and dried. The yield of crude product, m.p. 320.5–323.0°, was 27.25 g. (99.2%). Recrystallization from about 200 ml. of nitrobenzene gave 25.17 g. (91.5%) of white fluffy needles, m.p. 323.5-324.5°.

Anal. Calcd. for $C_{13}H_8BrNO$: C, 56.9; H, 2.92; N, 5.11; Br, 29.1. Found: C, 57.3; H, 2.97; N, 5.14; Br, 28.8.

B. 2-Bromophenanthridone by Cyclization. 2-Acetamido-5-bromobiphenyl (I).—The acetylation of 2-aminobiphenyl was conducted in benzene solution using acetic anhydride. On recrystallization from cyclohexane the product melted at 118.5–120.5° (lit.[6] m.p. 121°). Bromination of the acetyl derivative in acetic acid followed by recrystallization of the product from cyclohexane gave I, m.p. 128–129° (lit.[6] 130°).

2-Bromophenanthridone (III).—A mixture of 30 g. of I, 200 ml. of ethanol and 25 ml. of 48% hydrobromic acid was refluxed for 1 hour, then 100 ml. of solvent was allowed to distill. The residue was diluted with water, made basic with ammonium hydroxide and extracted well with ether. The ethereal extracts were dried ($MgSO_4$) and stripped of solvent, giving 25.1 g. of 2-amino-5-bromobiphenyl (IV), a pale pinkish-tan oil which crystallized readily on seeding (a seed was obtained by triturating a drop of oil with ligroin while cooling in Dry Ice). It was used directly in the next step.

A solution of 24.8 g. (0.10 mole) of 2-amino-5-bromobiphenyl (IV) in 100 ml. of toluene was added slowly to a solution of 50 g. (0.50 mole) of phosgene in 150 ml. of toluene, whereupon a white precipitate formed. The mixture was refluxed 1.5 hours and the clear pinkish-tan solution was stripped of solvent giving a quantitative yield of crude 5-bromo-2-biphenylyl isocyanate (V). It was used in the next step without distillation.

The isocyanate V was dissolved in 100 ml. of chlorobenzene and this solution was added dropwise with stirring to a suspension of 20.0 g. (0.15 mole) of powdered anhydrous aluminum chloride in 100 ml. of chlorobenzene. The mixture was warmed gently, then cooled and filtered. The white filter cake was washed with benzene and dried, then decomposed with cold dilute hydrochloric acid and filtered. The product was washed well with hot water, then methanol, and dried. The yield of crude product was 21.1 g. (77% from I). A sample recrystallized from nitrobenzene formed fluffy white needles, m.p. 323.0–324.0°. No noticeable depression in the melting point occurred with a mixture of this material and the product obtained by the bromination of phenanthridone.

Anal. Calcd. for $C_{13}H_8BrNO$: C, 56.9; H, 2.92; N, 5.11; Br, 29.1. Found: C, 57.0; H, 2.82; N, 5.13; Br, 29.1.

(6) H. A. Scarborough and W. A. Waters, *J. Chem. Soc.*, 89 (1927).

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A New Method of Purifying α,β,γ,δ-Tetraphenylporphine

BY J. H. PRIESTHOFF AND C. V. BANKS

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α,β,γ,δ-Tetraphenylporphine is prepared by the reaction of pyrrole with benzaldehyde in a sealed tube. Aronoff and Calvin[1] prepared the free-base porphine by this method. Ball, Dorough and Calvin[2] found the yield could be increased to about 10% if the zinc complex salt was prepared. The zinc was subsequently removed by the action of 6 *N* hydrochloric acid.

Although it was reported that the reaction product could be filtered and purple, crystalline tetraphenylporphine obtained, this was found not to be the case in any one of the twenty reactions carried out in this Laboratory. The product of the reaction was a black, tarry mass and could not be filtered. Although the tarry by-product could be extracted with acetone and crystalline zinc tetraphenylporphine obtained, about 5 g. of the complex were lost per liter of acetone used. Therefore, a new method was developed in which the zinc complex was decomposed with acid and the free-base-tar solution chromatographed on activated alumina (Aluminum Company of America, Grade F-20). The free-base eluate was concentrated and chromatographed on Magnesol (Westvaco Chemicals, S. Charleston, West Virginia; dry cleaning grade), yielding pure tetraphenylporphine.

