mercury is employed instead of an amalgam, an acid-resisting film is formed the ordinary life of which, however, is shorter than that of films formed with complex liquid amalgams.

The complex amalgam employed may be almost any dilute mercury solution. One such is a mixture of 5 g. of solder, 5 g. of Wood's metal, 2.5 g. of zinc and 80 g. of mercury, solution being effected with heat. Such a liquid also has the curious property of wetting clean, polished glass surfaces with ease.

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STUDIES IN QUINOLINE SYNTHESES

BY WILLIAM LYALL BARR

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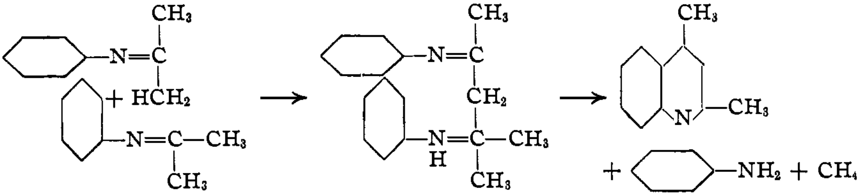
Historical.—The Skraup synthesis is variously formulated as involving intermediate formation of (I) acrolein anil, (II) β-anilinopropionaldehyde or (III) the anil of this aldehyde. The literature affords no definite evidence for the formation of a type I intermediate; there are results compatible with the formation of an intermediate of either type II or type III, but not of type I. Thus Murmann[1] obtained 2-phenylquinoline, not 4-phenylquinoline, by the condensation and oxidation of cinnamaldehyde and aniline, and Blaise and Maire[2] formed 4-ethylquinoline from anilinoethyl ethyl ketone heated with aniline hydrochloride.

From the work of Beyer, Engler and Riehm, and Knoevenagel, the last named investigator has shown[3] that quinoline formation from simple ketones or aldehydes and aromatic amines proceeds by the intermediate formation of ketylidene or alkylidene anils, which form dimerides and then quinoline derivatives; *e. g.*, from aniline and acetone



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[1] Murmann, *Monatsh.*, **25**, 621 (1904).

[2] Blaise and Maire, *Bull. soc. chim.*, [4] **3**, 658, 667 (1908).

[3] Beyer, *J. prakt. Chem.*, [2] **31**, 47 (1885); **32**, 125 (1885); **33**, 393 (1886); *Ber.*, **20**, 1767 (1887); Engler and Riehm, *ibid.*, **18**, 2245 (1885); Knoevenagel and v. Baehr, *ibid.*, **55**, 1912 (1922); Knoevenagel and Goos, *ibid.*, **55**, 1929 (1922); Knoevenagel, Wagner and v. Baehr, *ibid.*, **56**, 2414 (1923).

Any mesityl oxide or similar condensation product of the aldehyde or ketone is broken down to give the simple anil. The dimerides here mentioned are akin to the type III intermediate.

Another piece of evidence for the formation of the type III intermediate is the production of quinoline by König and Seifert[4] from $C_6H_5NHCH=CHCH=NC_6H_5$ heated with zinc chloride.

Theoretical.—Formation of a type I compound would involve reaction at only one double bond of a conjugate system, which is improbable, especially at a high temperature. Condensation of aniline with acrolein may be expected to be by the usual 1,4-addition. Polarity effects would lead to $C_6H_5NHCH_2CH=CHOH$, which can rearrange to the type II compound; but at the high temperature of the reaction, in the presence of aniline and the dehydrating agent, sulfuric acid, it is exceedingly unlikely that the aldehyde group would remain unattacked during the comparatively slow process of ring formation. Furthermore, as will be shown later, β-anilinopropionaldehyde polymerizes spontaneously to a substance from which no quinoline can be obtained.

Interaction of this aldehyde with aniline, however, would yield the type III compound, able to form quinoline by oxidation and splitting off of aniline, as shown by the work of Knoevenagel and of König and Seifert.

