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 $C_{18}H_{13}N_3SO_2$: 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 $C_{18}H_{15}NSO_2$: C, 69.88; H, 4.89. Found: C, 69.46; H, 4.91.

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

(7) O. Goll, *C. A.*, **28**, 654 (1934). German Patent 577,631.

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

BY LEONARD STEINBACH AND ERNEST I. BECKER[1]

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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.

with malonic acid in pyridine was reported to give β-(2-naphthoyl)-acrylic acid[2] according to the equation

$$ArCOCHO + CH_2(COOH)_2 \xrightarrow{\text{pyridine}} ArCOCH{=}CHCOOH + CO_2 + H_2O$$

It was the purpose of this investigation to extend this procedure to other aroylacrylic acids.

o-, *m*- and *p*-nitrophenylglyoxals were prepared by the selenium dioxide oxidation in acetic acid of the corresponding nitroacetophenones. The isolation of the nitrophenylglyoxals was accomplished with some difficulty. It was necessary to distil them below about 130° to avoid sudden decomposition.[3] Most often the glyoxals were used soon after preparation because they polymerized slowly. However, it was found that the ground up, glassy polymer could be used equally well. *m*- and *p*-nitrophenylglyoxals were obtained in 50 and 60% yields, respectively, but *o*-nitrophenylglyoxal was obtained in crude state only.

As model experiments for the condensation, malonic acid was condensed with phenylglyoxal to give β-benzoylacrylic acid in 35% yield and with 2-naphthylglyoxal to give β-(2-naphthoyl)-acrylic acid in 45% yield (reported[2] 12%). Then, 1-naphthylglyoxal afforded β-(1-naphthoyl)-acrylic acid in 53% yield. The physical properties of the two naphthoylacrylic acids agree with the assignment made by Martin and Stoffyn[4,5] and Grummitt and Arters[6] and serve to corroborate their structures.

Finally, *o*-, *m*- and *p*-nitrophenylglyoxals were condensed to the corresponding aroylacrylic acids in yields of 11, 25 and 41%, respectively. *o*-Nitrobenzoylacrylic acid had already been reported by Sakan[7] in about 5% over-all yield starting with ethyl *o*-nitrobenzoylacetate. *m*-Nitrobenzoylacrylic acid can be made by the direct nitration of β-benzoylacrylic acid in 90% yield.[8]

It has thus been shown that β-aroylacrylic acids can be synthesized by the condensation of malonic acid with an arylglyoxal in pyridine solution and that this procedure may have advantages for the introduction of electron-withdrawing groups in the aryl ring.

Experimental[9,10]

m-Nitrophenylglyoxal.—A solution of 39 g. (0.30 mole) of selenous acid, 24 g. of water and 150 ml. of acetic acid were refluxed for one hour with 49.8 g. (0.30 mole) of *m*-nitroacetophenone. Precipitated selenium was filtered from the cooled reaction mixture and the filtrate was distilled. After removing the water and acetic acid at 15 mm., 27 g. (0.151 mole, 50%) of the yellow product distilled at 118–128° (0.6 mm.).

Anal. Calcd. for $C_8H_5NO_4$: C, 53.64; H, 2.81; N, 7.82; oximation equiv., 89.6. Found: C, 53.21; H, 2.92; N, 7.80; oximation equiv., 88.8.[11]

On standing the viscous liquid became a glassy solid with an indefinite melting point of 37–46°.

3-(*m*-Nitrophenyl)-quinoxaline.—A mixture of 1.8 g. (0.010 mole) of *m*-nitrophenylglyoxal and 1.1 g. (0.010 mole) of *o*-phenylenediamine and 20 ml. of alcohol were refluxed for one hour on a steam-bath. Filtration of the crude mixture gave 2.4 g. (0.096 mole, 96%) of the tan, crude product, m.p. 187–188°. Recrystallization from benzene and then ethanol afforded the colorless product, m.p. 190–191°.

Anal. Calcd. for $C_{14}H_9N_3O_2$: C, 66.92; H, 3.61; N, 16.73. Found: C, 66.81; H, 3.70; N, 16.57.

p-Nitrophenylglyoxal.—Starting with *p*-nitroacetophenone[13] and using the same procedure as for the *m*-isomer, the *p*-compound was obtained in 60% yield as an intensely yellow material, b.p. 108–123° (1 mm.). Upon cooling a solution of the glyoxal in boiling water, a crystalline hydrate was obtained, m.p. 97–100° (reported[14] m.p. 98–100°).

