standard. The new Coleman Regional Spectrophotometer was used. The accuracy of the instrument compares very favorably with that of other apparatus, usually visual in operation, used for the same purpose. The compounds were weighed directly into volumetric flasks, made up to volume, and an aliquot taken if necessary. The concentrations used were in the neighborhood of  $0.001 \ M$ . The extinction coefficients were calculated from Beer's law.

## Summary

1. Several new copper inner complexes of closely related ortho-hydroxy azo dyes of 2-naph-thol have been prepared.

2. The complexes have been isolated in the crystalline state and are all sufficiently soluble in organic solvents to permit absorption spectra measurements.

3. The absorption spectra of phenanthrenequinone monoxime, chrysenequinone monoxime, and ten of their metal inner complexes were measured in pyridine solution and the observed variations discussed.

4. The absorption spectra of thirteen orthohydroxy azo dyes and the thirteen corresponding copper inner complexes were measured in nitrobenzene and the observed variations discussed.

5. The color of the inner complexes in both cases is apparently influenced less by the character of the substituent group in the organic portion than by the formation of the chelate bond.

SEATTLE, WASHINGTON RECEIVED MARCH 15, 1940

[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

## $\alpha$ - and $\beta$ -N-Dialkylamino- $\alpha$ , $\beta$ -unsaturated Ketones

By Norman H. Cromwell

Although  $\beta$  - N - dialkylamino -  $\alpha$ , $\beta$ -unsaturated ketones have been prepared by André,<sup>1</sup> by adding secondary amines to phenylacylacetylenes, it seems desirable to use cheaper, more readily obtainable starting materials.

The condensation of benzoylacetone with ammonia and primary amines has been shown by Beyer<sup>2</sup> to give 1-phenyl-3-aminobutene-2-one-1 and 1-phenyl-3-N-alkylaminobutene-2-one-1, respectively, or their tautomeric imines. Also Combes<sup>3</sup> has shown that acetylacetone could be condensed with diethylamine to give 2-N-diethylamino-pentene-2-one-4.

The investigation of Ruhemann and Watson<sup>4</sup> has led these workers to the conclusion that dibromobenzalacetophenone reacted with ammonia and amines to give  $\beta$ -amino- $\alpha$ , $\beta$ -unsaturated ketones. The more recent work of Dufraisse, *et al.*,<sup>5</sup> has shown conclusively that the main product from this type of reaction is not the  $\beta$ - but the  $\alpha$ -amino- $\alpha$ , $\beta$ -unsaturated ketone. Dufraisse was interested in this reaction, mainly, as a means of preparing 1,2-diketones.

The research described in the present paper is

(1) André, Compt. rend., 152, 525 (1911); Ann. chim., [8] 29, 575 (1913).

an extension of these methods to the preparation of the following unsaturated amino ketones

$$\begin{array}{cccc} C_{6}H_{5} & -CO & -CH = C - CH_{3} \\ & & & & \\ & & & N(C_{2}H_{5})_{2} \\ I \\ C_{6}H_{5} & -CH = C - COC_{6}H_{5} \\ & & & & C_{6}H_{5}COCH = C - C_{6}H_{5} \\ & & & & \\ & & N(C_{2}H_{5})_{2} \\ & & & N(C_{2}H_{5})_{2} \\ II \\ III \\ \end{array}$$

The unsaturated amino-ketone II was prepared from the corresponding dibromide, while I and III were prepared by the condensation of diethylamine with the corresponding 1,3-diketones. The yield of compound III was too low to make this method of preparative value, and is reported here merely for reasons of comparison with the readily obtainable compound I. Both of these condensations had to be carried out in sealed tubes above 100°.

The structure of II was elucidated by its hydrolysis to the corresponding 1,2-diketone, which was identified through a suitable derivative. The structure of I was apparent by analogy with the investigations of Beyer,<sup>2</sup> while III had been prepared from benzoyl-phenylacetylene, previously, by André.<sup>1</sup>

The study of these two reactions and their products is being extended.

<sup>(2)</sup> Beyer, Ber., 20, 2180 (1887); ibid., 24, 1669 (1891).

<sup>(3)</sup> Combes and Combes, Bull. soc. chim., [3] 7, 778 (1892).

<sup>(4)</sup> Ruhemann and Watson, J. Chem. Soc., 85, 1181 (1904).

<sup>(5)</sup> Dufraisse and Moureu, Bull. soc. chim., [4] 41, 861 (1927).

# Experimental<sup>6</sup>

(I) 1-Phenyl-3-N-diethylaminobutene-2-one-1.—A mixture of benzoylacetone (5 g.), diethylamine (4.5 g., a one mol excess), and one small drop of concd. hydrochloric acid was heated ( $110^{\circ}$ ) in a sealed tube for thirty-six hours, and then allowed to stand at room temperature for ten days. The light orange solution was dissolved in ether and shaken with several portions of water to remove excess diethylamine. Most of the unreacted benzoylacetone was also removed in this process. Evaporation of the ether gave light yellow crystals (4.1 g.) which on recrystallization from low boiling petroleum ether gave almost colorless rods, m. p. 70-71°.

