

with those of two bromoperfluorobenzenes obtained as by-products in the pyrolysis of tribromofluoromethane.

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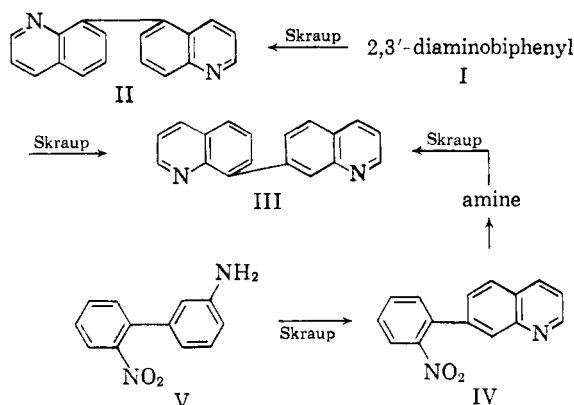
The Behavior of 2,3'- and 3,3'-Diaminobiphenyl in the Skraup Reaction. Synthesis of 5,8'-, 7,8'-, and 5,7'-Biquinolines¹

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In a Skraup reaction 2,3'-diaminobiphenyl should be capable of yielding two biquinolines (5,8' and 7,8'), both hitherto unreported. These have now been isolated. The proof of their identity is as follows:



3-Amino-2'-nitrobiphenyl (V), subjected to a Skraup reaction, yielded a single product, which has been shown to be 7-(o-nitrophenyl)quinoline (IV), since on reduction followed by deamination it yielded the known 7-phenylquinoline. Reduction of IV followed by a Skraup reaction yielded III, which was identical with one of the biquinolines obtained from I. Since I could only yield two possible biquinolines, the other must have been II.

From 3,3'-diaminobiphenyl a Skraup reaction might be expected to yield three biquinolines (5,5'; 7,7'; and 5,7'). Of these the first two are known.² In this laboratory two of these have been

isolated —7,7', identified by mixed melting point with an authentic specimen, and one which melts much lower than either of the symmetrical ones, and must be the 5,7' isomer.

Experimental

2,3'-Dinitrobiphenyl.—The following procedure was found preferable to that previously described.³ To 350 ml. of concentrated nitric acid there was added, with stirring, 15 g. of 3-nitrobiphenyl, and the temperature raised to 65°. At this point solution occurred and heating was discontinued. After cooling, the precipitated solid was removed by filtration, washed with water, dried at 100°, and digested with 500 ml. of absolute methanol. The insoluble portion (3,4'-dinitrobiphenyl) was removed and the solution evaporated, yielding 5 g. of 2,3'-dinitrobiphenyl, m.p. 113–115°.

2,3'-Diaminobiphenyl.—This was prepared by the catalytic (10% palladium-on-carbon) reduction of the dinitro compound in ethanol. The product obtained after removal of the solvent was used in the following reaction without further purification.

Skraup Reaction on 2,3'-Diaminobiphenyl.—A mixture of 15.8 g. of 2,3'-diaminobiphenyl (unpurified after the catalytic reduction of 2,3'-dinitrobiphenyl), 48 ml. of concentrated sulfuric acid, 16 ml. of water, 36 g. of *m*-nitrobenzenesulfonic acid, and 60 g. of glycerol was heated with stirring under reflux at 130–140° for 2 hr. It was then poured on ice and made alkaline with sodium hydroxide solution. The resulting precipitate was removed by filtration, dried, and extracted, as well as the filtrate, with benzene. After removal of the tarry residue, the benzene was evaporated and the resulting oil eluted over alumina first with benzene-petroleum ether, then with benzene, and finally with chloroform. From the first elutions there was obtained, after crystallization from benzene-petroleum ether, 3.5 g. (15.9%) of a substance melting at 107–108°.

Anal. Calcd. for $C_{18}H_{12}N_2$: C, 84.35; H, 4.72. Found: C, 84.28; H, 4.85.

The final elutions yielded 0.9 g. (4.1%) of a substance melting at 190–191° after crystallization from benzene-petroleum ether (90–100°). The pure biquinoline melts at 193–194°.

