only by redetermining the optical properties of crystals obtained from the original source. Strüver[9] obtained his material from the lichens *Zeora sordida* and *Usnea barbata*. Kappen[10] obtained *l*-usnic acid from *Usnea barbata* and the *d*-usnic acid from *Usnea longissima*.

A lichen collected by one of us (F.T.J.) and identified by the University of California Botany Department as *Usnea californica* Herre has yielded crystals of usnic acid[11] having optical and crystallographic properties identical with those of the material obtained from *Ramalina reticulata* reported above. This evidence makes it practically certain that Kappen's values for the refractive indices of usnic acid are in error. His method for determining the indices is not clearly stated but the implication is that it was a goniometric method utilizing the usnic acid crystal as a prism. The sample from *Usnea californica* was too small to test for optical rotation but the material is probably the dextrorotatory isomer. Abderhalden[11] lists only the *d* isomer from any of the *Usneas;* consequently Kappen must have obtained his *l*-usnic acid from a lichen mistakenly identified as *Usnea barbata*.

Acknowledgments.—We wish to express our thanks to Merle Ballantyne for taking the X-ray diffraction photographs, to Oliver Emerson for determining the molecular weight, and to N. Floy Bracelin for help in the preparation of Fig. 2 and for assistance in finding a source of *Usnea californica*. We also thank Phyllis Gardner, herbarium botanist of the University of California, and C. W. Dodge of Washington University and the Missouri Botanical Garden for their assistance in finding and identifying the *Usnea californica* Herre.

Summary

The optical properties of usnic acid isolated from the lichens *Ramalina reticulata*, *Parmelia moliuscula*, and *Usnea californica* Herre have been determined. The crystals obtained from chloroform solution are orthorhombic with indices $\alpha = 1.611$, $\beta = 1.710$, and $\gamma = 1.772$. These values differ markedly from those originally reported for usnic acid. X-Ray diffraction photographs of these crystals give $a = 19.10$ Å. parallel to β, $b = 20.39$ Å. parallel to γ, and $c = 8.09$ Å. parallel to α. The space group is probably $D_2^4 - P2_12_12_1$ but may be $D_2^3 - P2_12_12$, and the density is 1.46 g./cc. There are two crystallographically unrelated sets of four molecules each in the unit cell.

ALBANY, CALIFORNIA RECEIVED SEPTEMBER 3, 1949

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[11] E. Abderhalden, "Biochemisches Handlexikon," Vol. 7, J. Springer, Berlin, 1912, p. 116.

[CONTRIBUTION FROM THE VENABLE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

2,4,6-Trinitrostyrene[1]

BY RICHARD H. WILEY[2] AND LYELL C. BEHR

Polynitrostyrenes have not been previously reported in the literature. It was felt that it would be of interest to attempt preparation of such compounds, and to observe their polymerizability, in view of recent reports of the successful polymerization of *m*-nitrostyrene[3] and *p*-nitrostyrene,[4] and of the fact that 1,3,5-trinitrobenzene is an efficient inhibitor of vinyl polymerization.[5] In this paper, we wish to report a successful synthesis of 2,4,6-trinitrostyrene and some attempts to polymerize it.

A method which has been successful in the synthesis of many substituted styrenes consists in the decarboxylation of the corresponding cinnamic acid. Attempts to prepare 2,4,6-trinitrocinnamic acid for use in this reaction have been unsuccessful in these laboratories. We have, however, obtained 2,4,6-trinitrostyrene by the series of reactions diagrammed below. Mannich condensations with 2,4,6-trinitrotoluene have been previously carried out using the free amine and formaldehyde solution in the presence of alkali,[6] but our experience was that this technique produced undesirable by-products (probably due to the action of the alkali) which were difficult to remove and which tended to make the product less stable. We therefore carried out the condensation in absolute alcohol, using the amine hydrochloride and paraformaldehyde. The hydrochloride (I) thus obtained was converted, without isolation, into the free base and thence to the methiodide (II). The over-all yields in this reaction varied from 15–40% of the theory. It should be noted that the free amine of the hydrochloride (I) was unstable, particularly in alkaline medium. Use of sodium carbonate, rather than the calcium salt, to free the base from the hydrochloride often resulted in profound decomposition. The methiodide (II) is also somewhat unstable on standing. Conversion to the styrene was carried out in an aqueous methanol solution, using silver oxide. Yields up to 65% of theoretical were obtained. Decom-

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[1] Work done under a contract with the Bureau of Ordnance, Department of the Navy.

