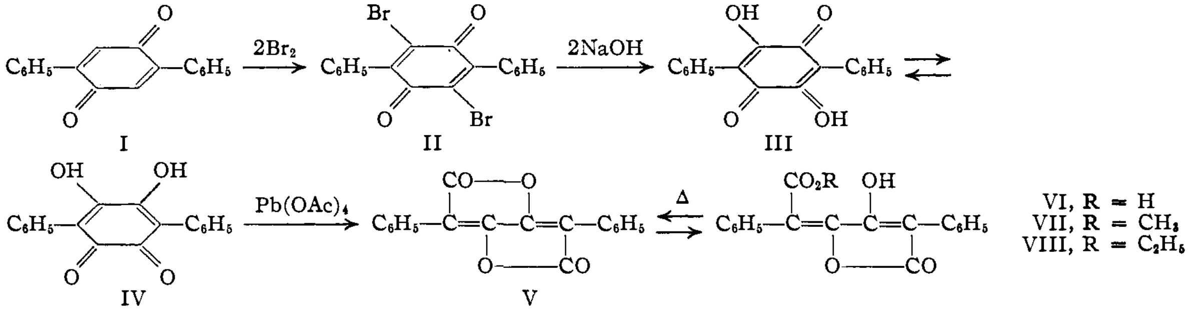
LOUISVILLE, KENTUCKY RECEIVED OCTOBER 10, 1949

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

The Synthesis of Vulpinic Acid from Polyporic Acid[1]

BY ROBERT L. FRANK, GEORGE R. CLARK AND JAMES N. COKER

In this communication we wish to report the oxidation of the fungus pigment polyporic acid (III)[2] by means of lead tetraacetate. This reaction has been made possible a new and total synthesis of vulpinic acid (VII)[3] and an examination of some of its derivatives, notably the "isovulpinic acid" described by Spiegel.[4]



VI, R = H
VII, R = CH_3
VIII, R = C_2H_5

Vulpinic acid is a yellow pigment found in a variety of lichens. Its structure was elucidated mainly by Spiegel[3] and by Karrer, Gehrckens and Heuss,[5] and confirmed by synthesis by Volhard.[6] It has recently been observed to be a powerful antibacterial agent *in vitro.*[7]

Polyporic acid (III) for this study was obtained both from the natural source, the fruit body of *Polyporus rutilans*, and by synthetic means. The rarity of the fungus, however, limits the value of the natural source.[8] Culture of the fungus has also not been a feasible source, because the pigment occurs only in the fruit body and not in the mycelium.[9]

The synthesis of polyporic acid (III) was accomplished by a modification (I–II–III) of the method of Shildneck and Adams.[10] In addition to the elimination of two steps of the previous method, the preparation of the starting material, 2,5-diphenyl-1,4-benzoquinone (I), has been improved by use of nitrous acid rather than chromic acid in oxidizing the mixture of quinone, quinhydrone and hydroquinone obtained in the phenylation of 1,4-benzoquinone. Fieser[11] has recently observed that nitrous acid is specific for this type of oxidation.

Reaction of lead tetraacetate with polyporic acid in boiling acetic acid occurs smoothly to give

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(1) Presented before the Division of Organic Chemistry at the Atlantic City meeting of the American Chemical Society, September 18–23, 1949.

(2) Kögl, *Ann.*, **447**, 78 (1926); Kögl and Becker, *ibid.*, **465**, 219 (1928).

(3) Spiegel, *ibid.*, **219**, 1 (1883).

(4) Spiegel, *ibid.*, **219**, 15 (1883).

(5) Karrer, Gehrckens and Heuss, *Helv. Chim. Acta*, **9**, 446 (1926).

(6) Volhard, *Ann.*, **282**, 1 (1894).

(7) Stoll, Renz and Brach, *Experientia*, **3**, 111, 115 (1947).

(8) *Polyporus rutilans* (*P. nidulans*) is reputed to be fairly common in some areas, notably Pennsylvania. The coöperation of a number of collectors during the relatively dry summer and fall of 1948, however, netted the authors less than an ounce of the dried fungus.

(9) Private communication, Dr. Leland Shanor and Mr. Richard K. Benjamin; see the following paper.

(10) Shildneck and Adams, THIS JOURNAL, **53**, 2373 (1931).

(11) Fieser, *ibid.*, **70**, 3165 (1948).