Experimental

In this work quinoline was detected in neutral aqueous emulsion or solution by the production with potassiomercuric iodide solution of a white amorphous precipitate which became yellow and crystalline on addition of dilute hydrochloric acid.[5] Recrystallized from hot water, this precipitate from quinoline melted at 144–146°.

The product of the direct interaction of acrolein and aniline, described by Mann,[6] was first studied; the observations that this base yielded no quinoline on treatment with sulfuric acid and arsenic oxide or nitrobenzene (Mann) or chromic acid (König) were confirmed. A similar negative result was found on oxidation with acid permanganate or ferric chloride. This base, $C_{18}H_{20}ON_2$, is evidently far more complex than the Skraup intermediate.

An attempt was made to carry out the series of reactions

$$C_6H_5NH_2 + ClCH_2CH_2CH(OEt)_2 \longrightarrow C_6H_5NHCH_2CH_2CHO \longrightarrow C_6H_5NHCH_2CH_2CH=NC_6H_5$$

Raeth's work[7] on this type of condensation of chloro-acetals with aromatic amines is spoiled by inconsistent nomenclature; and König and

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[4] König and Seifert, *Ber.*, **56**, 1853 (1923).

[5] Donath, *ibid.*, **14**, 1769 (1881).

[6] Mann, *J. Chem. Soc.*, **121**, 2178 (1922).

[7] Raeth, *Ber.*, **57**, 550, 715 (1924).

Buchheim[8] have shown that in some of his work Raeth failed to identify the product correctly, and that no cyclization had occurred.

Direct interaction in dry ethereal solution of 1 mole of aniline and 1 mole of β-chloropropionacetal yielded aniline hydrochloride and, presumably, acrolein acetal. Use of excess aniline (2.5 moles) yielded aniline hydrochloride and a brown viscous liquid which, after removal of most of the aniline by distillation *in vacuo*, changed to a dark red solid gum, soluble in alcohol and acetone, which would not crystallize or distil without decomposition even *in vacuo*. The last traces of aniline could not be removed; yield, 20–25%; N, 7.0% (anilinopropionacetal, N, 6.3%). This crude residue yielded a tiny amount of quinoline on treatment with sulfuric acid and arsenic oxide or nitrobenzene. As free aniline was present, no conclusion can be drawn as to the mechanism of the reaction.

Acid hydrolysis of this substance yielded, instead of β-anilinopropionaldehyde, a pink sticky gum which gave no aldehyde tests. An apparent polymer of this aldehyde was obtained by interaction of the chloro-acetal and a large excess of aniline in ether shaken with a saturated solution of sodium bicarbonate; distillation of the mixed bases in steam removed aniline and effected hydrolysis, leaving a brown resin soluble only in acetone and nitrobenzene; N, 9.4%; mol. wt. in nitrobenzene, 495 (anilinopropionaldehyde, N, 9.4%; mol. wt., 149). This aniline-free substance yielded no quinoline.

All attempts to condense the crude anilinopropionacetal base with aniline by the action of concd. hydrochloric acid or 70% sulfuric acid proved unsuccessful. Hence the type III intermediate was not obtained, and no conclusion can be drawn as to its place in the Skraup synthesis.

Attempts were made to effect cyclization with propionanilide and with allylaniline.

Propionanilide could not be made to undergo ring formation by heating with zinc dust, or with nitrobenzene and zinc chloride or sulfuric acid; nor by passing through a hot tube in air alone or over lead oxide.

Koenigs[9] obtained quinoline from allylaniline vapor passed over lead oxide in a hot tube. Cyclization to quinoline was attempted under the conditions of the Skraup reaction.

Ten g. of allylaniline and 20 g. of sulfuric acid with 8 g. of nitrobenzene or 20 g. of arsenic oxide dried at 170° were refluxed for several hours, and the dark viscous mixture worked up for quinoline. There was much charring and production of tarry matter. Quinoline was detected in small quantities in every case; yield, about 1%. Picric acid was tried in place of nitrobenzene (*vide* Murmann), but it made the reaction explosively violent.

