some control of reflux by rotation of the condenser and allowing recovery of condensate solidified on the walls of the condenser. The same apparatus was used for continuous removal of piperazine–water mixture in the dehydrations carried out at atmospheric pressure.

Autoclave reactions were carried out in an American Instrument Co. hydrogenation bomb of 750-ml. capacity, electrically heated and provided with a rocker for agitation.

Materials.—Dioxane was purified by long (ten to twenty hours) reflux of commercial dioxane with aniline and metallic sodium, followed by fractional distillation. N-(2-Hydroxyethyl)-ethenediamine from Carbide and Carbon Chemicals Corp. was distilled; other intermediates were prepared.[3]

Preparation of Piperazine at Atmospheric Pressure.—One hundred and fifty grams of N-(2-hydroxyethyl)-ethenediamine containing 5 g. of Raney nickel catalyst were heated under a distillation column for two and one-half hours. Distillate of b. p. about 120° slowly was collected; 75 g. of tarry resin remained in the still-pot. The distillate, 57 g. of aqueous piperazine, contained piperazine in amount equivalent to a 32% yield, determined by titration with 0.1 *N* acid (brom phenol blue indicator): benzoyl deriv., m. p. 191.7–192.8° (from alc.); dibenzoylpiperazine, m. p. 192.1–193.0°; mixed m. p. 191.7–193.0°. With diethylcarbitol as diluent, twelve hours were required for reaction, giving 34% yield.

TABLE I

SYNTHESIS OF PIPERAZINE FROM N-(2-HYDROXYETHYL)-ETHENEDIAMINE. AUTOCLAVE METHOD

g.	Catalyst	Reactant, g.	Dioxane, ml.	Reaction time, hr.	Reaction temp., °C.	Yield, %	Recovered amino-alc., g.
60	Copper–chromium oxide	156[a]	1050	3	275	45	[b]
30	Raney nickel	156[a]	1050	3	200	50	[b]
10	Raney nickel	85	400	3	200	51	0
15	Act. alumina	150	200	3	300	20	82
30	Silica gel	279	None	3	300	17.4	150
30	Cupric oxide	150	200	3	275	43	[b]
30	Iron (H_2 red.)	150	200	3	300	26	0

[a] Composites of three runs, 52 g. reactant per run. [b] Not determined.

(3) Kitchen and Pollard, *J. Org. Chem.*, **8**, 342 (1943).

Autoclave Method for Piperazine Preparation.—The autoclave was charged with 150 g. of N-(2-hydroxyethyl)-ethenediamine in 200 ml. of dioxane, 5–30 g. of catalyst was added, and reaction was carried out for three hours at a temperature in the range 200–300° (Table I). The reaction mixture, filtered from catalyst, was distilled; dioxane-water azeotrope distilled at 87°, then dioxane at 100–103°, and finally piperazine at 140–150°.

Raney nickel appeared the catalyst of choice; copper–chromium oxide, activated alumina, silica gel, cupric oxide and iron (hydrogen reduced) were intermediate in effectiveness. Low yields were obtained with palladium/Norit (225–246°, 13%) and fuller's earth (300°, 5%); and little or no piperazine was obtained when the catalyst was platinum/Norit (180–230°), vermiculite (300°), barium oxide (300°), chromic oxide (280°), stannous oxide (300°) or Norit (300°).

Preparation of 2-Methylpiperazine.—Two hundred and twenty-five grams of N-(2-hydroxypropyl)-ethenediamine in 350 ml. of dioxane was autoclaved with 10 g. of Raney nickel under 200 p. s. i. (cold) of hydrogen for five hours at 185–203°. Yield of 2-methylpiperazine was 121 g. (52% yield; 70%, based upon unrecovered starting material).

2-Methylpiperazino-bis-(phenylthiourea), from benzene–absolute alcohol; gave a m. p. 189.0–189.9° (cor.).

