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

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(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) Borshe 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).

to yield 20.7 g. (81%) of the amine, distilling at 150° at 2 mm. The amine rapidly picks up carbon dioxide from the air to form a white solid carbonate, but this can be prevented by distilling and storing under nitrogen.

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

The hydrochloride of the amine was recrystallized from anhydrous ethanol and melted at 217.5–218.5°.

Anal. Calcd. for $C_{15}H_{18}NCl$: N, 5.66; Cl, 14.34. Found: N, 5.59; Cl, 14.33.

bis-(γ,γ-Diphenylpropyl)-amine.—Upon reducing β,β-diphenylpropionitrile under ammonia, 10% of the secondary amine was obtained which distilled at 270° at 2 mm. Hydrogenating in the absence of ammonia increased the yield to 24%.

Anal. Calcd. for $C_{30}H_{31}N$: N, 3.46. Found: N, 3.42.

The hydrochloride of the amine melted at 193–194° after one recrystallization from ethanol.

Anal. Calcd. for $C_{30}H_{32}NCl$: N, 3.17; Cl, 8.06. Found: N, 3.10; Cl, 8.04.

4-Pyrone.—Chelidonic acid[17] was decarboxylated to 4-pyrone.[2]

N-(9-Aminofluorenyl)-4-pyridone.—To 50 ml. of anhydrous ethanol in a 100-ml. beaker were added 1 g. of 4-pyrone and 1.91 g. of 9-aminofluorene. The solution was evaporated down to about 10 ml., cooled and filtered. The pale yellow crystals were recrystallized twice from benzene yielding 1.1 g. (41%) of a white product melting at 177° dec.

Anal. Calcd. for $C_{18}H_{13}NO$: N, 5.36. Found: N, 5.30.

The following N-substituted 4-pyridones were prepared in the same manner.

N-(α,α-Diphenylmethyl)-4-pyridone.—α,α-Diphenylmethylamine was condensed with 4-pyrone to yield 42.3% of a product which melted at 169.5–170.5° after two recrystallizations from benzene.

Anal. Calcd. for $C_{18}H_{15}NO$: N, 5.33. Found: N, 5.48.

N-(β,β-Diphenylethyl)-4-pyridone.—β,β-Diphenylethylamine and 4-pyrone yielded 31% of a nearly white material melting at 159–160° following two recrystallizations from benzene.

Anal. Calcd. for $C_{19}H_{17}NO$: N, 5.10. Found: N, 5.00.

N-(γ,γ-Diphenylpropyl)-4-pyridone.—Condensing, γ,γ-diphenylpropylamine and 4-pyrone yielded a light brown viscous liquid that resisted attempts to purify it.

N-(β,γ-Diphenylpropyl)-4-pyridone.—Condensation experiments with β,γ-diphenylpropylamine and 4-pyrone yielded viscous liquids similar to that described above.

Attempts to prepare salts of the last two compounds resulted in the formation of brownish-red oils that could not be characterized.

N-(α,α-Diphenylmethyl)-chelidamic Acid.—Condensation was effected by treating 1.8 g. of chelidonic acid with 1.8 g. of α,α-diphenylmethylamine in 50 ml. of anhydrous ethanol. The pale yellow solid that formed after evaporating down the solution was washed with ethanol and yielded 2.8 g. (84%) of a white solid melting at 210° dec.

Anal. Calcd. for $C_{20}H_{15}NO_5$: N, 4.01. Found: N, 3.75.

N-(β,γ-Diphenylpropyl)-chelidamic Acid.—Equimolar amounts of β,γ-diphenylpropylamine and chelidonic acid were condensed as above to yield 76.6% of a pale yellow solid melting at 210° dec.

Anal. Calcd. for $C_{22}H_{19}NO_5$: N, 3.63. Found: N, 3.67.

N-(γ,γ-Diphenylpropyl)-chelidamic Acid.—γ,γ-Diphenylpropylamine and chelidonic acid were condensed to yield 79% of a nearly colorless product melting at 220° dec.

Anal. Calcd. for $C_{22}H_{19}NO_5$: N, 3.63. Found: N, 3.40.

Summary

1. Five new N-aralkyl-4-pyridones have been synthesized: α,α-diphenylmethyl-, β,β-diphenylethyl-, 9-aminofluorenyl-, β,γ-diphenylpropyl- and γ,γ-diphenylpropyl-. The latter two are viscous liquids that resisted attempts to purify them.

2. Three new N-aralkyl chelidamic acids were also prepared: α,α-diphenylmethyl-, β,γ-diphenylpropyl- and γ,γ-diphenylpropyl-.

3. The yields of β,β-diphenylethylamine and β,γ-diphenylpropylamine prepared from their nitriles has been increased over those reported in the literature.

4. The methods of preparation and constants of γ,γ-diphenylpropylamine and bis-(γ,γ-diphenylpropyl)-amine and their hydrochlorides are described for the first time.

BROOKLYN, N. Y. RECEIVED NOVEMBER 1, 1946

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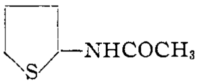
[17] "Organic Syntheses," Coll. Vol. II, p. 126 (1943).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Diazo Reactions in the Thiophene and Furan Series

BY CHARLES D. HURD AND HILL M. PRIESTLEY[1]

One of the rules in dye chemistry is that when an arylamine is acetylated, its power to couple with diazonium salts is destroyed. Thus, aniline will couple but acetanilide will not.[2] The present investigation has demonstrated that this limitation does not apply to the thiophene or furan series. Aceto-2-thiophenamide[3] (I), the thiophene analog of acetanilide, couples rapidly with sodium *p*-nitrobenzenediazotate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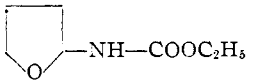
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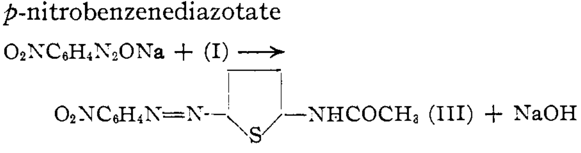

Still more remarkable is the fact that the coupling may be carried out with *p*-nitrobenzenediazonium

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[1] Present address: Pepsodent (Lever Brothers), Chicago, Illinois.

[2] König and Kohler, *Ber.*, **54**, 981 (1921), obtained a 20% yield of an azo dye by allowing to react for five days at 0° a mixture of diazotized *p*-nitroaniline and aceto-1-naphthylamide.

[3] The names aceto-2-thiophenamide and 2-thiophenamine are used in preference to the abridged names aceto-2-thiophenide and 2-thiophenine, respectively.