

bon tetrachloride was added. To this mixture was added 0.5 ml. of dry bromine and 0.200 g. (0.0015 mole) of aluminum chloride. The bromine color disappeared. One milliliter of dry bromine was added and the AlCl_3 went into solution. On standing overnight the bromine color disappeared and the AlCl_3 settled out. This procedure was repeated until the bromine color remained. The solution was filtered through glass wool and the excess bromine and carbon tetrachloride removed *in vacuo*. The residue was distilled. The fraction boiling $153\text{--}155^\circ$ (25 mm.) was collected; yield 3.19 g. of a clear, colorless liquid, b.p. $270\text{--}271^\circ$ (atm.) (lit. 275° (740 mm.)) (57.9%).

One gram of the preceding liquid was heated on a steam-bath with 3 ml. of water for 15 minutes. The water was evaporated and on cooling a white crystalline material solidified, m.p. $48\text{--}49^\circ$. This material gave no depression of melting point when admixed with authentic α -bromoacetic acid.

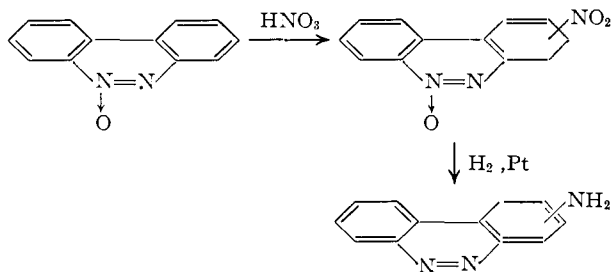
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Nitration of Benzo(c)cinnoline

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Although the compound benzo(c)cinnoline has been known for some time, all reported derivatives have been made indirectly. The formation of two monoaminobenzo(c)cinnolines by reduction of the appropriate mononitrobenzo(c)cinnoline-6-oxide prepared by nitration of benzo(c)cinnoline-5-oxide with fuming nitric acid has been reported.³ Al-



though these mononitro and monoamino compounds were identified by reduction to triaminobiphenyl and cyclized to aminocarbazoles, dipole measurements have raised considerable doubt concerning the structure proof.⁴

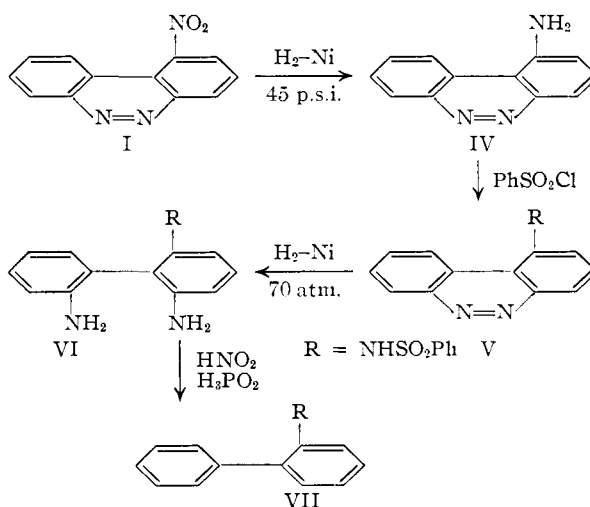
Nitration of benzo(c)cinnoline with mixed sulfuric and nitric acids at 30° gave a mixture from which three compounds (I, II and III) could be isolated with difficulty. Nitration with potassium nitrate and sulfuric acid generally gave the same products as nitration with mixed acids, but the yields were not as high. In the course of these nitrations, it was found that the nitric acid, whether used as such or formed from a salt, must be fairly pure for the best yields and easiest separation of products. As nitration conditions were made milder in order to make isolation easier, compound III no longer was formed. Compound III is most likely either a dinitrobenzo(c)cinnoline or a mononitro product formed by nitration at a less reactive

center. Either of these reactions would be expected to occur under more strenuous conditions.

Nitration with mixed acids at $0\text{--}5^\circ$ gave a mixture of I and II in 57.7 and 12.1% yield, respectively. These compounds, whose elemental analyses correspond to that expected for a mononitro derivative, were best isolated by extraction in a Soxhlet extractor. The major isomer, melting at $160\text{--}161^\circ$, was removed first by extraction with Skellysolve B. Two recrystallizations from ethanol were usually sufficient to purify this isomer. Occasionally the compound must be treated with Norite in acetone to remove the last of a red impurity which occurs in the nitration. The minor isomer, melting at 230° , was extracted with ethanol. This isomer, being much less soluble, was purified by washing with hot ethanol.