Preparation of 2-Phenylpiperazine.—One hundred and eight grams of N-(2-hydroxy-2-phenylethyl)-ethenediamine in 300 ml. of dioxane, agitated with 20 g. of Raney nickel at 220° for three and one-half hours, yielded 32 g. (32% yield) of crude 2-phenylpiperazine, a yellow oil of $n^{30}D$ 1.5766 and b. p. 124–146° (10 mm.) which crystallized to a mush on standing. Redistilled, it boiled mainly at 138° (10 mm.). Purified by three recrystallizations from hexane, it had m. p. 87.5–87.8° (cor.). Dihydrochloride, from aqueous alcohol, gave a m. p. *ca* 335° (dec.). *Anal.* Calcd. for $C_{10}H_{16}N_2Cl_2$: Cl, 30.15. Found: 29.35. Dinitroso deriv., m. p. 69.9–70.2° (cor.) (from methanol); diacetyl deriv., m. p. 70.1–71.2° (cor.) (hexane); picrate (prepared in alcohol), m. p. *ca.* 276° (dec.) (cor.).

Summary

Preparation of piperazine, 2-methylpiperazine and 2-phenylpiperazine, a new compound, by catalytic cyclodehydration of hydroxyethylethenediamines is described.

GAINESVILLE, FLORIDA RECEIVED AUGUST 29, 1946

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Synthesis of 4-Hydroxyquinolines. X. Quinoline Derivatives with Sulfur-Containing Substituents[1]

BY CHARLES C. PRICE,[2] NELSON J. LEONARD AND GARDNER W. STACY[3]

In continuation of studies in the 4-hydroxyquinoline series[4] it appeared of interest to prepare some quinolines with sulfur-containing substituents. The 6-substituted quinoline derivatives are the most convenient examples of this type of compound since the possibility of ambiguity of structure on ring closure is eliminated.

The application of the ethoxymethylenemalonic ester synthesis[4] to *p*-aminophenyl sulfide (I) proceeded successfully to produce 6,6′-bis-[4-(4-diethylamino-1-methylbutylamino)-quinolyl] sulfide (VII). One unusual and interesting feature was the apparent oxidation of the sulfide to sulfoxide during replacement of the 4-hydroxyl group by chlorine (V → VI), and the subsequent reduction of the sulfoxide during treatment with 1-amino-4-diethylaminopentane (VI → VII).

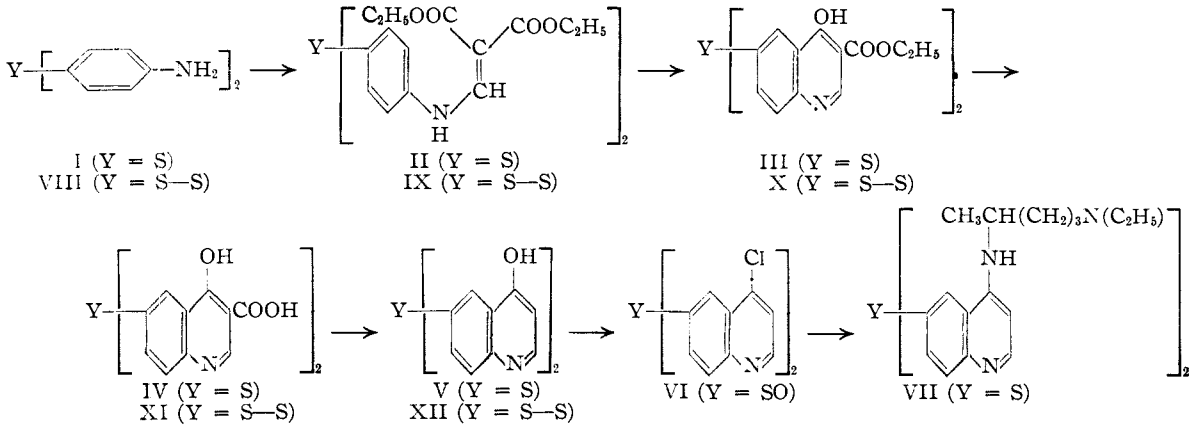
Application of this synthesis to *p*-aminophenyl

(1) The work described in this paper was carried out under a contract, recommended by the Committee on Medical Research, between the Office of Scientific Research and Development and the University of Illinois.

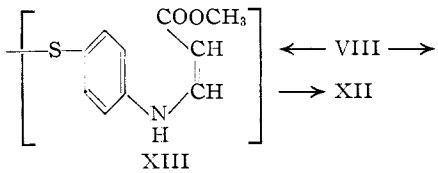
(2) Present address: University of Notre Dame, Notre Dame, Indiana.

