

so that discrepancies at the higher temperatures presumably have their origin in one or both of these components of C_p . We conclude, then, that one or more of the medium-valued frequencies, possibly ν 17,¹¹ have been assigned values somewhat too low, and/or that the constant b in the expansion formula¹² has been set somewhat too high.

Acknowledgment.—The authors wish to thank Dr. R. C. Lord, Jr., of the Department of Chemistry for many helpful discussions.

(11) See ref. 5, p. 68.

(12) The constant a which gives the lattice portion of the expansion term, presumably is essentially correct because of the satisfactory agreement below 170°K.

Summary

1. The heat capacity of benzene- d_6 has been measured throughout the temperature range 100–320°K. with an accuracy of about 2%.

2. A comparison of the experimentally observed values of C_p with those calculated by a semi-theoretical method indicates that the low frequencies in the benzene- d_6 molecule have been correctly assigned.

3. The possibility that one or more of the medium-valued frequencies have been assigned values which are too low is presented.

BALTIMORE, MD.

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[CONTRIBUTION FROM THE KNIGHT CHEMICAL LABORATORY, UNIVERSITY OF AKRON]

The Halogenation of *m*-Diphenylbenzene. II. The Monoiodo Derivative¹

BY WALTER A. COOK AND KATHRYN HARTKOFF COOK

In a previous communication² the authors reported the preparation and proof of structure of the monochloro and monobromo derivatives of *m*-diphenylbenzene. The present communication describes the preparation of the analogous monoiodo derivative from the corresponding amine. The latter compound was prepared by ammonolysis of the monochloro and monobromo derivatives.

Experimental

Ammonolysis Experiment.—The ammonolysis studies were carried out in a steel bomb of 500-ml. capacity, electrically heated and equipped with a bimetallic thermostat, safety diaphragm valve, pressure gage and Hoke pressure regulator valve. The details of a typical run are given as follows: 12 g. of 4-chloro-*m*-diphenylbenzene, 340 ml. of 28% aqueous ammonia, 2 g. of cuprous chloride, 1.26 g. of calcium oxide and 2 g. of copper tinsel were heated with continuous agitation for thirty hours at 190° and 800–850 pounds pressure. After cooling the bomb contents were transferred to a 600-ml. beaker, the aqueous ammonia layer decanted and the reaction residue washed with water. The reaction product was dissolved in ether, filtered and saturated with dry hydrogen chloride gas. The precipitated and dried crude 4-amino-*m*-diphenylbenzene hydrochloride weighed 6 g. The ether layer, after subsequent washing with water and evaporation, yielded 2.5 g. of unreacted monochloro derivative. The combined yields of crude amine hydrochloride from several runs was purified by moistening with dil. hydrochloric acid and allowed to stand for several hours in contact with glacial acetic acid. After filtration it was washed with diluted hydrochloric acid and water. It was then converted into the free base with 6 *N* potassium hydroxide solution containing

a trace of ammonium hydroxide and filtered. Recrystallization from 95% ethanol yielded pure 4-amino-*m*-diphenylbenzene, m. p. 74°. Similarly a specimen of the amine prepared by the Wardner and Lowy³ method, and purified as described above, melted at 74°, although these authors reported a value of 64°. Mixed melting points of these products as well as a specimen of the amine prepared by Dr. Russell Jenkins⁴ of Monsanto Chemical Co. agree with our value of 74°. The structure of the amine was recently reported by France, Heilbron and Hey,⁵ although they were unable to solidify their specimen. A phenylthiourea derivative of 4-amino-*m*-diphenylbenzene was prepared in the usual way; m. p. 135°.

Anal. Calcd. for $C_{20}H_{20}N_2S$: N, 7.36; S, 8.43. Found: N, 7.51; S, 8.60.

4-Iodo-*m*-diphenylbenzene.—From 28 g. of the corresponding amine hydrochloride, 18.6 g. of a pale yellow oil b. p. (1 mm.) 235–240° (cor.) was obtained by diazotization and treatment with potassium iodide in the usual manner. The oil solidified after standing for several days and on crystallization from absolute ethanol melted at 67°.

Anal. Calcd. for $C_{18}H_{13}I$: I, 35.65. Found: I, 35.41.

Attempts to oxidize this compound to a substituted phenylbenzoic acid resulted in such small yield of product that it could not be isolated.

The authors acknowledge the helpful assistance of Professor D. E. Anderson in the design and construction of the bomb in which the ammonolysis studies were undertaken.

Summary

1. The preparation and properties of 4-iodo-*m*-diphenylbenzene are described.

(3) Wardner and Lowy, *ibid.*, **54**, 2510 (1932).

(4) Private communication to the authors.

(5) France, Heilbron and Hey, *J. Chem. Soc.*, 1283–1292 (1939).

(1) Presented before the Division of Organic Chemistry at the Memphis meeting of the American Chemical Society, in April, 1942.

(2) Cook and Cook, *This Journal*, **55**, 1212 (1933).