Again, effort was made to nitrate under milder conditions. However, nitration of benzo(c)cinnoline did not occur with a mixture of nitric and acetic acids even at 80° for four hours.

The major nitration product was identified by conversion to a known monosubstituted biphenyl. By taking advantage of the fact that the azo group of benzo(c)cinnoline is stable to stannous chloride and hydrochloric acid, sodium hydrosulfite, Raney nickel and low pressure hydrogen, hydrogen and platinum, and sodium amalgam and alcohol, a nitro group may be reduced without disturbing the benzo(c)cinnoline nucleus. In fact, the first three named reagents have been used to convert the nitro compound, I, to its corresponding amine, IV. This amine was protected during the following reactions by conversion to its benzenesulfonamide, V. The azo group of the sulfonamide was reduced to the expected diamine VI with Raney nickel and hydrogen at 70 atmospheres.³ Deamination of the diamine was accomplished by allowing the tetrazonium salt formed by reaction of the diamine with nitrous acid to stand in hypophosphorous acid. This work was patterned after a reported deamination of substituted diaminobiphenyls.⁵ The 2-benzenesulfonamidobiphenyl, VII, which resulted from these reactions, was compared with the benzenesulfonamide of authentic 2-aminobiphenyl.



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(3) F. King and T. King, *J. Chem. Soc.*, 824 (1945).

(4) K. Calderbank and R. LeFevre, *ibid.*, 649 (1951).

(5) S. Ross and I. Kuntz, *THIS JOURNAL*, 74, 1297 (1952).

The ultraviolet spectra of the two samples were identical, and a mixed melting point of the two showed no depression. The major nitration product of benzo(c)cinnoline has, therefore, been identified as 1-nitrobenzo(c)cinnoline.

Since the major product is the 1-isomer, it would be expected that the minor product, II, would be the 3-isomer. Reduction of II with Raney nickel and low pressure hydrogen gave an amine melting at 198–200°. It is interesting to note that hydrogen and platinum did not give clean results, though Raney nickel and hydrogen did. The amine appeared to be converted to a diazonium derivative in the usual manner, but neither pouring the diazonium salt into boiling 57% sulfuric acid,⁶ nor allowing the salt to warm slowly converted it into an identifiable product. It was hoped that the known 3-hydroxybenzo(c)cinnoline would be formed.⁷ Of the four possible monoaminobenzo(c)cinnolines, three are known. These melt at 167, 234 and 194–195°. Whether the monoaminobenzo(c)cinnoline obtained by reduction of the minor nitration product is the same as that which is reported to melt at 194–195°, or is the fourth possible amine, is not known. Physical appearance does not clarify the problem since all the amines are yellow or gold and form deep blue solutions in acid.

Experimental

1-Nitrobenzo(c)cinnoline.—A solution of 150 ml. of concentrated sulfuric acid and 50 ml. of pure concentrated nitric acid was cooled to 0°. To the stirred solution was added 30 g. of benzo(c)cinnoline over a 90-minute period. The solution was stirred at 0–5° for an additional 7.5 hours and then poured onto 300 g. of ice. Concentrated ammonium hydroxide was added until the solution had just become milky. After adding the minimum amount of concentrated hydrochloric acid necessary to eliminate the cloudiness, the precipitated product was removed by vacuum filtration. The thoroughly dried product (30.2 g.) was placed in the thimble of a Soxhlet extractor and extracted with Skellysolve B until the solution in the upper chamber was nearly colorless. Evaporation of the solvent produced 24.9 g. of product melting at 133–137°. Two recrystallizations from ethanol yielded 20.1 g. (54%) of 1-nitrobenzo(c)cinnoline melting at 160–161°. (In cases in which the melting point was lower than this or the compound was contaminated with a red impurity, further purification was effected by dissolving the compound in concentrated hydrochloric acid and precipitating with base, or by treatment with Norite in acetone.)

Anal. Calcd. for $C_{12}H_7N_3O_2$: C, 63.99; H, 3.13; N, 18.67. Found: C, 63.05; H, 3.20; N, 18.26.

Ethanol was then run through the material remaining in the thimble of the Soxhlet extractor until no more product was being extracted. The solid which had been extracted was removed by filtration to give 4.5 g. (12.1%) of x-nitrobenzo(c)cinnoline melting at 230°.

Anal. Calcd. for $C_{12}H_7N_3O_2$: C, 63.99; H, 3.13; N, 18.67. Found: C, 63.37; H, 3.08; N, 19.07.

Evaporation of the solvent yielded a solid which was dissolved in hot ethanol, separated from the more insoluble impurities by filtration while hot, and reprecipitated by cooling to give an additional 1.4 g. (3.75%) of 1-nitrobenzo(c)cinnoline melting at 157–158°.