(3) Present address: Department of Biochemistry, Cornell University Medical College, New York, New York.

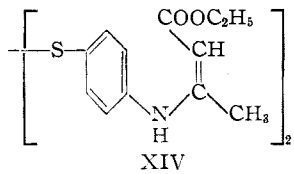
(4) Price and co-workers, THIS JOURNAL, **68**, 1204, 1251, 1253, 1255, 1256, 1279, 1282 (1946); **69**, 371, 374 (1947).



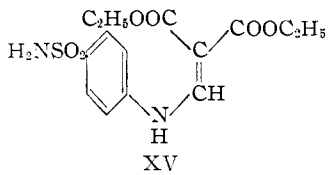
disulfide (VIII) was successful up to the stage of decarboxylation of the quinoline acid (XI). Decarboxylation could not be induced to proceed satisfactorily under a wide variety of conditions. An attempt to circumvent the decarboxylation step by direct cyclization of the acrylate derivative[4] (XIII → XII) was also unsuccessful.



XIII



XIV



XV

The condensation product (XIV) of *p*-aminophenyl disulfide with acetoacetic ester was prepared and characterized, as was the condensation product (XV) of sulfanilamide with ethoxymethylenemalonic ester. Attempts at thermal cyclization of XIV and XV to 4-hydroxyquinoline derivatives were unsuccessful.

Experimental[5]

p-Aminophenyl Sulfide (I).—To 165 g. (0.598 mole) of *p*-nitrophenyl sulfide[6] was added 990 g. (4.40 moles) of stannous chloride dihydrate dissolved in 975 ml. (11.7 moles) of concentrated hydrochloric acid. To initiate the reaction the mixture was warmed on the steam-bath to about 65°. The reaction mixture was heated at 80–90° for nearly five hours and then poured into an ice-cold solution of 1290 g. of sodium hydroxide dissolved in 3230 ml. of water.

The crude *p*-aminophenyl sulfide was separated by filtration. For recrystallization it was dissolved in 500 ml. of ethanol, the hot solution was filtered, and 500 ml. of water containing about one gram of sodium hydrosulfite was added. *p*-Aminophenyl sulfide crystallized in small white needles, m. p. 110–111°[7]; yield, 106 g. (81.6%).

bis-(*p*-(β,β-Dicarbethoxyvinylamino)-phenyl) Sulfide (II).—One hundred and twenty grams (0.560 mole) of *p*-aminophenyl sulfide and 252 g. (1.16 moles) of ethoxymethylenemalonic ester were heated at 70–105° for one hour, and then at 105–150° for an additional hour. A sample of the product was purified for analysis by recrystallization from ethanol, m. p. 103.5–105.5°.

Anal. Calcd. for $C_{28}H_{32}N_2O_8S$: C, 60.40; H, 5.80; N, 5.03. Found: C, 60.21; H, 5.82; N, 5.16.

6,6′-bis-(3-Carbethoxy-4-hydroxyquinolyl) Sulfide (III).—The acrylate just described was dissolved in 500 ml. of diphenyl ether and then added over a period of one-half hour to 2 liters of diphenyl ether at 250°. After one hour, the product was removed by filtration of the cooled mixture; yield 242 g. (92.5%); m. p. 325–327° (dec.).

Anal. Calcd. for $C_{24}H_{20}N_2O_6S$: C, 62.05; H, 4.34; N, 6.03. Found: C, 61.79; H, 4.30; N, 6.28.

6,6′-bis-(3-Carboxy-4-hydroxyquinolyl) Sulfide (IV).—Hydrolysis was accomplished by heating 242 g. of III with 835 ml. of 2.5 *N* sodium hydroxide at the reflux temperature for fifteen minutes. The reaction mixture was treated in the usual manner and acidified with 400 ml. of 6 *N* hydrochloric acid. The product was obtained in a yield of 189 g. (89%); m. p. 295–297° (dec.).

Anal. Calcd. for $C_{20}H_{12}N_2O_6S$: C, 58.82; H, 2.96; N, 6.86. Found: C, 58.73; H, 3.10; N, 6.67.