Anal. Calcd. for $C_{18}H_{12}N_2$: C, 84.35; H, 4.72. Found: C, 84.29; H, 4.75.

3-Amino-2'-nitrobiphenyl.—The method of Arcos and Miller was used.⁴

7-(o-Nitrophenyl)quinoline.—In a three-necked flask equipped with a mechanical stirrer, reflux condenser, and dropping funnel were placed 22 g. of 3-amino-2'-nitrobiphenyl, 14.2 g. of arsenic acid, 30 g. of concentrated sulfuric acid, and 7 ml. of water. To the stirred mixture was added dropwise 37 g. of glycerol at a temperature of 100°. The temperature of the surrounding oil bath was then raised until the inside temperature reached 130–140° and was maintained there for 3 hr. The contents of the flask were then poured on ice and neutralized with aqueous sodium hydroxide. The resulting precipitate was dried and extracted with boiling benzene, the benzene removed, and the residue extracted with petroleum ether (b.p. 60–70°). Evaporation and crystallization from the same solvent yielded 3 g. (12.8%) of product, m.p. 77–78°.

Anal. Calcd. for $C_{15}H_{10}N_2O_2$: C, 71.99; H, 4.03. Found: C, 72.08; H, 3.99.

7-(o-Aminophenyl)quinoline.—To a solution of 45 g. of stannous chloride dihydrate in 200 ml. of concentrated hydrochloric acid maintained at 10° was added 10 g. of 7-(o-

(1) This work was supported by a grant from the Committee on Research and Publications of Temple University.

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(3) W. Blakey and H. A. Scarborough, *J. Chem. Soc.*, 3000 (1927).

(4) J. C. Arcos and J. A. Miller, *J. Org. Chem.*, **21**, 651 (1956).

nitrophenyl)quinoline. The reactants were stirred for 1 hr. at 10° and then for 3 hr. while the reaction mixture came to room temperature. After dissolving the tin complex in hot water, the solution was made alkaline with aqueous sodium hydroxide, extracted with benzene, and the latter evaporated. The residue was crystallized from water-acetone. The yield of pure amine was 5.3 g. (60%), m.p. 125–127°.

Anal. Calcd. for $C_{15}H_{12}N_2$: C, 81.79; H, 5.49. Found: C, 81.69; H, 5.60.

On deamination with sodium nitrite and dilute sulfuric acid in ethanol, 7-phenylquinoline was obtained, m.p. 58–59°, and unchanged when mixed with an authentic specimen.⁵

7,8'-Biquinoline.—To a mixture of 8.8 g. of 7-(*o*-aminophenyl)quinoline, 11.4 g. of arsenic acid, and 25 ml. of 85% phosphoric acid in a three-necked flask equipped with a mechanical stirrer and reflux condenser was added 3.4 g. of freshly distilled acrolein at a temperature of 100°. After heating for 1 hr. at this temperature, the contents of the flask were poured on ice and neutralized with aqueous sodium hydroxide. The resulting precipitate was dried and extracted with 200 ml. of boiling benzene. The residue from the evaporation of the benzene was then extracted with 100 ml. of petroleum ether (b.p. 90–100°). After concentration to 50 ml., the solution was allowed to stand for several days at room temperature, whereupon crystals were deposited. Recrystallization from the same solvent yielded 0.05 g. (0.5%) of biquinoline, m.p. 193–194°. A mixed melting point with the high-melting biquinoline prepared from 2,3'-diaminobiphenyl showed no depression.

3,3'-Dinitrobenzidine.—The following modification of the original procedure⁶ was used: Bis *p*-toluenesulfonylbenzidine⁷ (30 g.) was added slowly to 150 ml. of concentrated nitric acid keeping the temperature between 40 and 50°. The mixture was then poured on ice and filtered. After washing with water the precipitate was crystallized from aqueous dimethyl formamide; yield, 27 g. (76.1%) of product melting at 215°. (The pure product melts at 220°.) The above material was hydrolyzed by dissolving it in 250 ml. of concentrated sulfuric acid, heating it for 2 hr. on the steam bath, and pouring into ice-water; yield, 14 g. of product, m.p. 270° (lit.,⁸ b.p. 275°).