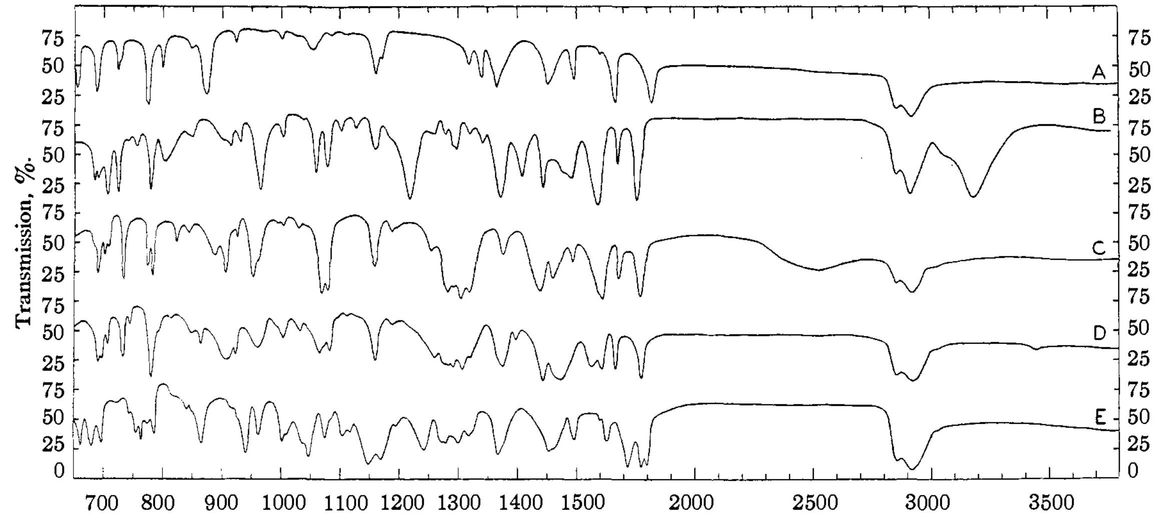

Fig. 1.—Infrared absorption spectra of crystalline compounds in Nujol suspension: A, pulvinic acid lactone (V); B, pulvinic acid (VI); C, vulpinic acid (VII); D, ethyl pulvinate and "isovulpinic acid" (VIII); E, acetyl derivative of ethyl pulvinate and of "isovulpinic acid."

pulvinic acid lactone (V) in 28% yield. The lactone is converted readily by acid hydrolysis to pulvinic acid (VI)(90%) and by methanolysis to vulpinic acid (VII) (90%).

We were surprised to note in the lead tetraacetate oxidation that reaction occurred as well in the absence of water as in the presence of one mole of water per mole of polyporic acid. On the basis of Structure III for polyporic acid this is unexpected, since Baer[12] has pointed out that α-hydroxy ketones are attacked by lead tetraacetate only if water is present to form a hydrate. One may postulate from this that a tautomeric structure (IV) can also exist for polyporic acid, and that it is this form which reacts with lead tetraacetate.

Spiegel[4] has described the formation of a by-product in the pyrolysis of vulpinic acid (VII) to pulvinic acid lactone (V). He considered this to be isomeric with vulpinic acid, and named it "isovulpinic acid." We have prepared the same by-product and find it is not an isomer of vulpinic acid but is instead identical with ethyl pulvinate (VIII), as judged by mixed m. p. determinations and comparisons of infrared absorption spectra of the esters as well as their acetyl derivatives. The compound can also be saponified to pulvinic acid (VI). Spiegel crystallized his material from ethanol, a procedure now known to form the ethyl ester (VIII) from pulvinic acid lactone (V).

Infrared absorption data have hitherto not been reported for structures of the pulvinic acid type and are therefore included here (Fig. 1). The lack of absorption in the region 3100–3800 cm.⁻¹ of the esters (VII and VIII, Fig. 1, C and D) may signify that these compounds exist in the keto form rather than the enolic form of Structures VII and VIII.

Experimental

All m. ps. are corrected.

2,5-Diphenyl-1,4-benzoquinone (I).—The method of Shildneck and Adams,[10] the reaction of benzene, 1,4-benzoquinone and aluminum chloride, with the same quantities of starting materials, gave 138 g. of the brownish-green mixture of quinone, quinhydrone and hydroquinone, m. p. 165–175°, reported by these authors. The mixture was oxidized in 10-g. portions as follows: a 10-g. suspension in 250 ml. of glacial acetic acid was boiled for fifteen minutes and filtered rapidly. The filtrate was heated to 100–105° in a flask equipped with a stirrer, a dropping funnel, a thermometer and a reflux condenser attached to a trap, and a solution of 8.0 g. (0.094 mole) of sodium nitrite in 10 ml. of water was added rapidly. After several minutes stirring, the mixture was poured into 600 ml. of ice water, additional water was added to bring the volume to 2800 ml., and the orange solid collected on a suction filter. The crude product (9.0 g.) was then dissolved in hot xylene, the solution filtered through a heated Büchner funnel containing a layer of Filter-Cel (to remove an insoluble oily material), and cooled to yield a mat of yellow crystals, m. p. 212–214° (lit.,[10] 214°), after several 5-ml. washes with cold benzene. The product weighed 5.0 g. (29% based on one mole of 1,4-benzoquinone; 87% based on three moles used up per mole of product. The true yield must lie somewhere between these figures.[13]

The oxidation of 100-g. amounts of the mixture from the Friedel–Crafts reaction was observed to give slightly lower yields.