6,6′-bis-(4-Hydroxyquinolyl) Sulfide (V).—One hundred and eighty-nine grams of 6,6′-bis-(3-carboxy-4-hydroxyquinolyl) sulfide was heated in 1.5 liters of diphenyl ether at 250° for one hour and fifteen minutes. During the latter part of the heating period the material fused to a solid mass. After the mixture was allowed to cool, the sintered mass was broken up and removed by filtration. This material was placed in 500 ml. of boiling glacial acetic acid. A thick, white paste was formed. The mass was cooled, filtered and dried. The yield of 6,6′-bis-(4-hydroxyquinolyl) sulfide (m. p. 340°) was 106 g. (72%).

6,6′-bis-(4-Chloroquinolyl) Sulfoxide (VI).—When 100 g. (0.312 mole) of 6,6′-bis-(4-hydroxyquinolyl) sulfide was added to 200 ml. of phosphorus pentachloride over a period of fifteen minutes, a vigorous exothermic reaction occurred. The mixture was heated in an oil-bath at 120° for three-quarters of an hour. Such a vigorous reaction ensued that the oil-bath had to be removed. After the reaction had subsided, the oil-bath was replaced and heating was continued for one-half hour at 100–105°. The

(5) All melting points are corrected. The microanalyses were carried out by Miss Theta Spoor, Miss Lillian Hruda and Mr. Howard Clark.

(6) Price and Stacy, THIS JOURNAL, **68**, 498 (1946).

(7) Nietzki and Bothof (*Ber.*, **27**, 3261 (1894)) reported a melting point of 109°.

temperature was raised to 150° and maintained for one hour.

After the reaction mixture had been cooled, ice was added with caution. The resulting solution was made alkaline (400 g. of sodium hydroxide in 3 liters of water). The product was collected by filtration, washed with 1.5 liters of water, and dried. The yield of crude material, m. p. 186–190°, was 85.5 g. (73%).

To obtain suitably pure 6,6′-bis-(4-chloroquinolyl) sulfoxide the compound was recrystallized four times from 500-ml. portions of Cellosolve. In each case the hot solution was treated with Norite. The yield of pure material was 26.3 g. (22.5%), m. p. 197–198°.

Anal. Calcd. for $C_{18}H_{10}Cl_2N_2OS$: C, 57.91; H, 2.70; N, 7.51; Cl, 19.00. Found: C, 57.94; H, 2.92; N, 7.65; Cl, 18.92.

6,6′-bis-[4-(4-Diethylamino-1-methylbutylamino)-quinolyl] Sulfide (VII).—Five grams (0.134 mole of 6,6′-bis-(4-chloroquinolyl) sulfoxide, 8.90 g. (0.0562 mole) of 1-amino-4-diethylaminopentane and 2.0 g. (0.0214 mole) of phenol were heated at 185–210° for sixteen hours. After the reaction mixture had cooled, it was poured into 50 ml. of 2 *N* hydrochloric acid. The dark-red acid solution was then neutralized with 20 ml. of 5 *N* sodium hydroxide. The resulting gummy precipitate was dissolved in 100 ml. of benzene, treated with Darco, and filtered. The yield of granular product (m. p. 175–180°) was 3.68 g. (45.8%). For analysis the material was recrystallized once from benzene and washed with ether, m. p. 181–182°.

Anal. Calcd. for $C_{36}H_{52}N_6S$: C, 71.95; H, 8.73; N, 13.99. Found: C, 71.63; H, 8.81; N, 13.79.

The **picrate** of this compound was prepared in the customary manner. Because of its extreme insolubility it could not be purified by recrystallization; m. p. 244–245° (dec.).

Anal. Calcd. for $C_{36}H_{52}N_6S \cdot 4C_6H_3N_3O_7$: C, 47.49; H, 4.25; N, 16.62. Found: C, 47.66; H, 4.21; N, 16.06, 16.15.

