

form 1.8 g. of solid was obtained, m.p. 260–265°. White crystals were obtained upon recrystallization from absolute ethanol, m.p. 292–294°.

*Anal.* Calcd. for  $C_4H_4N_3OCl$ : C, 33.00; H, 2.77; N, 28.87. Found: C, 33.55; H, 3.21; N, 28.25.

*4-Aminoimidazo[4,5-d]pyridazine* (XXIV). 4-Methylmercaptoimidazo[4,5-d]pyridazine, X (1.3 g., 0.008 mole), was placed in a 500 ml. stainless steel bomb with 150 ml. of ethanol containing approximately 9 g. of ammonia. The same procedure was followed as in the preparation of compound VIII. The yield was 1.0 g. (87%) of crude product. On a

Kofler micro hot stage, water was given off at approximately 215°. The crude product was recrystallized twice from ethanol. A tan solid was obtained with a decomposition point of approximately 315°.

*Anal.* Calcd. for  $C_8H_7N_3O$ : N, 45.73. Found: N, 45.53.

Infrared spectra were determined on the following compounds: V, VI, VII, VIII (anhydrous), IX, X, XI, XII, XIII, XV, XVI, and XXIV.

ALBUQUERQUE, N. M.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

## Dibenzopentalene<sup>1</sup>

CHEN C. CHUEN<sup>2</sup> AND STUART W. FENTON

Received April 7, 1958

A new synthesis of 1,2:5,6-dibenzopentalene is described.

In 1952 Blood and Linstead<sup>3</sup> described a synthesis of the hydrocarbon 1,2:5,6-dibenzopentalene (I). This red compound is the simplest relative of pentalene which has been prepared. Bicyclo-[3.3.0]octa-1,4-diene-3,6-dione, which might be considered to be the ketonic form of a pentalenediol, has been prepared<sup>4</sup> but could not be induced to enolize. The present work describes a new synthesis of I and some of its reactions.

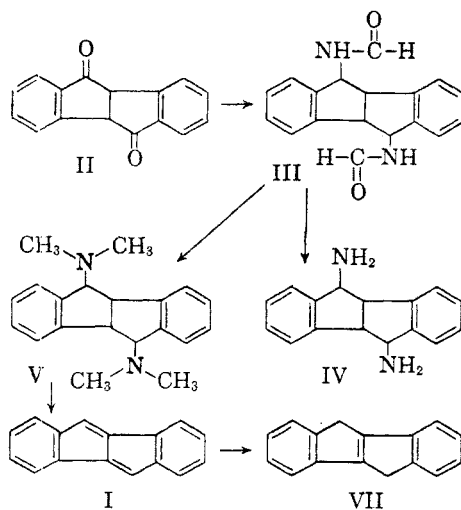
The key intermediate in the present sequence was 9,12-diphensuccinadione (II) which was prepared in 50–70% yield by cyclization of *meso*-diphenylsuccinic acid with hot, concentrated sulfuric acid. Treatment of II with formamide and formic acid

yielded the bisformyl derivative (III) in 69% yield. Acid hydrolysis of this amide gave the base, 9,12-diaminodiphensuccindane (IV) which was characterized as the dipicrate. This diamine was readily methylated with formic acid and formaldehyde to give the ditertiary amine (V). V was extremely hygroscopic and formed a dipicrate which was obtained as a dihydrate. The water of crystallization was removed by prolonged heating under reduced pressure. The ditertiary amine (V) was also obtained directly from III by treatment with a solution of formic acid in formalin. Treatment of V with methyl iodide yielded the methiodide (VI).

When an aqueous solution of VI was basified at room temperature, two molecular equivalents of trimethylamine were eliminated giving the blood red dibenzopentalene (I) in 30% yield. The usual procedure for the Hofmann elimination reaction involving treatment of the methiodide with silver oxide followed by thermal decomposition of the quaternary hydroxide proved to be rather ineffective in this case as the product tended to coat the insoluble oxide and prevent further reaction.