Based on a preparation of acrolein by Wohl and Mylo[10] from glycerol vapor passed over heated magnesium sulfate, a synthesis of quinoline was attempted from the vapors of aniline and glycerol aspirated in air or carbon dioxide over magnesium sulfate at 370–400°, with nitrobenzene vapor or lead oxide as oxidizing agent. No quinoline could be detected in the products of the reaction.

To try to reduce the number of distillations in steam in the Skraup synthesis from three to two, transformation of excess aniline to phenol with nitrous acid was tried in the

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[8] König and Buchheim, *Ber.*, **58**, 2868 (1925).

[9] Koenigs, *ibid.*, **12**, 453 (1879).

[10] Wohl and Mylo, *ibid.*, **45**, 2046 (1912).

acid reaction mixture after distillation in steam to remove nitrobenzene and dilution with water. These attempts were unsuccessful, for though excess nitrous acid was shown to be present, the resulting quinoline contained a considerable amount of aniline. The destruction of aniline was incomplete even with the clear reaction mixture obtained by the method of Cohn and Gustavson.[11]

The author wishes to express his grateful thanks to Dr. J. K. H. Inglis for his kind interest and helpful advice in this investigation.

Summary

1. As neither β-anilinopropionaldehyde nor its acetal or anil could be obtained pure, nothing can be concluded as to the constitution of the Skraup intermediate.

2. Allylaniline can yield small quantities of quinoline by oxidation in solution.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

NITRIDATION STUDIES. I. INTRODUCTION. II. MERCURIC NITRIDE AND BISMUTH NITRIDE AS NITRIDIZING AGENTS[1]

BY IMAN SCHURMAN AND W. CONARD FERNELIUS

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I. INTRODUCTION

The term "nitridation" or "nitridation reaction"[2] has been applied to all those reactions which for the ammonia system of compounds are essentially similar to oxidation reactions for the familiar water compounds or for those reactions in which nitrogen plays a part analogous to that played by oxygen in ordinary simple processes of oxidation.

Numerous examples of nitridation reactions are known.[3]

The only agents to be examined to any extent, however, are hydrazoic

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[11] Cohn and Gustavson, THIS JOURNAL, **50**, 2709 (1928).

[1] The material presented in this paper is from a portion of a thesis submitted by Iman Schurman in partial fulfilment of the requirements for the Degree of Master of Science at The Ohio State University.

[2] (a) Browne and Welsh, THIS JOURNAL, **33**, 1728 (1911); Franklin, *J. Phys. Chem.*, **27**, 169 (1923); *cf.* Goldberg, THIS JOURNAL, **34**, 886 (1912). Turrentine [*ibid.*, **34**, 386 (1912)] calls hydrazoic acid a nitridizing agent because many of the reactions of hydrazoic acid are similar to those of nitric acid, an oxidizing agent. (b) Cady and Taft [*Science*, **62**, 403 (1925)] have proposed the terms "electronation" and "delectronation" to be used in place of "reduction" and "oxidation" in the broad sense. Accordingly "nitridation" would be a particular type of "delectronation."

[3] Franklin, *J. Phys. Chem.*, **27**, 169 (1923); THIS JOURNAL, **46**, 2142 (1924); "Reactions in Liquid Ammonia," Columbia University Press, New York, **1927**, p. 16; Bergstrom, THIS JOURNAL, **48**, 2324 (1926); *J. Phys. Chem.*, **32**, 440 (1928); Strain, THIS JOURNAL, **49**, 1558 (1927); **50**, 2220 (1928); **51**, 271 (1929); Chuck, "Dissertation," Stanford University, **1925**; Turrentine, Ref. 2a; Goldberg, Ref. 2a.