Anal. Calcd. for $C_8H_5NO_4$: oxim. equiv., 89.6. Found: oxim. equiv., 92.3. Calcd. for $C_8H_7NO_5$ (hydrate): oxim. equiv., 98.6. Found: oxim. equiv., 100.0.

The quinoxaline melted at 191–192° (reported[14] m.p. 186–188°).

o-Nitrophenylglyoxal.—Starting with *o*-nitroacetophenone[15] the glyoxal was obtained only in the crude state. With ethanol as the solvent for the oxidation,[11] this was also true. The material was used after removal of the solvent without further purification.

3-(*o*-Nitrophenyl)-quinoxaline.—Refluxing a solution of the crude glyoxal with *o*-phenylenediamine in ethanol followed by three recrystallizations from ethanol (charcoal) gave the colorless product, m.p. 114.8–115.2°.

Anal. Calcd. for $C_{14}H_9N_3O_2$: C, 66.92; H, 3.61; N, 16.73. Found: C, 67.08; H, 3.56; N, 16.73.

β-Benzoylacrylic Acid.—Ten milliliters of pyridine was added in one portion to a stirred mixture of 7.6 g. (0.050 mole) of phenylglyoxal monohydrate and 5.2 g. (0.050 mole) of malonic acid. An exothermic reaction took place and raised the temperature from 30 to 40°. A gas was evolved and solution took place rapidly. After having been stirred for four hours and standing overnight, the mixture was semi-solid. The mass was dissolved with 40 ml. of 10% aqueous sodium carbonate solution and extracted with three 50-ml. portions of benzene. Acidification of the aqueous layers with concentrated hydrochloric acid at 5–10° gave an oil which crystallized on shaking with the mother liquor. Filtration gave 9.6 g. of crude acid, which then was dissolved in 250 ml. of water at 80° and filtered to remove a small quantity of a viscous oil. To the clear filtrate at 80°, 7.5 g. of concentrated hydrochloric acid was added and the solution was stirred for several minutes and then cooled to 5°. The precipitate was collected, dried over sulfuric acid and recrystallized twice from benzene to give 3.0 g. (0.015 mole, 34%) of yellow β-benzoylacrylic acid, m.p. 95–96° (m.m.p. 95–96° with authentic material prepared *via* the Friedel and Crafts reaction).

β-(2-Naphthoyl)-acrylic Acid.—Ten milliliters of pyridine was added to a stirred mixture of 5.05 g. (0.025 mole) of naphthylglyoxal monohydrate[16] and 2.6 g. (0.025 mole) of malonic acid. Heat was evolved and after stirring for one hour the mass had practically solidified. After standing for 18 hours the mass had liquefied and gas was evolved. The mixture was dissolved with 50 ml. of 5% aqueous sodium carbonate solution at 10–15°. After extracting the alkaline solution with four 50-ml. portions of benzene, the

(2) M. Goldman and E. I. Becker, *Nature*, **170**, 35 (1952).

(3) Crude samples of *m*-nitrophenylglyoxal decomposed suddenly when distillation above 1 mm. was attempted.

(4) Martin and Stoffyn[5] prepared their acids by separating the products of the Friedel and Crafts reaction with naphthalene and maleic anhydride while Grummitt and Arters[6] added the corresponding naphthylzinc halides to maleic anhydride.

(5) R. H. Martin and P. Stoffyn, *Bull. soc. chim. Belges*, **59**, 83 (1950).

(6) O. Grummitt and A. A. Arters, unpublished M.S. thesis of A.A.A., Western Reserve University, Cleveland 6, Ohio, June, 1951.

(7) T. Sakan, *J. Chem. Soc. Japan*, **63**, 1545 (1942); *C. A.*, **41**, 3072d (1947).

(8) M. T. Bogert and J. J. Ritter, THIS JOURNAL, **47**, 526 (1925).

(9) Melting points are not corrected.

(10) Analyses were performed by Dr. K. Ritter, Microanalytisches Laboratorium, Basel 2, Switzerland.

(11) The oximation procedure used was that of Stillman and Reed[12] and consistently gave values of 97–99% purity for these compounds.