The identity of I was established by mixture melting point, comparison of infrared and ultraviolet spectra, and comparison of x-ray diffraction patterns of this substance with an authentic sample prepared according to the method of Blood and Linstead.<sup>3</sup> Reduction of I with zinc and acetic acid gave 10-diphensuccindene (VII) in 77% yield. The mixture melting point and infrared spectrum of VII were identical with that of an authentic sample.<sup>5</sup>

Dibenzopentalene polymerized fairly readily. When I was heated at the reflux temperature with glacial acetic acid, an amorphous yellow product was obtained which was insoluble in toluene, benzene, chloroform, ether, or alcohol. A similar prod-



(1) Supported in part by a grant from the Rohm & Haas Co., Philadelphia.

(2) Abstracted from the M.S. Thesis of Miss Chen C. Chuen, University of Minnesota, January 1954.

(3) C. T. Blood and R. P. Linstead, *J. Chem. Soc.*, 2263 (1952).

(4) C. T. Blood and R. P. Linstead, *J. Chem. Soc.*, 2255 (1952).

(5) S. Wawzonek, *J. Am. Chem. Soc.*, 62, 745 (1940).

uct was obtained when attempts were made to nitrate I in glacial acetic acid.

#### EXPERIMENTAL<sup>5</sup>

*9,12-Diphensuccinadione* (II). A modification of Roser's<sup>7</sup> procedure was employed which involved the rapid addition of 20 g. of *meso*- $\alpha,\beta$ -diphenylsuccinic acid<sup>8</sup> to 50 ml. of concentrated sulfuric acid at 150°. When solution was complete, the reaction mixture was poured onto a stirred mixture of ice and water. The solid product was washed with water, treated with 100 ml. of 10% aqueous sodium carbonate, washed with water, and then air dried. After recrystallization from 95% ethanol, 8.55 g. (50.8%) of II was obtained, m.p. 211–213°.

*The Bisformyl derivative of 9,12-diaminodiphensuccindane* (III). A solution containing 10 g. (0.043 mole) of II in 15 ml. of 90% formic acid and 100 ml. of formamide was heated at the reflux temperature for 24 hr. Dilution with water gave a crude orange product. Recrystallization from 95% ethanol yielded 8.64 g. (69.1%) of III, m.p. 265–267°.

*Anal.* Calcd. for  $C_{13}H_{16}N_2O_2$ : C, 73.95; H, 5.52. Found: C, 73.54; H, 5.86.

*9,12-Diaminodiphensuccindane* (IV). A mixture of 5.0 g. (0.017 mole) of II and 50 ml. of 5% hydrochloric acid was heated under reflux for 24 hr. After filtration and basification with 40 ml. 10% aqueous sodium hydroxide, the product was extracted with chloroform. On evaporation of the solvent, 3.74 g. (95%) of IV was obtained which melted at 48–57° after one recrystallization from chloroform-ether. A sample of IV was converted to a yellow-orange picrate by treatment of an ethanolic solution of the base with picric acid. After recrystallization from absolute alcohol, it melted at 242–243°.

*Anal.* Calcd. for  $C_{25}H_{20}O_{14}N_8$ : C, 48.51; H, 3.19; N, 16.15. Found: C, 48.07; H, 3.23; N, 15.86.

*9,12-Bisdimethylaminodiphensuccindane* (V). *Method A.* A solution of 2.90 g. (0.0125 mole) of IV in a mixture of 40 ml. of 88% formic acid and 16.5 g. of 40% formalin was

(6) Melting points were determined with a Fisher-Johns melting point apparatus and are uncorrected.

(7) W. Roser, *Ann.*, **247**, 153 (1888).

(8) A. Lapworth and J. A. McRae, *J. Chem. Soc.*, **83**, 995 (1903).

heated at the reflux temperature for 12 hr. After the excess formic acid and formaldehyde had been removed by distillation at reduced pressure, the residue was neutralized with 5% aqueous sodium hydroxide. An oil separated which was extracted with ether. Removal of the ether by distillation gave 2.90 g. (80.5%) of crude product, m.p. 80–83°. After several recrystallizations from 1:1 aqueous ethanol, 1.5 g. (41.7%) of the colorless base was obtained, m.p. 82–83°.