3,6-Dibromo-2,5-diphenyl-1,4-benzoquinone (II).—To a vigorously stirred solution of 1.1 g. (0.0042 mole) of 2,5-diphenyl-1,4-benzoquinone in 75 ml. of hot glacial acetic acid was added 5.5 g. (0.034 mole) of bromine. The solution was heated at 95–100° for one hour, then cooled and 550 ml. of water added. The resulting suspension was refluxed, with use of a gas trap, for fifteen minutes to coagulate the dibromoquinone. The orange crystals were collected on a filter, washed with two 10-ml. portions of

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(12) Baer, THIS JOURNAL, 62, 1597 (1940).

(13) Basing the yield on three moles of quinone assumes the reaction of one-third of the quinone with benzene, the other two-thirds serving to oxidize the primary product to the diphenylbenzoquinone. Since this oxidation is not complete, more than one-third of the quinone must have been available to undergo the reaction with benzene. A calculation of the true yield would have to take this unknown quantity into account.

cold water, and dried at 50–60° to yield 1.55 g. (88%) of product, m. p. 221–223°. Recrystallization from benzene, giving the product in 80% recovery, raised the m. p. only slightly, to 223–224° (lit.,[10] 224°).

When the procedure was adapted to 50-g. batches, the yield was 92%.

Polyporic Acid (III).—From 3,6-Dibromo-2,5-diphenyl-1,4-benzoquinone: The procedure of Shildneck and Adams,[10] using up to 90 g. of the dibromoquinone, gave polyporic acid in yields of 80–95%, m. p. 303–305° with sublimation (lit.,[10] 305°).

From *Polyporus rutilans*.—The method of Kögl[2] was employed. The yield of pigment, m. p. 304–305° with sublimation, was 23% of the weight of air-dried fungus.

Pulvinic Acid Lactone (V).—Three grams (0.0103 mole) of polyporic acid was dissolved in 600 ml. of glacial acetic acid by refluxing for ten minutes in a three-necked flask equipped with a reflux condenser, dropping funnel and mechanical stirrer. To the well-stirred solution was then added 4.55 g. (0.0105 mole) of lead tetraacetate dissolved in 20 ml. of warm glacial acetic acid. Heating was continued for one hour. The solution was then concentrated to 75 ml. by heating under reduced pressure, cooled to 5–10°, and the yellow pulvinic acid lactone collected on a suction filter. It was washed with two 5-ml. portions of cold methanol and dried in air to yield 1.1 g. (37%) of product pure enough for subsequent reactions, m. p. 210–215°. One recrystallization from chloroform gave 0.85 g. (28%) of minute yellow plates, m. p. 220–221° (lit.,[3] 220–221°). An attempt to apply to polyporic acid the procedure of Kögl and Becker[2] for the analogous oxidation by means of hydrogen peroxide of the pigment atromentin yielded only traces of yellow crystals, m. p. 217–218°.

Vulpinic Acid (VII).—A suspension of 3.3 g. (0.0114 mole) of pulvinic acid lactone in 200 ml. of methanol and 5 ml. of concentrated hydrochloric acid was refluxed for fifteen minutes, then filtered rapidly while hot. The yellow filtrate, concentrated *in vacuo* to a volume of 40 ml. and cooled in ice, yielded a mass of yellow crystals. One recrystallization from 50 ml. of methanol gave 3.3 g. (90%) of short yellow plates melting constantly at 145–146° (lit.,[3] 148°).

Anal.[14] Calcd. for $C_{19}H_{14}O_5$: C, 70.81; H, 4.34. Found: C, 70.81; H, 4.57.

The acetyl derivative of vulpinic acid, prepared by refluxing 0.5 g. (0.0014 mole) with 5 ml. of acetyl chloride for fifteen minutes, pouring the mixture slowly into 50 ml. of water, and recrystallizing the resulting crystals from methanol, melted at 149–150° (lit.,[5] 148°).

Ethyl Pulvinate (VIII).—This was prepared in the same manner as was vulpinic acid from 3.3 g. (0.0114 mole) of pulvinic acid lactone, 200 ml. of absolute ethanol and 5 ml. of concentrated hydrochloric acid. The product was 3.5 g. (92%) of yellow plates, m. p. 124–125°. One recrystallization from absolute ethanol raised the m. p. to 126–127° (lit.,[3] 127–128°).

The acetyl derivative was prepared by the procedure used for the vulpinic acid derivative. Two recrystallizations from absolute ethanol gave short cream-colored plates melting constantly at 139–140° (lit.,[15] 143–144°).