***p*-Aminophenyl Disulfide (VIII).**—In a 12-liter flask, equipped with reflux condenser and mechanical stirrer, were placed 369 g. (2.35 moles) of *p*-chloronitrobenzene, 1475 g. (6.15 moles) of sodium sulfide monohydrate, and 3700 ml. of water.[8] With vigorous stirring this mixture was then heated at the reflux temperature for fifteen hours. At the end of this time the flask was cooled, the sludge was removed by filtration, and the filtrate was concentrated to 2.5 liter. In order to obtain the disulfide the concentrate was divided into two equal parts and, while the temperature of the reaction mixture was maintained at 65–70°, 140 ml. of 30% hydrogen peroxide was added to each. The crude *p*-aminophenyl disulfide was removed by filtration. For the two runs the combined yield of crude product amounted to 238 g. (82.5%). This material was recrystallized by dissolving in 1.5 liters of hot ethanol and 1.5 liters of water containing sodium hydrosulfite to inhibit discoloration through oxidation. The yield of pure *p*-aminophenyl disulfide (m. p. 80–81°) was 189 g. (65%).

bis-(*p*-(β,β-Dicarbethoxyvinylamino)-phenyl) Disulfide (IX).—Thirty grams (0.121 mole) of *p*-aminophenyl disulfide was heated with 52.3 g. (0.242 mole) of ethoxymethylenemalonic ester at 90–115° for ten minutes. After the vigorous evolution of ethanol had subsided, heating was continued for one hour at 115–125°. Acrylate formation was then complete and the acrylate was used directly for the next reaction in the series.

In order to isolate a sample of this intermediate for analysis a small portion of the oil was crystallized from a limited volume of ethanol. Crystallization was successful, however, only when the ethanolic solution was maintained at a temperature of 45°. The acrylate was obtained as a bright yellow, crystalline solid, m. p. 87–89°.

Anal. Calcd. for $C_{28}H_{32}N_2O_8S_2$: C, 57.11; H, 5.48; N, 4.76. Found: C, 57.30; H, 5.73; N, 4.85.

(8) Lantz, French Patent 714,682; *Chem. Zentr.*, **103**, I, 1828 (1932).

6,6′-bis-(3-Carbethoxy-4-hydroxyquinolyl) Disulfide (X).—While the temperature of the acrylate intermediate (IX) was still at about 100°, it was dissolved in 150 ml. of diphenyl ether. This solution was added from a dropping funnel over a period of ten minutes to 300 ml. of refluxing diphenyl ether. Formation of the quinoline derivative was apparently complete after the mixture had been maintained at the reflux temperature for an additional five minutes. The product was removed by filtration and washed several times with petroleum ether (b. p. 30–60°); yield 43 g. (60%); m. p. 321–322°, with decomposition.

This compound was quite insoluble in a wide variety of solvents. In order to prepare a sample for analysis a small amount was placed in a Soxhlet extraction apparatus and subjected to continuous extraction with glacial acetic acid and ethanol and the solid separated from the extract.

Anal. Calcd. for $C_{24}H_{20}N_2O_6S_2$: C, 58.05; H, 4.06; N, 5.64. Found: C, 57.93; H, 4.11; N, 5.87.

6,6′-bis-(3-Carboxy-4-hydroxyquinolyl) Disulfide (XI).—In 385 ml. of 2.5 *N* sodium hydroxide solution, 59 g. of 6,6′-bis-(3-carbethoxy-4-hydroxyquinolyl) disulfide was heated under reflux for fifteen minutes. The mixture was filtered to remove insoluble material and then acidified with 90 ml. of concentrated hydrochloric acid.

The quinolinecarboxylic acid, m. p. 275° (dec.), was separated by filtration; yield 43.0 g. (82.5%). This material was very insoluble, and again a sample for analysis had to be prepared by the extraction technique.

Anal. Calcd. for $C_{20}H_{12}N_2O_6S_2$: C, 54.54; H, 2.75; N, 6.36. Found: C, 54.08; H, 3.08; N, 6.11.

bis-(*p*-β-Carbomethoxyvinylaminophenyl) Disulfide (XIII).—*p*-Aminophenyl disulfide (2.5 g., 0.0101 mole) was dissolved in 25 ml. of 50% acetic acid. To this with stirring were added simultaneously from two dropping funnels 12.5 ml. of glacial acetic acid and a solution of 2.5 g. of methyl sodioformylacetate in 12.5 ml. of water. After most of the formylacetate solution has been added, a yellow precipitate began to form. The crude product (0.5 g.) was separated by filtration. After several recrystallizations from Cellosolve, the material melted at 187°.