*Anal.* Calcd. for  $C_{20}H_{24}N_2$ : C, 82.14; H, 8.27; N, 9.58. Found: C, 82.05; H, 8.46; N, 9.95.

*Method B.* The bis-formyl derivative was converted directly to IV by heating a mixture containing 3.60 g. of III (0.0125 mole), 40 ml. of 88% formic acid, and 16.5 g. of 40% formalin at the reflux temperature for 12 hr. The product was isolated as described under method A. After recrystallization 0.98 g. (27.2%) of IV was obtained, m.p. 83–84.5°.

*Dimethiodide of 9,12-Bisdimethylaminodiphensuccindane* (VI). A solution of 4.5 g. (0.0125 mole) of IV in 100 ml. of methanol was heated under reflux with 8.7 g. (0.061 mole) of methyl iodide for 24 hr. The pale yellow salt which precipitated during this period was recrystallized from 2:1 aqueous ethanol to yield 6.1 g. (69.3%) of the dihydrate of VI, m.p. 270° (decomp.).

*Anal.* Calcd. for  $C_{22}H_{30}N_2I_2 \cdot 2H_2O$ : C, 43.13; H, 5.60; N, 4.58. Found: C, 43.39; H, 5.87; N, 4.56.

*Dibenzopentalene* (I). To a mixture of 700 ml. of benzene and 50 ml. of saturated aqueous sodium hydroxide, 4.0 g. (0.007 mole) of VI dissolved in 30 ml. of water was added with stirring. An atmosphere of nitrogen was maintained in the flask. The hydrocarbon layer became blood red. After 2 hr. the benzene layer was separated and dried. On removal of the bulk of the benzene, red crystals of I separated. The product after recrystallization from 95% ethanol weighed 0.4 g. (28.2%). The compound softened at 270° and decomposed at 285°. Identity of this material was established by comparison of x-ray powder patterns, ultraviolet and infrared spectra with those of a sample prepared by the method of Blood and Linstead.<sup>3</sup>

When 0.09 g. (0.00044 mole) of VI, 20 ml. boiling acetic acid was treated with zinc dust, a colorless solution was obtained from which 0.07 g. (77%) of 10-diphensuccindene, m.p. 204–208° was isolated. A mixture of this material with an authentic sample of 10-diphensuccindene<sup>6</sup> melted at 204–208°.

MINNEAPOLIS, MINN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

## Absorption Spectra of Tetracyclones. V<sup>1</sup>

VINCENT F. D'AGOSTINO,<sup>2</sup> MICHAEL J. DUNN,<sup>2</sup> ARTHUR E. EHRLICH,<sup>2</sup> AND ERNEST I. BECKER<sup>3</sup>

Received April 11, 1958

Four *p*-phenoxy-, four *p*-phenylthio, and four *o*-fluoro-substituted tetracyclones (tetraphenylcyclopentadienones) have been prepared in order to study their electronic spectra. When referred to the spectrum of the parent compound, the maxima at 342  $m\mu$  and at 512  $m\mu$  shift in accordance with the previous correlations: a substituent in the 3- and/or 4-phenyl ring affects principally the band at 342  $m\mu$  while a substituent in the 2- and/or 5-phenyl ring affects principally the band at 512  $m\mu$ . Electron-releasing phenoxy and phenylthio groups shifted their bands bathochromically.

Substitution in the ortho position by fluorine affected the substituted path most, but in this case the shift was to shorter wave lengths with lower intensity. The shift was accompanied by an intensification of the band associated with the unsubstituted path.

The purpose of this investigation was to test the previously published interpretation of the absorp-

tion spectrum of tetracyclone (tetraphenylcyclopentadienone) using the following groups: phenoxy and phenylthio in the para positions and fluoro in the ortho positions. First the syntheses and then the spectra are discussed.

*Synthesis of tetracyclones.* Most of the desired

(1) Part IV: *J. Am. Chem. Soc.*, **77**, 60 (1955).

(2) From the M.S. theses of V. F. D. (1957), M. J. D. (1955), and A. E. E. (1955).

(3) To whom inquiries should be directed.