All nitrations were carried out in essentially the same way as that given above. Reaction time, temperature and reagents were altered, but the reaction and subsequent isolation procedures were standardized.

1-Aminobenzo(c)cinnoline.—A solution of 2 g. of 1-nitrobenzo(c)cinnoline in 100 ml. of methanol was hydrogenated

at 45 pounds with 1 g. of Raney nickel for 45 minutes. The nickel catalyst was removed by filtration. After evaporating the solution to half volume, the solution was diluted with 250 ml. of water. The precipitate which settled was collected by filtration to give 1.4 g. (81%) of crude 1-aminobenzo(c)cinnoline melting at 155–157°. (Highest melting point of pure amine is 167°.)

X-Aminobenzo(c)cinnoline.—The minor nitration isomer (m.p. 230°) was reduced in a manner identical to that given above to give a 57.5% yield of a gold solid melting at 198–200°.

1-Benzenesulfonamidobenzo(c)cinnoline.—A solution of 3.2 g. (0.0164 mole) of 1-aminobenzo(c)cinnoline (m.p. 155–157°), 3 g. (0.171 mole) of benzenesulfonyl chloride and 30 ml. of pyridine was allowed to stand for 4 days at room temperature. At that time 35 ml. of water and 75 ml. of 6 *N* hydrochloric acid were added. The oil which separated was dissolved in 25 ml. of concentrated hydrochloric acid, treated with Norite, and liberated by addition of solid sodium carbonate to give a yellow product which upon recrystallization from ethanol weighed 1.3 g. (23.6%) and melted at 211–213°. Upon standing, the solution from which the oil had been separated yielded an additional 2 g. of product melting at 200–208° which may be purified in the same manner as used for the oil.

Anal. Calcd. for $C_{18}H_{18}N_2SO_2$: C, 64.44; H, 3.91; N, 12.68. Found: C, 64.28; H, 3.92; N, 12.22.

2,2'-Diamino-6-benzenesulfonamidobiphenyl.—A mixture of 2.6 g. of 1-benzenesulfonamidobenzo(c)cinnoline, 1 g. of Raney nickel and 100 ml. of ethanol was shaken in a hydrogenation bomb at 70° under a hydrogen pressure of 70 atmospheres for two hours. When the temperature had dropped to 40°, the pressure was released. After the nickel had been removed by filtration, the solution was treated with Norite for five hours at 25° and then evaporated to give 1.4 g. of impure material which was used in the following experiment without further purification.

2-Benzenesulfonamidobiphenyl.—To a solution of 1.4 g. of impure 2,2'-diamino-6-benzenesulfonamidobiphenyl in 31 ml. of 3.4 *N* hydrochloric acid cooled to 0°, was added 1.2 g. of sodium nitrite over a 15-minute period. After the solution had stood at 0° for one hour, 30.2 g. of precooled 50% hypophosphorus acid was added with stirring over a 15-minute period. (Foaming was quite pronounced at this point.) The mixture was kept at 0° for 42 hours. The solid which separated was extracted with 15 ml. of hot benzene. The solid isolated by evaporation of the benzene was dissolved in acetone and treated with Norite. Evaporation of the acetone gave a light brown solid melting at 113°. Two recrystallizations from ethanol gave 0.01 g. (0.42%) of product melting at 116–117.5°.

Authentic 2-Benzenesulfonamidobiphenyl.—A solution of 1.4 g. (0.006 mole) of authentic 2-aminobiphenyl, 1.5 g. (0.0085 mole) of benzenesulfonyl chloride and 30 ml. of pyridine was allowed to stand at room temperature for 4 days. The solution was then diluted with 100 ml. of water and 10 ml. of 37% hydrochloric acid. The precipitate which separated was recrystallized twice from ethanol to give 1.0 g. (39%) of the expected product melting at 117–118°.

Anal. Calcd. for $C_{18}H_{16}NSO_2$: C, 69.88; H, 4.89. Found: C, 69.46; H, 4.91.

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A Synthesis for β -Aroylacrylic Acids Substituted with Electron-withdrawing Groups

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Except for the *m*-nitro group, the introduction of an electron-withdrawing group into the aryl ring of β -aroylacrylic acids is lengthy. The usual Friedel and Crafts reaction has not been employed and does not appear promising for such compounds. Recently, the condensation of 2-naphthylglyoxal

(1) To whom inquiries should be directed.

(6) R. Manske, in Gilman's "Organic Syntheses," Coll. Vol. I. John Wiley and Sons, Inc., New York, N. Y., 1941, p. 404.

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