(12) K. Stillman and R. M. Reed, *Perfumery Essent. Oil Records*, **23**, 278 (1932).

(13) L. M. Long and H. D. Troutman, THIS JOURNAL, **71**, 2473 (1949).

(14) C. Musante and V. Parrini, *Gazz. chim. ital.*, **81**, 451 (1951).

(15) G. A. Reynolds and C. R. Hauser, *Org. Syntheses*, **30**, 70 (1950).

(16) L. N. Goldyrev and I. Ya Postovskiĭ, *J. Gen. Chem.* (*U.S.S.R*), **10**, 39 (1940); *C. A.*, **34**, 4732[7] (1940).

aqueous layer was acidified at 10° with concentrated hydrochloric acid to give 6 g. of a pasty yellow solid. Recrystallization from 50% ethanol (charcoal) afforded 2.5 g. (0.011 mole, 45%) of yellow crystals, m.p. 167–168° (reported 163–165°, 164–166°,[2] 166–167°[5]).

β-(1-Naphthoyl)-acrylic Acid.—Using the procedure for the 2-naphthoyl isomer, starting with the same quantities of 1-naphthylglyoxal monohydrate[16] and malonic acid and crystallizing the yellow product finally from 50% ethanol, β-(1-naphthoyl)-acrylic acid was obtained in 53% yield, m.p. 148.5–149.5° (reported 145–147°, 148–149°[5]). No depression was observed on admixture with a sample prepared *via* the Friedel and Crafts reaction.[17]

β-(*m*-Nitrobenzoyl)-acrylic Acid.—At 10–15°, 7.0 g. (0.067 mole) of malonic acid was added gradually to a solution of 12 g. (0.067 mole) of *m*-nitrophenylglyoxal in 35 ml. of pyridine. After stirring for 15 minutes and standing for 20 hours, the mixture was cooled to 10–15° and to it was added 170 ml. of 5% aqueous sodium carbonate solution. While maintaining this temperature, the alkaline solution was extracted with four 150-ml. portions of benzene and then acidified with concentrated hydrochloric acid. Recrystallization of the crude product from 1.5 l. of 1.9% hydrochloric acid gave 3.4 g. (0.015 mole, 25%) of yellow β-(*m*-nitrobenzoyl)-acrylic acid, m.p. 190–191°.

Anal. Calcd. for $C_{10}H_7NO_5$: C, 54.30; H, 3.19; N, 6.33; neut. equiv., 221. Found: C, 54.45; H, 3.30; N, 6.45; neut. equiv., 221.

No depression was observed on admixture with a sample prepared by the direct nitration of β-benzoylacrylic acid.[8]

β-(*p*-Nitrobenzoyl)-acrylic Acid.—Using the procedure for the *m*-isomer and starting with 3.84 g. (0.019 mole) of *p*-nitrophenylglyoxal monohydrate, there was obtained 1.76 g. (0.0080 mole, 41%) of yellow product, m.p. 165.0–166.5° (from 1.9% hydrochloric acid).

Anal. Calcd. for $C_{10}H_7NO_5$: C, 54.30; H, 3.19; N, 6.33; neut. equiv., 221. Found: C, 54.29; H, 3.34; N, 6.37; neut. equiv., 222.

β-(*o*-Nitrobenzoyl)-acrylic Acid.—This material was prepared in the same manner as that for the other two isomers. Starting with the crude reaction product obtained by the oxidation of 6.5 g. (0.039 mole) of *o*-nitroacetophenone and 4.0 g. (0.039 mole) of malonic acid there was obtained 0.8 g. (0.0036 mole, 11%) of light yellow needles, m.p. 173.0–173.5° (from 1.9% hydrochloric acid).

Anal. Calcd. for $C_{10}H_7NO_5$: C, 54.30; H, 3.19; N, 6.33; neut. equiv., 221. Found: C, 54.38; H, 3.24; N, 6.48; neut. equiv., 222.

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(17) This sample was kindly supplied by Dr. M. Goldman.