Experimental

Zinc tetraphenylporphine was prepared by the method of Ball, Dorough and Calvin,[2] involving reaction of 5 ml. of pyrrole, 10 ml. of benzaldehyde, 10 ml. of pyridine and 5 g. of zinc acetate in a special Carius tube or bomb of about 40-ml. capacity (2.4 × 10 cm.). Nitrogen was bubbled through the reactants for one-half hour before the bomb was sealed. The bomb size was later increased to about 400-ml. capacity (5.0 × 20 cm.) with appropriate increase in the quantity of reactants.

The bomb was placed in a pipe jacket which was then sealed with caps and placed in an oven at 200° for 48 hours. After cooling to room temperature, the bomb was removed from the pipe jacket, opened, and the contents washed into a beaker with sufficient chloroform to ensure complete dissolution. An equal volume of 6 *N* hydrochloric acid was added to the beaker and the mixture stirred vigorously for two hours. The acidic solution was then neutralized with ammonium hydroxide.

The entire contents of the beaker were poured into a special U-tube, Fig. 1. The stirrer (A) forced the water through the chloroform solution and the wash water drained off at (C). The flow of water and the speed of stirring were carefully regulated to obtain optimum washing. If the stirring is too fast, the chloroform solution will be carried through the overflow with the water; if it is too slow, the method is inefficient. The washing time for a run made in a 400-ml. bomb was from 4 to 6 hours.

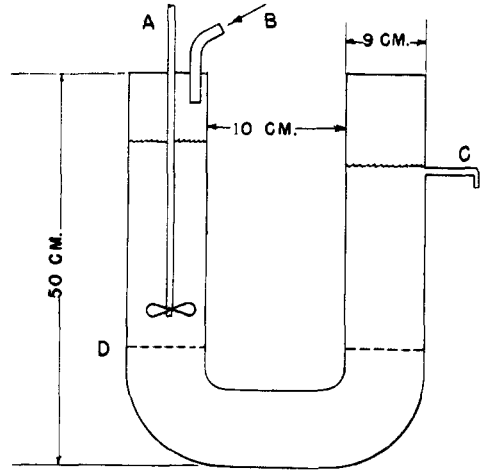

Fig. 1.—Apparatus for washing chloroform solution of TPP: A, stirrer; B, water inlet; C, water outlet; D, level of chloroform.

The chloroform solution was separated from the water and chromatographed on a column (8 × 63 cm.) of activated alumina. The column was packed by tapping the sides of the column with the hand while the alumina was being introduced. Throughout the developing and eluting procedures the flow rates were maintained at 40 to 50 ml. per

(1) S. Aronoff and M. Calvin, *J. Org. Chem.*, **8**, 205 (1943).

(2) R. H. Ball, G. D. Dorough and M. Calvin. THIS JOURNAL, **68**, 2278 (1946).

minute. Fresh chloroform was used to develop the bands, of which there were three. The free-base porphine formed a reddish-purple band which was washed through the column and collected. The tarry by-products remained near the top of the column as a brown-black band. Any zinc complex which was not decomposed by the acid formed a purple band intermediate between the porphine and the tarry band. The zinc complex could be recovered, by eluting with acetone, and subsequently reprocessed. The free-base porphine obtained from this procedure was about 95% pure.

The chloroform solution of the porphine was concentrated by evaporation and chromatographed on Magnesol. The Magnesol column (a 13 × 15 cm. sintered-glass filter funnel) was packed using suction and the column developed under the same conditions with fresh chloroform. Four bands were obtained on this column, from top to bottom they were: tan-green, light green, brown and dark green. The dark green band was tetraphenylporphine, the tan-green and the light green bands contained considerable tetraphenylchlorin and some tetraphenylporphine. The brown band was not characterized.

The column was permitted to go "dry" under suction. It was then inverted on a glass plate and shaken gently to remove the packing in one piece. The bands were separated mechanically and dried. After drying, the individual bands were packed into appropriately sized columns and eluted. The dark green porphine band was treated first with acetone and then with chloroform. The acetone caused the green Magnesol to turn reddish purple. The chloroform concentrated the porphine and washed it through the column. It was necessary to add alternately acetone and then chloroform until the porphine was completely eluted.

The eluted chloroform solution of the porphine was evaporated to dryness and spectrophotometrically pure tetraphenylporphine was obtained.[3]

Using the above procedure about 80 g. (18% yield on the basis of pyrrole) of pure tetraphenylporphine was prepared. This procedure may also be followed using talc as an adsorbent instead of Magnesol. However, the flow of solvent through talc is considerably slower than through Magnesol. An even greater advantage of Magnesol is that approximately five times more porphine could be chromatographed on it than on talc. About 5 g. of crude porphine could be chromatographed on the 13 × 15 cm. column of Magnesol.