2. Further proof of the structure of Wardner and Lowy's mononitro and monoamino derivatives is presented.

3. A corrected m. p. of 74° for 4-amino-*m*-di-

phenylbenzene is reported. For characterization purposes, the phenylthiourea derivative is also described.

AKRON, OHIO

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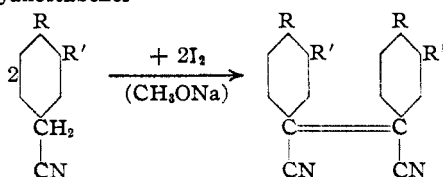
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

Symmetrical Cyanostilbenes

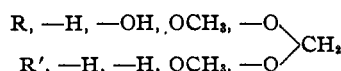
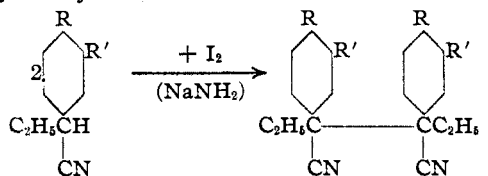
BY JOSEPH B. NIEDERL AND ALBERT ZIERING¹

In a previous communication² the preparation of unsymmetrical cyanostilbenes was presented. The purpose of this communication is to give report on the preparation of symmetrical and variously ring and side-chain substituted cyanostilbenes and dihydrostilbenes related in structure to diethylstilbestrol. The ring substituents included the following: nitro, amino, hydroxy, acetoxy, methoxy, dimethoxy and methylenedioxy groups, while the side-chain substituents comprised either hydrogen or ethyl groups. The method of preparation of these compounds consisted in self-condensation of the respective benzyl nitriles by means of iodine in the presence of sodium methoxide or sodium amide as follows³

Dicyanostilbenes



Dicyanodihydrostilbenes:



Experimental

α,α' -Dicyanostilbenes.—One-tenth mole of the respective benzyl nitrile (*p*-methoxy-3,4-methylenedioxy-3,4-dimethoxy) was dissolved in 65 cc. of absolute methyl alcohol. To this solution 25.4 g. of iodine, dissolved in 130 cc.

of absolute ether, was added, followed by the dropwise addition of a solution of 4.6 g. of sodium in 70 cc. of absolute methyl alcohol.³ The precipitated solid was filtered and recrystallized from ethyl acetate. All dicyanostilbenes were colored and gave positive unsaturation tests with potassium permanganate dissolved in acetone; yields, 35% (approx.). The 4,4'-dihydroxy derivative was prepared by diazotizing the corresponding amine,⁴ acetylating the resulting solid and then hydrolyzing the acetate with alkali to the phenolic derivative.

α,α' -Dicyanodihydrostilbenes.—One-tenth mole of phenylethylacetonitrile was added dropwise to a suspension of sodamide (0.1 mole) in 150 cc. of anhydrous ether. The mixture was refluxed until the evolution of ammonia had ceased. To this was then added slowly 0.05 mole of iodine in 100 cc. of absolute ether.³ The precipitated solid was filtered, washed with water and recrystallized from ethanol. All dicyanodihydrostilbenes were colorless and the unsaturation tests with potassium permanganate in acetone were negative; yields, 25% (approx.).

Piperonylethylacetonitrile was treated in the same manner and the final reaction product was recrystallized from dioxane; yield, 25%.

The piperonylethylacetonitrile was prepared by first treating 3,4-methylenedioxybenzyl nitrile with diethyl carbonate in the presence of sodium at 60° in benzene to yield the ethyl piperonylcynoacetate (b. p. 161° at 3 mm.). This ester was then ethylated in the usual manner with ethyl iodide and sodium ethoxide in absolute ethanol to give the ethyl piperonylethylcynoacetate (m. p. 72°) which was then hydrolyzed with alkali in the cold to the piperonylethylcynoacetic acid (m. p. 110°). The acid was decarboxylated by heating to 180°. The resulting piperonylethylacetonitrile boiled at 174° at 15 mm.

The corresponding phenolic derivative was prepared by nitrating phenylethylacetonitrile with fuming nitric acid at 0° to yield the *p*-nitrophenylethylacetonitrile (b. p. 165° at 3 mm.). The nitro compound was converted to the dihydrostilbene by means of iodine and sodium methoxide.⁵ The resulting dihydrostilbene was then reduced to the amine, which was then diazotized and finally hydrolyzed to the phenolic derivative, which was recrystallized from benzene containing a little alcohol.

Physiological Tests.—All compounds were subjected to the Fluhmann^{5,6} test for estrogenic activity. Most re-

(1) Abstracted from Part II of the thesis presented by A. Ziering to the Graduate School of New York University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1942.

(2) J. B. Niederl and A. Ziering, *THIS JOURNAL*, **64**, 885 (1942).

(3) Knoevenagel and Chalanay, *Ber.*, **25**, 285 (1892).

(4) Heller, *Ann.*, **332**, 280 (1904).

(5) Fluhmann, *Endocrinology*, **18**, 705 (1934).

(6) Deckert, Mulhall and Swiney, *J. Lab. Clin. Med.*, **23**, 85 (1937).