Anal. Calcd. for  $C_{14}H_{19}NO$ : N, 6.45; C, 77.36; H, 8.82. Found: N, 6.40; C, 77.48; H, 8.84.

This compound gave clear solutions with dilute mineral acids, which on heating reformed benzoylacetone.

(II)  $\alpha$ -N-Diethylaminobenzalacetophenone.---To a cooled (0°) absolute ethyl alcohol (20 ml.) suspension of benzalacetophenone dibromide (20 g.), diethylamine (12.0 g., a two mol excess) was added rapidly with stirring. The dibromide dissolved and the solution turned a deep red color, evolving some heat. After standing at room temperature for eighteen hours the precipitated diethylamine hydrobromide (16.5 g.) was filtered from the mixture with the addition of dry ether to the solution. Evaporation of the solvent *in vacuo* gave a red oil, which crystallized on adding low boiling petroleum ether to give orange-red crystals (13.5 g.), m. p. 50–54°. Recrystallization from low boiling petroleum ether gave orange rosets, m. p. 51–53°.

Anal. Caled. for  $C_{19}H_{21}NO$ : N, 5.01; C, 81.67; H, 7.58. Found: N, 5.00; C, 81.65; H, 7.60.

This product darkened on standing and developed an isocyanide-like odor. Its ether solution precipitated a color-

(6) All analyses for nitrogen were determined by the Kjeldahl method by Mr. Clifford Hollenbeck of the Graduate College of the University of Nebraska, and micro C-H analyses by Mr. Edward Renfrew of the University of Minnesota. less hydrochloride with dry hydrogen chloride, m. p.  $106-110^{\circ}$ , which dissolved in water to precipitate the orange unsaturated amino ketone.

**Hydrolysis of (II)**.—Freshly recrystallized (II) (2.0 g.) was heated on the steam-bath (thirty minutes) with 15% sulfuric acid (25 cc.). The product was an oily solid (1.4 g.) which on recrystallizing from dilute alcohol gave colorless needles; m. p.  $60-63^{\circ}$ . This product gave better than a 90% yield of the phenylenediamine derivative of benzyl phenyl diketone, m. p.  $98-99^{\circ}$ .<sup>7</sup>

(III)  $\beta$ -N-Diethylaminobenzalacetophenone.—A mixture of dibenzoylmethane (5 g.), diethylamine (3.26 g., a one mol excess), and one small drop of concd. hydrochloric acid was heated  $(150^{\circ})$  in a sealed tube for sixty-six hours, and then allowed to stand at room temperature for sixteen days. The reaction mixture was worked up as for (I) to give a light yellow oil from which only dibenzoylmethane could be crystallized. However, on dissolving this oil in dry ether and passing in dry hydrogen chloride an oily hydrochloride was precipitated. This product was well washed with ether and then decomposed in a saturated solution of sodium bicarbonate. This decomposition was carried out in a separatory funnel in the presence of ether, and the precipitated amino-ketone was immediately extracted from the aqueous layer. Evaporation of the ether gave an almost colorless solid (0.65 g.), m. p. 58-59°, which on recrystallization from low boiling petroleum ether gave almost colorless rods, m. p. 61–62°. The product had all of the properties of the product of André,1 being completely soluble in mineral acids, from which it is precipitated unchanged by dilute alkali.

#### Summary

One new  $\alpha$ -dialkylamino- $\alpha,\beta$ -unsaturated ketone, and a new  $\beta$ -dialkylamino- $\alpha,\beta$ -unsaturated ketone have been prepared from readily available starting materials, in good yields.

(7) Jörlander, Ber., 50, 416 (1917).

LINCOLN, NEBRASKA RECEIVED APRIL 8, 1940

#### [CONTRIBUTION FROM THE RESEARCH LABORATORIES OF MERCK & Co., INC.]

# Erythrina Alkaloids. VIII. Studies on the Constitution of Erythramine and Erythraline

## BY KARL FOLKERS AND FRANK KONIUSZY

Erythramine was isolated originally from the seeds of *Erythrina sandwicensis* Deg. and *Erythrina subumbrans* (Hassk.) Merr.<sup>1</sup> It was later isolated from the seeds of *Erythrina glauca* Willd. together with erythraline and erythratine,<sup>2</sup> and the alkaloid erythraline was isolated from five additional species of *Erythrina*. Although the isolation of erythramine from *Erythrina glauca* was facilitated by large amounts of seeds, it is

probable that many species which have yielded and will yield erythraline also contain erythramine. Since these species yielding erythramine and erythraline represent several groups and subgroups of the genus,<sup>3</sup> it seems probable that knowledge on the constitution of these two alkaloids will be significant for at least one broad group of *Erythrina* alkaloids.

<sup>(1)</sup> Folkers and Koniuszy, THIS JOURNAL, 61, 1232 (1939).

<sup>(2)</sup> Folkers and Koniuszy, ibid., 62, 436 (1940).

<sup>(3)</sup> Krukoff, Brittonia, 3, No. 2, 205 (1939); Krukoff, J. Arnold Arboretum, 20, 225 (1939); Folkers and Unna, J. Am. Pharm. Assoc., 28, 1019 (1939).