Anal. Calcd. for $C_{22}H_{18}O_6$: C, 69.84; H, 4.76. Found: C, 69.99; H, 4.93.

"Isovulpinic Acid."—The description of Spiegel[4] was followed as closely as possible. One gram (0.0031 mole) of vulpinic acid was heated in a glass sublimation tube at 275–300° for two hours. The sublimate was pulvinic acid lactone. The residue was leached with 200 ml. of hot absolute ethanol in 15-ml. portions, the ethanolic solution evaporated to dryness on a steam cone, and the residue from this extracted with 25 ml. of cold saturated aqueous sodium carbonate to yield an orange solution with a slight green fluorescence. To this was added 10 ml. of concentrated hydrochloric acid with the temperature maintained at 5–10°. The resulting yellow precipitate was collected on a filter, washed twice with 10-ml. portions of cold water, and redissolved in 50 ml. of absolute ethanol. The solution was concentrated to half its volume and cooled. Recrystallization of the resulting yellow crystals from absolute ethanol yielded *ca.* 0.3 g. of short yellow plates, m. p. 126–127°.

Anal. Calcd. for $C_{20}H_{16}O_5$: C, 71.43; H, 4.76. Found: C, 71.50; H, 5.00.

A mixture of this material with ethyl pulvinate melted at 126–127°. Its acetyl derivative, prepared precisely as that of ethyl pulvinate, melted at 139–140°, as did its mixture with the acetyl derivative of ethyl pulvinate. Hydrolysis of the compound by means of calcium hydroxide according to the directions below for pulvinic acid from ethyl pulvinate gave pulvinic acid. Infrared spectra of chloroform solutions of "isovulpinic acid" and ethyl pulvinate were identical, as were the spectra of their respective acetyl derivatives.

Evidence that the transformation of vulpinic acid (VII) to ethyl pulvinate (VIII) occurred by the intermediate formation of pulvinic acid lactone (V) was obtained as follows: Vulpinic acid (VII) is not converted to ethyl pulvinate (VIII) by boiling ethanol or boiling ethanolic hydrogen chloride. Vulpinic acid is stable for at least several hours to cold aqueous sodium carbonate. Pulvinic acid (VI) is not esterified by boiling for three hours with absolute ethanol. On the other hand, pulvinic acid lactone (V) dissolves slowly on refluxing with absolute ethanol to yield ethyl pulvinate, even in the absence of hydrochloric acid.

Pulvinic Acid (VI).: From Ethyl Pulvinate (VIII).—Refluxing of 1.0 g. (0.0030 mole) of ethyl pulvinate in 40 ml. of saturated aqueous calcium hydroxide, followed by cooling and filtration, yielded a yellow solution of the neutral calcium salt of pulvinic acid. Acidification at 5° with 5 ml. of concentrated hydrochloric acid yielded a flocculent precipitate, coagulated by allowing it to stand in an ice-bath. One recrystallization from benzene gave 0.80 g. (87%) of orange plates, m. p. 216–217° (lit.,[6] 215–216°).

From Pulvinic Acid Lactone (V).—A suspension of 0.50 g. (0.00172 mole) of the lactone was refluxed for fifteen minutes in 25 ml. of 2% aqueous sodium hydroxide. The orange solution was filtered, cooled to 0–5°, acidified with 3 ml. of cold concentrated hydrochloric acid, and the precipitate washed with cold water and dried *in vacuo*. Recrystallization from benzene gave 0.48 g. (91%) of crystalline acid, m. p. 216–217°. Mixed m. ps. of this material with that obtained by calcium hydroxide hydrolysis of ethyl pulvinate and of "isovulpinic acid" were not depressed.

Infrared Spectra.—The determinations were kindly carried out by Miss Elizabeth Petersen using a Perkin-Elmer Model 12B infrared spectrometer with rock salt optics. We are indebted to Miss Petersen and to Dr. Werner Herz for helpful discussions of the spectra.

Acknowledgment.—We wish to express our appreciation to the large number of persons, botanists and otherwise, who undertook to help us obtain specimens of *Polyporus rutilans*, and one of us (G. R. C.) wishes to thank the Sunbeam Corporation for financial assistance.

Summary

1. A direct synthesis of the lichen pigment vulpinic acid has been accomplished by lead tetraacetate oxidation of polyporic acid.

2. The synthesis of polyporic acid from 1,4-benzoquinone has been improved.

3. "Isovulpinic acid," described by Spiegel in 1883 as an isomer of vulpinic acid, has been shown to be identical with ethyl pulvinate.

URBANA, ILLINOIS RECEIVED AUGUST 15, 1949

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[14] Microanalyses were carried out by Miss Emily Davis.

[15] Zopf, *Ann.*, **284**, 116 (1895).