identical with those observed for these solutions can be obtained by linear combination of curves A and N. The acid form (A) is stable in acid solutions and exists in (rapidly reversible) equilibrium with the neutral form (N) in solutions of intermediate acidity.

In basic solutions pheophytin undergoes an irreversible reaction producing a single substance whose absorption spectrum is represented by curve B. If a basic solution containing this reaction product is neutralized with acid, the absorption spectrum of the resulting solution has its principal maxima at λ4120 and 6480 Å. In dilute solutions of strong base (or of moderate concentrations of aliphatic amines), the irreversible reaction of pheophytin to form the product (B) is measurably slow. There is no evidence for the transient existence, in any of these solutions, of a reversible, intermediate basic form of pheophytin.

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N-Phenylpyrrolidine[1]

BY CARL J. OLSEN AND ARTHUR FURST[2]

RECEIVED FEBRUARY 2, 1953

By passing tetrahydrofuran and aniline over activated alumina at 400°, Yur'ev and Minkina[3] obtained N-phenylpyrrolidine in 45.5% yield. Bourns, Embleton and Hansuld,[4] by carefully controlling feed rate, molar ratios and temperature conditions, increased the yield to 88%.

A study was made to see if the desired product could be obtained by merely heating tetrahydrofuran and aniline in an autoclave with a Lewis acid. When aluminum chloride was used as a catalyst N-phenylpyrrolidine was obtained in 42% yield. It was subsequently found possible to obtain a 20% yield in the presence of aluminum chloride at atmospheric pressure.

Experimental

Pressure Reaction.—A mixture of 4.0 g. (0.043 mole) of aniline, 5.7 g. (0.054 mole) of anhydrous aluminum chloride and 4.0 g. (0.056 mole) of tetrahydrofuran was placed in an autoclave, and the pressure was brought up to 1000 lb./sq. in. with nitrogen gas. The mixture was heated to 240° and rocked for 24 hours. The amber colored semi-solid reaction product was made basic with sodium hydroxide solution and extracted with ether. The ether was removed and N-phenylpyrrolidine was recovered by distillation under reduced pressure; b.p. 106–109° (6 mm.), yield 2.7 g. (0.018 mole) or 42.6%, m.p. *ca.* 13°, picrate, m.p. 116–118°, lit. value[3] 116°. No depression of melting point was noted when authentic picrate was mixed with product above.

Other catalysts used and yields were: hydrogen chloride (3.2%), sulfuric acid (no yield), phosphorus pentoxide (31.6%), activated alumina (no yield).

Atmospheric Pressure.—Anhydrous aluminum chloride, 28.5 g. (0.210 mole), was added in portions to 20.0 g. (0.215 mole) of aniline. The temperature rose to *ca.* 150°. With constant stirring, 20.0 g. (0.276 mole) of tetrahydrofuran was added drop by drop. The solution darkened. The temperature was maintained at 150–160° by heating. After one-third of the tetrahydrofuran was added the temperature dropped. The reaction mixture was heated to reflux and the remainder of the tetrahydrofuran added. Refluxing was continued two more hours.

On cooling, the solution was made basic, steam distilled, and the distillate extracted with ether. A yield of 6.1 g. (0.042 mole), 19.8%, N-phenylpyrrolidine was obtained.

Acknowledgment.—This investigation was supported by a grant-in-aid from the Research Corporation. Tetrahydrofuran was kindly supplied by E. I. du Pont de Nemours and Co.

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[1] Taken in part from the Master of Science Thesis of Carl J. Olsen, June, 1952.

[2] Department of Pharmacology and Therapeutics, Stanford University School of Medicine, San Francisco, California.

[3] Yu. K. Yur'ev and G. A. Minkina, *J. Gen. Chem.* (*USSR*), **1**, 2945 (1937); *C. A.*, **32**, 5399 (1938).

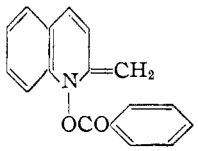
[4] A. N. Bourns, H. W. Embleton and M. K. Hansuld, *Can. J. Chem.*, **30**, 1 (1952).