CONTRIBUTION NO. 241 FROM THE
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IOWA STATE COLLEGE, AMES, IOWA

(3) The absorption spectra were compared with an authentic sample kindly supplied by G. D. Dorough, Washington University, St. Louis, Missouri.

(4) Work was performed at the Ames Laboratory of the Atomic Energy Commission.

Reduction of δ-Lactones by Catalytic Hydrogen

BY EVANS B. REID AND JOEL R. SIEGEL

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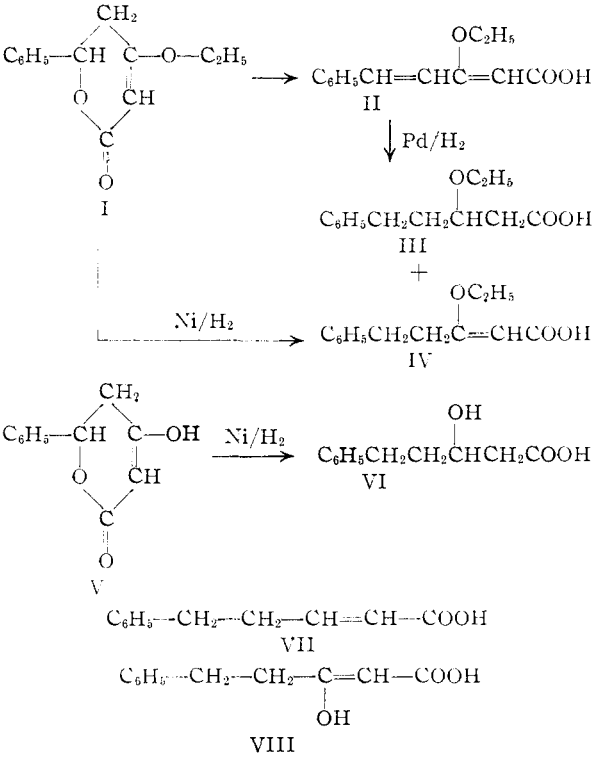
In a recent study of the chemical properties of 4-ethoxy-6-phenyl-5,6-dihydro-2-pyrone[1] (I) the lactone ring of the latter was opened by treatment with base and the resultant 3-ethoxy-5-phenyl-2,4-pentadienoic acid (II) was subjected to catalytic hydrogenation using 5% palladium black supported on barium sulfate. This led to three products, *viz.*, an unidentified oil, considered possibly to be 2-ethoxy-4-phenylbutane, the expected 3-ethoxy-5-phenylvaleric acid (III) and a different compound, m.p. 109–112°, that gave analytical figures approximating those calculated for 3-hydroxy-5-phenylvaleric acid (VI). Although this product was not obtained in a pure state, it and the ethereal degradation product were considered entirely likely in view of certain hydrogenolyses observed by other workers.[2]

(1) E. B. Reid and W. R. Ruby, THIS JOURNAL, **73**, 1054 (1951).

(2) J. M. Sprague and H. Adkins, *ibid.*, **56**, 2669 (1934).

It is the purpose of the present paper to show that this conclusion, in so far as it concerns the impure hydrogenation product, m.p. 109–112°, was in error, and also to place on record our observations regarding the hydrogenolysis of 4-hydroxy-6-phenyl-5,6-dihydro-2-pyrone (V) and of the ethyl enol ether of the latter compound I.



Upon further purification the impure product was freed of a gummy contaminant, and then had m.p. 114–115.5°. By direct comparison with 3-hydroxy-5-phenylvaleric acid (VI) (*vide infra*), dissimilarity was established.

In separate experiments it was demonstrated that reduction of the ethoxypyrone I by means of hydrogen and Raney nickel, afforded the same material exclusively, identity being established by means of mixed melting point determinations, and by the fact that the infrared absorption spectra of both products, either mulled in mineral oil or taken in chloroform solution, were virtually superposable.

Analysis of the material showed it to be a dihydro derivative of 3-ethoxy-6-phenyl-1,3-pentadienoic acid (II) and the weak acidity of the compound (solubility in carbonate, insolubility in bicarbonate solutions) was confirmed by the presence, in the infrared absorption spectrum, of a strong band at 5.92 μ (carboxyl absorption). Three structures thus became possible for the new acid, two of them being the olefinic isomers of 3-ethoxy-6-phenyl-2-pentenoic acid (IV). That the substance is in fact IV, and that it cannot have the double bond elsewhere than in the 2-position, is shown by the following evidence.

In the infrared the ethylenic absorption band shows strongly at 6.18 μ, which corresponds exactly with the position of the ethylenic absorption of the ethoxy-pyrone I, in which the ethoxylated carbon