3,3'-Dinitrobiphenyl.—To a mixture of 20 g. of 3,3'-dinitrobenzidine, 400 ml. of ethanol and 100 ml. of dilute (1–1) sulfuric acid there was added slowly with shaking 40 g. of solid sodium nitrite. The contents of the flask were then refluxed for 1 hr. on a steam bath, and poured on ice. The resulting precipitate was removed by filtration, dried, and extracted with benzene. After removal of the benzene the residue was crystallized from ethyl cellosolve; yield, 13 g. (73.0%), m.p. 193–194° (lit.,⁸ b.p. 196–198°).

3,3'-Diaminobiphenyl.—This was prepared in the same way as 2,3'-diaminobiphenyl, and used in the following reaction without further purification.

Skraup Reaction on 3,3'-Diaminobiphenyl.—The procedure was the same as that for 2,3'-diaminobiphenyl, except that 15.3 g. of 3,3'-diaminobiphenyl was used with proportionate amounts of other reagents. On evaporation, the benzene extract solidified. Two crystallizations from benzene yielded 4.2 g. (14.7%) of a solid melting at 168–169°, and unchanged when mixed with a sample of 7,7'-biquinoline prepared by the method of Ueda.² Elution of the first filtrate from the above material with benzene over alumina yielded 3.5 g. of pure product (16.5%), m.p. 128–129°.

Anal. Calcd. for $C_{18}H_{12}N_2$: C, 84.35; H, 4.72. Found: C, 84.08; H, 4.69.

Separation of Sesquiterpenes by Partition Chromatography

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The formation of pi complexes between olefins and silver salts has been the subject of numerous studies and has been utilized for isolation purposes through crystallization, countercurrent extraction, or vapor phase chromatographic techniques.

In connection with work on naturally occurring sesquiterpenes where a complementary method to vapor phase chromatography was desired, preliminary experiments with a partition chromatographic technique based upon the olefin-silver ion complex formation was investigated. Although the work had to be interrupted before the method had been thoroughly standardized, the preliminary results have proven useful in certain cases.^{1–3}

Because of the lipophilic character of sesquiterpenes a reversed phase technique was employed, using glass fiber paper impregnated with hexadecane and aqueous methanol containing a high concentration of silver fluoborate as the mobile phase.⁴ Silver nitrate was too insoluble to be used and concentrated aqueous silver fluoborate solutions were found to cause strong swelling of cellulose paper. Furthermore, glass fiber paper has a finer grain and offers less resistance to the mobile phase than ordinary filter paper.

After drying the developed chromatograms either by brief heating or by treatment with thionyl chloride vapor, the spots were detected by passing the paper through a solution of antimony pentachloride in chloroform. The drying process appeared to be the ambiguous part of the procedure and reproducible results were obtained only with some practice.

Using an irrigant containing approximately 90 ml. of methanol, 6 ml. of water, and 30 g. of silver fluoborate per 100 ml., the following R_f values were observed: α -Cedrene (0.15), cuparene (0.25), and thujopsene (0.46). On omitting the silver salt there was no or little separation, and the migration rates were very low. With increasing water concentration the R_f values were found to decrease. This fact was taken advantage of when dealing with polyunsaturated compounds (cf. ref. 2) or alcohols. Thus some cadinol mixtures were well

(1) C. Enzell, *Acta Chem. Scand.*, **15**, 1303 (1961).

(2) H. S. Barreto and C. Enzell, *ibid.*, **15**, 1313 (1961).

(3) J. Runeberg, *ibid.*, **14**, 1985 (1960).

(4) Concentrated aqueous solutions of silver fluoborate have been shown to extract volatile olefins such as ethylene out of gas mixtures. H. G. van Raay and U. Schwenk, U. S. Patent 2,913,505.

(5) F. H. Case and C. J. Buck, *J. Org. Chem.*, **21**, 697 (1956).

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(8) C. C. Barker and F. D. Casson, *J. Chem. Soc.* 4185 (1953).