The Benzoylation of Quinaldine Oxide

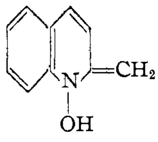
BY IRWIN J. PACHTER

RECEIVED FEBRUARY 27, 1953

The reaction of quinaldine oxide (I) with benzoyl chloride and sodium hydroxide was investigated by Henze[1] who obtained a compound, $C_{17}H_{13}NO_2$, which was formulated as IIa. Upon treatment with either acid or alkali the compound was converted to a new substance, $C_{10}H_9NO$, isomeric with quinaldine oxide. This substance reacted with Fehling solution and Tollens reagent, but not with phenylhydrazine or hydroxylamine. Structure IIIa was suggested for the debenzoylated product.[1]



IIa



IIIa

A substance of structure IIIa would undergo facile tautomerism to quinaldine oxide, particularly under the conditions employed in effecting debenzoylation. It may therefore be discounted as a possibility. A more likely product would be 2-quinolinemethanol (IIIb) which, being analogous to an α-ketol, would be expected to undergo oxidation in Fehling solution and Tollens reagent. A reaction scheme for the formation of IIIb, involving attack of hydroxyl ion or water on the methylene group of IIa with concurrent elimination of benzoate ion or benzoic acid, can readily be formulated.

The syntheses described by Henze were repeated. The identity of the debenzoylated product with a sample of 2-quinolinemethanol prepared from methyl quinaldate by reduction with lithium aluminum hydride[2,3] was established by mixture melting point determination and infrared spectroscopy.

The infrared spectrum of the compound formulated as IIa was examined. The absence of bands indicative of a terminal methylene group suggested that the product might be 2-quinolinemethyl benzoate (IIb). To test this possibility, IIIb was rebenzoylated. The compound thus obtained was

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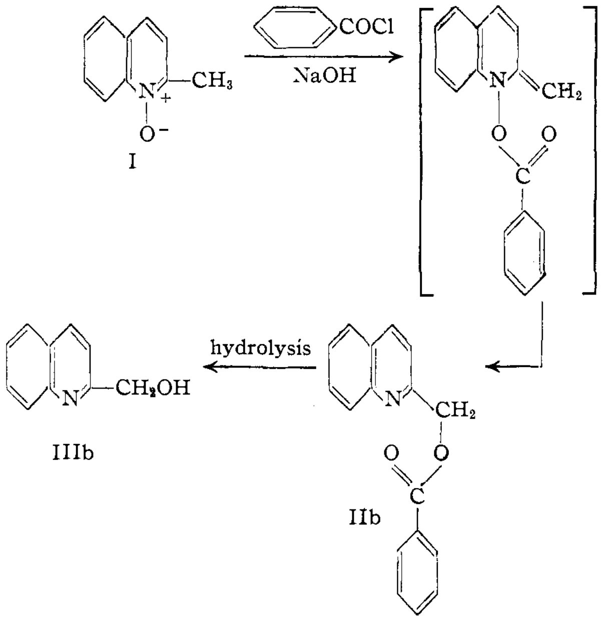
[1] M. Henze, *Ber.*, **69**, 534 (1936).

[2] C. E. Kaslow and W. R. Clark, *J. Org. Chem.*, **18**, 55 (1953).

[3] The author is grateful to Professor C. E. Kaslow for supplying this authentic sample.

found to be identical with that formed directly from quinaldine oxide and benzoyl chloride. Reaction with rearrangement thus occurs when quinaldine oxide is treated with benzoyl chloride. The subsequent formation of IIIb from IIb is the result of simple hydrolysis.



In isolating IIb, Henze acidified the benzoylation product with hydrochloric acid, purified the hydrochloride, and then liberated IIb with alkali. It was possible that the acidification transformed initially-formed IIa to IIb. An experiment avoiding acidification was therefore performed. The product isolated directly from the alkaline benzoylation mixture proved to be identical with that obtained *via* the hydrochloride.

A simplified method for the preparation and purification of quinaldine oxide hydrate is described.

Experimental[4]

Quinaldine Oxide Hydrate.—To 20 g. of freshly distilled quinaldine was added 22 g. of 30% aqueous hydrogen peroxide and 60 ml. of acetic acid. The solution was heated at 55° for 20 hours. It was then cooled in ice and slowly treated with a solution of 80 g. of potassium hydroxide in 100 ml. of water. Quinaldine oxide hydrate separated as a dark oil and soon solidified. It was filtered and the filtrate was extracted with 30 ml. of chloroform. The chloroform was evaporated from the extract and the residue was combined with the main product and added to 300 ml. of benzene. The mixture was distilled until water no longer came over with the benzene. The light yellow benzene solution was then decanted from dark brown insoluble materials, cooled, and stirred with a few ml. of water. The quinaldine oxide hydrate, which separated as almost colorless needles, was filtered and dried to give 16.2 g. of product, m.p. 75–76°. Recrystallization from water raised the m.p. to 77–78°.