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The Action of Lithium Aluminum Hydride on a β-Lactam[1]

BY MERRILL E. SPEETER AND WILLIAM H. MARONEY

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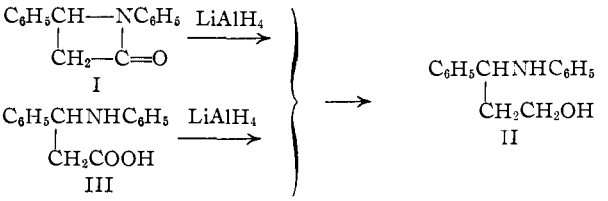
The facile preparation of substituted pyrrolidines, piperidines and other polymethylenimines through the action of lithium aluminum hydride on the corresponding lactams has been reported by a number of investigators.[2–5] It thus appeared possible that relatively uninvestigated compounds of the azetidine series might be obtained through the action of lithium aluminum hydride on azetidinones (β-lactams). To test this possibility 1,4-diphenylazetidinone, which is readily obtainable through a Reformatsky reaction with benzalaniline,[6] was reduced with lithium aluminum hydride both in ether and in tetrahydrofuran solution. In these reductions no azetidine was produced as ring opening took place concurrent with the reduction of the carbonyl group and only 3-anilino-3-phenyl-1-propanol (II) could be isolated. This compound was obtained in 88% yield and a careful examination of the recrystallization mother liquors failed to yield any second product.



An independent synthesis of II was desired and this was accomplished through the lithium aluminum hydride reduction of the acid III.[7] Only a poor yield of II was obtained in this reduction, but it might be expected that III would yield a highly insoluble complex with lithium aluminum hydride which would reduce with difficulty.

The formation of carbinols in the lithium aluminum hydride reduction of cyclic amides rarely has been reported. Morrison, Long and Königstein[8] treated 4-methyl-2,2-diphenyl-3-morpholone with lithium aluminum hydride and in addition to the expected morpholine derivative isolated 3-hydroxy-4-methyl-2,2-diphenylmorpholine.[9]

Experimental

Lithium Aluminum Hydride Reduction of 1,3-Diphenylazetidinone.—A solution of 33 g. (0.15 mole) of 1,4-diphenylazetidinone was prepared in 400 ml. of dry tetrahydrofuran. This solution was added with stirring to 6.4 g. (0.17 mole) of lithium aluminum hydride dissolved in 350 ml. of tetrahydrofuran. A moderately exothermic reaction was observed during the addition. The mixture was concentrated to a volume of 200 ml., after the addition and the cooled solution diluted with 500 ml. of ether. Excess lithium aluminum hydride was destroyed with ether–alcohol and several hundred ml. of 10% sodium hydroxide was added with vigorous stirring. The ether layer was decanted and the alkali layer agitated with several 200-ml. portions of ether. The combined ether solutions were washed with water, dried over potassium carbonate and concentrated. The remaining oil crystallized and after two recrystallizations from toluene the material melted at 87–88°. The product weighed 28 g. and an additional 2 g. was obtained from the

(1) Abstracted from a senior research paper submitted by W. H. Maroney to Kalamazoo College in partial fulfillment of the requirements for the A.B. degree.

(2) P. Karrer and P. Portmann, *Helv. Chim. Acta*, **31**, 2088 (1948).

(3) R. B. Moffett, *J. Org. Chem.*, **14**, 862 (1949).

(4) L. Ruzicka, M. Kobelt, O. Häfliger and V. Prelog, *Helv. Chim. Acta*, **32**, 544 (1949).

(5) See also the review "Reductions by Lithium Aluminum Hydrides," by W. G. Brown, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, Chapter 10.

(6) H. Gilman and M. E. Speeter, THIS JOURNAL, **65**, 2255 (1943).

(7) H. T. Clarke, J. R. Johnson and R. Robinson, editors, "The Chemistry of Penicillin," Princeton University Press, Princeton, N. J., 1948, p. 977.

(8) A. L. Morrison, R. F. Long and M. Königstein, *J. Chem. Soc.*, 952 (1951).

(9) The referee has pointed out the work of A. Stoll, A. Hofmann and T. Petrzilka, *Helv. Chim. Acta*, **34**, 1544 (1951), which indicates that carbinols have been obtained from some lithium aluminum hydride reductions in the ergot alkaloid field. Also, A. Mustafa, *J. Chem. Soc.*, 2435 (1952), isolated arylsulfonylaminocarbinols from the $LiAlH_4$ reduction of N,N'-diaryl-α-sulfonyldianthranilides.