Anal. Calcd. for $C_{20}H_{20}N_2O_4S_2$: C, 57.67; H, 4.84; N, 6.73. Found: C, 57.75; H, 5.08; N, 6.90.

bis-[*p*-(β-Carbethoxy-α-methylvinylamino)-phenyl] Disulfide (XIV).—Fifty grams (0.202 mole) of *p*-aminophenyl disulfide and 50 g. (0.431 mole) of acetoacetic ester were allowed to stand together for a period of ten hours. The reaction was catalyzed by a drop of concentrated hydrochloric acid. The yield of crude product was 92.0 g. (97.5%). After recrystallization from ethanol, the material melted at 109°.

Anal. Calcd. for $C_{24}H_{28}N_2O_4S_2$: C, 60.99; H, 5.97. Found: C, 60.94; H, 6.14.

Ethyl α-Carbethoxy-β-(*p*-sulfonamidoanilino)-acrylate (XV).—Eighty-six grams (0.50 mole) of sulfanilamide and 108 g. (0.50 mole) of ethoxymethylenemalonic ester were heated at 115° with stirring for a period of one-half hour. The crystalline mass obtained was recrystallized from 800 ml. of ethanol, m. p. 149°, yield 147 g. (86%).

Anal. Calcd. for $C_{14}H_{18}N_2O_6S$: C, 49.11; H, 5.26. Found: C, 49.20; H, 5.32.

Summary

1. 6,6′-bis-[4-(4-Diethylamino-1-methylbutylamino)-quinolyl] sulfide has been prepared through the ethoxymethylenemalonic ester synthesis.

2. The parallel synthesis of the analogous disulfide failed because 6,6′-bis-(3-carboxy-4-hydroxyquinolyl) disulfide could not be decarboxylated successfully.

3. The preparation of bis-(*p*-(β-carbomethoxyvinylamino)-phenyl) disulfide, bis-[*p*-(β-carbeth-

oxy-α-methylvinylamino)-phenyl] disulfide, and ethyl α-carbethoxy-β-(*p*-sulfonamidoanilino)-acrylate has been described.

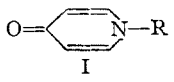
URBANA, ILLINOIS RECEIVED DECEMBER 26, 1946

[CONTRIBUTION FROM THE POLYTECHNIC INSTITUTE OF BROOKLYN AND THE RESEARCH LABORATORY OF BENZOL PRODUCTS CO.]

N-Aralkyl Derivatives of 4-Pyridone and Chelidamic Acid

BY STANLEY K. FREEMAN,[1] WILLIAM F. RINGK AND PAUL E. SPOERRI

The first simple method for the preparation of 4-pyrone was introduced by Willstätter and Pummerer[2] in 1904. This work opened a field of study that would appear to have interesting possibilities although it has not been made the subject of many investigations. Only a few reports can be found in the literature concerning N-alkyl- and N-aryl-4-pyridones (I).



I

where R is Me,[3] 1-naphthyl,[3] phenyl,[4] *p*-methoxyphenyl,[5] 4′-pyridyl.[6]

The present paper deals with the syntheses of some N-aralkyl derivatives of 4-pyridone and a few N-aralkyl chelidamic acids that were also prepared during the course of this investigation. 4-Pyrone and chelidonic acid were condensed with a number of aralkyl primary amines to form these derivatives.

9-Aminofluorene[7] and α,α-diphenylmethylamine[8] were prepared by the reduction of the oximes. Four other amines were synthesized by the catalytic reduction of the corresponding nitriles under ammonia with Raney nickel catalyst. β,β-Diphenylethylamine previously reported[9] in 30% yield was prepared in 76% yield. An attempt to synthesize this amine directly from diphenylacetamide by hydrogenating in the presence of a copper-chromium catalyst was unsuccessful. β,γ-Diphenylpropylamine was obtained in 88% yield from 1-phenylcinnamyl nitrile. The amine has been prepared[10] in 60% yield by catalytic reduction. Hydrogenation of β,β-diphenylpropionitrile resulted in 81% of γ,γ-diphenylpropylamine along with 10% of bis-(γ,γ-diphenylpropyl)-amine. According to a publication of the Department of Commerce,[11] the primary amine has been prepared in Germany during the war, but no constants or method of preparation are given. β,β-Diphenylpropionitrile has been reported[12] to melt at 100°, but we have found the melting point to be 89.5–90.5°. Carrying out the reduction of this nitrile in the absence of ammonia resulted in a 24% yield of the secondary amine which has not been recorded previously.