2-Quinolinemethyl Benzoate.—To 0.5 g. of 2-quinolinemethanol was added 20 ml. of water, 2 ml. of 10% aqueous sodium hydroxide and 0.5 g. of benzoyl chloride. The mixture was stirred until the pale yellow oil solidified. The product was filtered and recrystallized from aqueous methanol to form clusters of almost colorless plates, m.p. 52–53°. The infrared spectrum and m.p. of the compound were identical with those of the product obtained from the reaction of quinaldine oxide hydrate with benzoyl chloride. There was no depression of m.p. upon admixture of the two samples.

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[4] It was reported[1] that the debenzoylated compound, now formulated as IIIb, gives a red color with ferric chloride in the alcoholic solution. In the present work, a yellow precipitate, but no red color, was observed. In other experiments, the results reported by Henze were obtained.

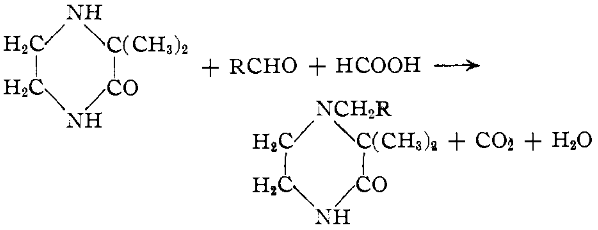
Leuckart Alkylation of 2-Piperazinones[1]

BY PHILIP RUBY AND PETER L. DEBENNEVILLE

RECEIVED FEBRUARY 20, 1953

The availability of 2-piperazinones by a new method developed in these laboratories,[2] suggested the possibility of alkylation on the amine nitrogens under Leuckart conditions. In this way, the amide nitrogen could be the site for a desired methylolation reaction without the complication of resin formation from the secondary amino group.

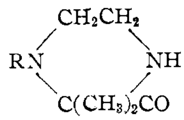
The alkylation may be illustrated by the series of compounds prepared from 3,3-dimethyl-2-piperazinone.[3]



Data for these reactions are given in Table I. Reaction proceeded smoothly at temperatures of 100–130°, resulting in good yields when aldehydes were used. Ketones failed to react even at high temperatures, and in all three cases tried, 4-formyl-2-piperazinone was the only product. The failure of ketones to react can probably be ascribed to the methyl groups in the 3-position, as well as to the fact that the piperazinone is a secondary amine. It has been noted that in the sequence ammonia, methylamine and dimethylamine, yields of 78,

TABLE I

ALKYLATED 3,3-DIMETHYL-2-PIPERAZINONES



R	Yield, %	M.p., °C.[a]	Empirical formula	Nitrogen,[b] % Calcd.	Found
Methyl	72	131–132	$C_7H_{14}N_2O$	19.7	19.2
Ethyl	27	164–165	$C_8H_{16}N_2O$	17.9	17.6
Isobutyl	60	136–138	$C_{10}H_{20}N_2O$	15.2	15.1
p-Chlorobenzyl	56	201–203	$C_{13}H_{17}N_2OCl$	11.1[c]	11.0[c]
3,4-Methylenedioxybenzyl[d]	35	190–193	$C_{14}H_{18}N_2O_3$	10.6	10.5
3,5,5-Trimethylhexyl	73	99–100	$C_{15}H_{30}N_2O$	11.1	11.2

[a] Uncorrected. [b] Kjeldahl method. [c] Calcd. for $C_{13}H_{17}N_2OCl$: Cl, 14.0. Found: Cl, 13.7. [d] From piperonal.

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[1] Communications should be directed to Peter L. deBenneville, Rohm & Haas Co., 5000 Richmond St., Philadelphia, Pa.

[2] V. T. Elkind, J. S. Strong and W. E. Craig, private communication.

[3] S. R. Aspinall, THIS JOURNAL, **62**, 1203 (1940).