[2] Present address: University of Louisville, Louisville, Kentucky.

[3] Wiley and Smith, *J. Polymer Sci.*, **3**, 444 (1948).

[4] Strassburg, Gregg and Walling, THIS JOURNAL, **69**, 2141 (1947).

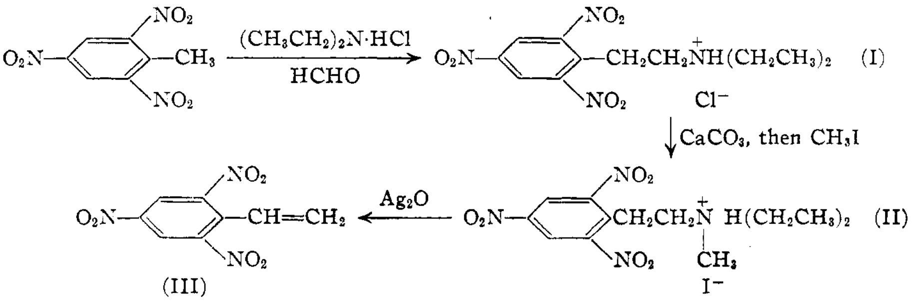
[5] Frank and Adams, *ibid.*, **68**, 908 (1946).

[6] Bruson and Butler, *ibid.*, **68**, 2348 (1946).

TABLE I

Compound, -ethane methiodide	Yield, %	M. p., °C.	Formula	Analyses, %: Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
1-Dimethylamino-2-(2,4,6-trinitrophenyl)-	18	142–144 d.	$C_{11}H_{15}IN_4O_6$	31.00	30.09	3.54	3.60	13.15	14.04
1-Diethylamino-2-(2,4-dinitrophenyl)-	24	133–135 d.	$C_{13}H_{20}IN_3O_4$					10.27	10.72
1-Dimethylamino-2-(2,4-dinitrophenyl)-	20	137–139 d.	$C_{11}H_{16}IN_3O_4$					11.02	10.83

position of the quaternary hydroxide occurred spontaneously at room temperature. The styrene was also obtained from the dimethyl analog of the methiodide.



Attempts to polymerize 2,4,6-trinitrostyrene in bulk with benzoyl peroxide, in solution with benzoyl peroxide and with boron trifluoride, and in emulsion with persulfate were unsuccessful. Copolymerizations with maleic anhydride in benzene solution, styrene in bulk and in emulsion, and isoprene in emulsion also failed. Evidence was accumulated, in fact, that the trinitrostyrene inhibits styrene polymerizations.

In an attempt to prepare 2,4-dinitrostyrene analogously, decomposition of the methiodide gave an apparently non-crystalline solid with approximately the proper composition. However, it decomposed without melting above 200° and was insoluble in the common organic solvents. It was soluble in dimethylformamide, but did not give a continuous film upon evaporation of the solvent. The Mannich condensation with *o*-nitrotoluene was unsuccessful.

Experimental Part

1-Diethylamino-2-(2,4,6-trinitrophenyl)-ethane Methiodide.—A mixture of 36.2 g. (0.16 mole) of 2,4,6-trinitrotoluene, 22.0 g. (0.20 mole) of diethylamine hydrochloride and 12.0 g. (0.40 mole) of paraformaldehyde in 200 cc. of absolute alcohol was mechanically stirred and heated at reflux for twenty-four hours. During this time, two further additions of 5 g. of paraformaldehyde were made. The flask was then cooled in ice, and 500 cc. of water with 10 cc. of concentrated hydrochloric acid added. The oil which formed was removed by extraction with ether and calcium carbonate was added cautiously to the yellow aqueous solution until an excess remained undissolved. The resulting mixture was extracted ten times with 200-cc. portions of ether, the ether extracts dried over anhydrous calcium chloride and evaporated under reduced pressure without heating. The amine was not further purified. An equal weight of methyl iodide was added, and after an induction period sometimes amounting to forty minutes, orange crystals began to form. Cooling was occasionally necessary after the reaction started. The mixture was allowed to stand for eight hours; the solid was removed by filtration and recrystallized from methanol–ethanol. The yield of orange crystals, m. p. 125–126° dec., was 22.3 g. or 30% of the theoretical.

Anal. Calcd. for $C_{13}H_{19}IN_4O_6$: C, 34.33; H, 4.22; I, 27.72; N, 12.34. Found: C, 34.08; H, 4.44; I, 27.58; N, 12.50.