Experimental

9-Aminofluorene.—Fluorenone-oxime was reduced to the amine following the method of Kerp.[13]

α,α-Diphenylmethylamine.—Benzophenone-oxime[14] was catalytically reduced[8] to the amine.

Diphenylacetonitrile.—Twenty-five grams of diphenylacetyl chloride[15] was dissolved in anhydrous ethyl ether and cylinder ammonia bubbled into the cooled solution. The white diphenylacetamide was filtered off and recrystallized from a 50–50 aqueous ethanol solvent. The resultant product weighed 19 g. (83%) and melted at 168–169°. Twenty grams of the amide was then refluxed with 25 g. of thionyl chloride until solution occurred, the excess thionyl chloride distilled off, and diphenylacetonitrile taken over under vacuum. Redistilling at 178° at 12 mm. yielded 14 g. (76.7%) of a colorless solid melting at 72–73.5°.

Anal. Calcd. for $C_{14}H_{11}N$: N, 7.25. Found: N, 7.05.

β,β-Diphenylethylamine.—Thirty-five grams of diphenylacetonitrile dissolved in anhydrous ethyl alcohol was charged into a high pressure bomb and 8 g. of Raney nickel and about 20 g. of liquid ammonia were added. The compound was reduced with hydrogen at an initial pressure of 2300 lb. per sq. in. and 100°. The catalyst was filtered off and the ethanol removed with the aid of a water pump. The amine distilled over at 134° at 2 mm. as a colorless liquid solidifying on standing to a white solid weighing 26 g. (76%) and melting at 42–43.5°.

Anal. Calcd. for $C_{14}H_{15}N$: N, 7.11. Found: N, 7.08.

Diphenylacetamide failed to reduce to β,β-diphenylethylamine employing a copper-chromium catalyst at 5000 lb. per sq. in. hydrogen pressure and 275°.

β,γ-Diphenylpropylamine.—Twenty-five grams of 1-phenylcinnamyl nitrile[16] was reduced in the same manner as the aforementioned nitrile to yield 22.7 g. (88%) of the colorless amine distilling at 171° at 6 mm.

Anal. Calcd. for $C_{15}H_{17}N$: N, 6.63. Found: N, 6.60.

β,β-Diphenylpropionitrile.—This nitrile was prepared according to the method of Kohler and Reimer[12] but was purified by a vacuum distillation (178° at 4 mm.) followed by a recrystallization from anhydrous ethanol. The product melted at 89.5–90.5° and an additional recrystallization did not raise the melting point. Kohler and Reimer reported a m. p. of 100°.

Anal. Calcd. for $C_{15}H_{13}N$: N, 6.76. Found: N, 6.70.

γ,γ-Diphenylpropylamine.—Twenty-five grams of β,β-diphenylpropionitrile was catalytically reduced as above

(1) From a thesis submitted by Stanley K. Freeman in partial fulfilment of the requirements for the degree of Master of Science, Polytechnic Institute of Brooklyn, 1946.

(2) Willstätter and Pummerer, *Ber.*, **37**, 3740 (1904).

(3) Smirnoff, *Helv. Chim. Acta*, **4**, 599–612 (1921).

(4) Borsche and Bonacker, *Ber.*, **54B**, 2678–2686 (1921).

(5) Rubtsov, *J. Gen. Chem., U. S. S. R.*, **7**, 1885–1895 (1937).

(6) Arndt and Kalischek, *Ber.*, **63**, 592 (1930).

(7) Schmidt and Soll, *Ber.*, **40**, 4258–4259 (1907).

(8) Winans, THIS JOURNAL, **55**, 2051 (1931).

(9) Rupe and Gisiger, *Helv. Chim. Acta.*, **8**, 338–351 (1925).

(10) Braun, Bayer and Cassel, *Ber.*, **60B**, 2602–2609 (1927).

(11) Office of the Publication Board, Department of Commerce, Report No. PB-981, p. 39.

(12) Kohler and Reimer, *Am. Chem. J.*, **33**, 338 (1905).

(13) Kerp, *Ber.*, **29**, 231 (1896).

(14) "Organic Syntheses," Coll. Vol. II, p. 70 (1943).

(15) Staudinger, *Ber.*, **44**, 1620 (1911).

(16) Freund, *Ber.*, **23**, 2859 (1890).