Recrystallization of the methiodide was carried out as rapidly as possible and using small quantities, because of the danger of decomposition. Occasionally, there crystallized along with the methiodide long dark needles of a compound whose structure has not been determined.

Anal. Found: C, 23.00; H, 3.48; N, 8.10; I, 50.21.

2,4,6-Trinitrostyrene.—To a solution of 4.6 g. of 1-diethylamino-2-(2,4,6-trinitrophenyl)-ethane methiodide in 100 cc. of methanol, there was added 100 cc. of water. The mixture was vigorously stirred while 5.0 g. of silver oxide was added. The solution immediately became blood-red; it was stirred for one minute and then filtered with suction through a layer of infusorial earth. The filter cake was washed with water until the washings were nearly colorless. The combined filtrate and washings were allowed to stand at room temperature for twelve hours. The precipitated 2,4,6-trinitrostyrene was removed by filtration, washed with water and air dried. It was recrystallized from a benzene–petroleum ether mixture, which removed a red, tarry material. The yield amounted to 1.2 g. (49% of theoretical) of yellow flakes or rhombs, m. p. 64–65°.

Anal. Calcd. for $C_8H_5N_3O_6$: C, 40.13; H, 2.18; N, 17.57. Found: C, 40.09; H, 2.44; N, 17.55.

Data for other methiodides, which were prepared similarly, are given in Table I.

2,4-Dinitrostyrene.—Two grams of 1-diethylamino-2-(2,4-dinitrophenyl)-ethane methiodide was dissolved in a mixture of 30 cc. of methanol and 20 cc. of water. The mixture was mechanically stirred and 3 g. of silver oxide added. The solution turned blue-violet. Vigorous stirring was continued for two minutes and then the mixture was filtered with suction through infusorial earth. The filtrate was allowed to stand twelve hours (it clouded almost immediately) and was then filtered. The material thus obtained was a bluish powder, which was insoluble in the common solvents, but soluble in dimethylformamide. When this solution was allowed to evaporate on a glass plate, the resulting residue was discontinuous. The material showed no crystalline form under the microscope. The yield obtained was 0.9 g.

Anal. Calcd. for $C_8H_6N_2O_4$: C, 49.48; H, 3.12; N, 14.44. Found: C, 49.15; H, 3.68; N, 14.27.

Attempts to Polymerize Trinitrostyrene. (a) Bulk.—Mixtures of styrene and trinitrostyrene of the following percentages of trinitrostyrene were allowed to stand in an oven at 62°: 100, 50, 25, 12.5, 5, 0%. Benzoyl peroxide (0.1% by weight of monomers) was used as initiator. The styrene tube showed evidences of polymerization after three hours; the others showed no increase in viscosity in one week. Under the same conditions 0.05% trinitrostyrene was found to inhibit styrene polymerization for three days.

(b) Solution.—A mixture of 1 g. of trinitrostyrene and 15 cc. of ethyl chloride was stirred at −50°, while gaseous boron trifluoride was passed into the mixture for one and one-half hours. The ethyl chloride was allowed to evaporate 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.

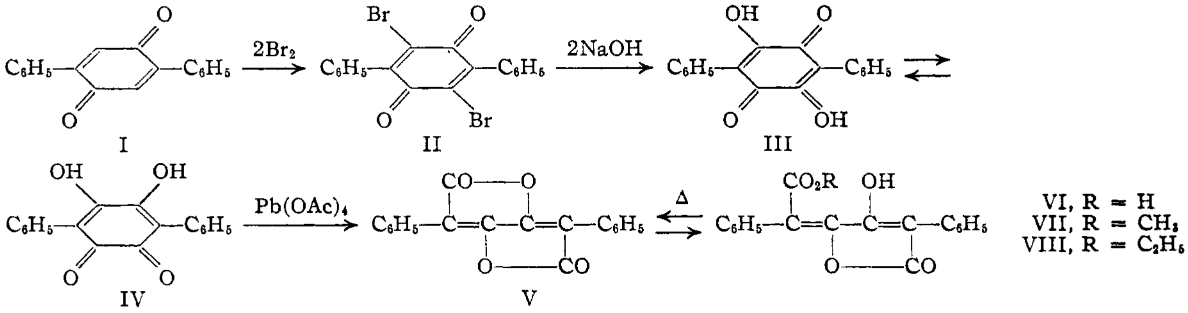
LOUISVILLE, KENTUCKY RECEIVED OCTOBER 10, 1949

[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]



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).