added slowly with stirring and cooling 116 g. (0.9 mole) of di-*n*-butylamine. When the addition was complete the reaction mixture was heated to 90° and the dropping funnel was replaced by a gas-inlet tube having a tip 0.5–1.0 mm. in diameter. To the gas-inlet tube was attached an ampoule containing 19.3 g. (0.45 mole) of ethylenimine.[9] The ampoule was immersed in a water-bath maintained at a temperature of 75–85°. At this temperature the ethylenimine was vaporized and bubbled into the stirred mixture at such a rate that the addition was complete in about thirty minutes. No external heating was necessary since the reaction was sufficiently exothermic to maintain reflux. When the addition of ethylenimine was complete the gas-inlet tube was replaced quickly with a rubber stopper to prevent sucking back of the reaction mixture. The mixture was stirred for an additional thirty minutes and was then transferred to a 3-liter three-necked flask equipped with reflux condenser and stirrer. The flask was immersed in an ice-bath and 500 g. of ice and water was added slowly through the condenser. To the almost solid mass which resulted there was added with stirring 300 g. of solid potassium hydroxide in small portions. When the mixture was cold the benzene layer was separated. The aqueous layer was extracted four times with 100-ml. portions of benzene. The combined benzene layers were dried over potassium hydroxide pellets, the solvent was distilled and the residue was distilled through a 12-in. helices-packed, partial take-off fractionating column.

Summary

1. The addition of primary and secondary amines to ethylenimine to form N-substituted ethylenediamines has been effected in anhydrous media using aluminum chloride as a catalyst.

2. Higher temperatures were required for the satisfactory addition of primary amines to ethylenimine than was the case for secondary amines.

3. Several types of primary and secondary amines were used.

IOWA CITY, IOWA RECEIVED MAY 7, 1946

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

The Beckmann Rearrangement in the Preparation of Aldehydes[1]

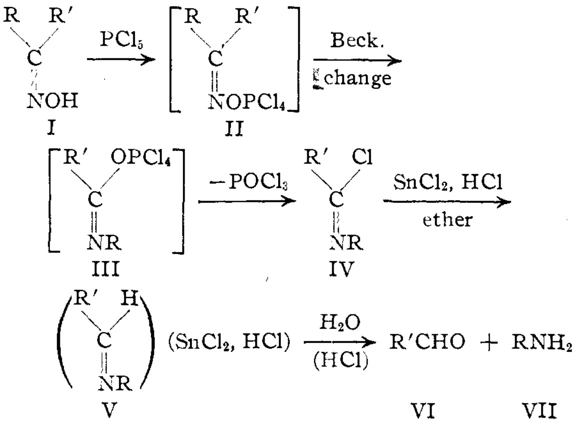
BY GEORGE H. COLEMAN AND RONALD E. PYLE

In this Laboratory we recently had occasion to prepare a considerable quantity of 1,2,3,4-tetrahydrophenanthrene-9-aldehyde. This compound had previously been prepared from the anilide[2] of the corresponding acid by treatment with phosphorus pentachloride and reduction of the product with stannous chloride. The anilide was prepared from 9-benzoyl-1,2,3,4-tetrahydrophenanthrene oxime by means of the Beckmann rearrangement.

It seemed possible from a consideration of the probable mechanism of the reaction that the aldehyde could be prepared directly from the oxime. This assumption was based on the probability that in the Beckmann rearrangement of the oxime an imidyl chloride was formed which was identical with that formed from the anilide in the previous method. Experimental trial has shown that such a procedure is possible and that satisfactory yields of 1,2,3,4-tetrahydrophenanthrene-9-aldehyde can be obtained by treatment of the corresponding oxime with phosphorus pentachloride and reduction of the product.

In order to gain additional information concerning its general applicability, the method has been studied further and used in the preparation of two other aromatic aldehydes, benzaldehyde and *p*-chlorobenzaldehyde. The intermediate imidyl chlorides have been isolated in both cases and other evidence with respect to the mechanism obtained.

It is postulated that the reaction can be explained by the following mechanism. The ketoxime (I) reacts with phosphorus pentachloride to form an ester (II) which undergoes a Beckmann rearrangement to form an intermediate (III). An imidyl chloride (IV) is formed from this by the loss of phosphorus oxychloride. This imidyl chloride is reduced by stannous chloride and separates as the stannous chloride, hydrogen chloride double salt of a Schiff base (V) which upon hydrolysis forms the desired aldehyde (VI) and a primary amine (VII).



In support of this mechanism the following experimental facts are presented. Hydrochloric acid and phosphorus oxychloride are formed in the reaction. The imidyl chlorides formed from diphenyl ketoxime and from *syn*-*p*-chlorophenyl phenyl ketoxime were isolated and were shown to be identical with the imidyl chlorides obtained from the corresponding anilides. Samples of both of the isolated imidyl chlorides were converted to the corresponding aldehydes by the

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[1] From a dissertation submitted by R. E. Pyle to the Graduate College of the State University of Iowa in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1946.

[2] Bachmann and Cronyn, *J. Org. Chem.*, **8**, 456 (1943).

standard procedure. The Schiff base was isolated from the double salt in both cases. These Schiff bases were identified by comparison with known compounds prepared from aniline and the corresponding aldehydes.

Experimental

1,2,3,4-Tetrahydrophenanthrene-9-aldehyde.—In a 1-liter, round-bottomed flask, 151 g. (0.5 mole) of 9-benzoyl-1,2,3,4-tetrahydrophenanthrene oxime (prepared by the method of Bachmann and Cronyn[2]) was suspended in 300 ml. of benzene and 120 g. (0.58 mole) of phosphorus pentachloride was added in small portions over a period of forty-five to sixty minutes with stirring and sufficient cooling to control the reaction. The mixture was refluxed on a steam-bath until the reaction was complete (about fifteen to twenty minutes). The benzene and phosphorus oxychloride were removed on a steam-bath at the pressure of a water suction pump.

The residue was dissolved in 215 ml. of ethylene chloride and the solution was cooled and added to an ice-cold solution, prepared by dissolving 390 g. of anhydrous stannous chloride in 1300 ml. of absolute ether saturated with dry hydrogen chloride. The solution was placed in a refrigerator and orange crystals began to form in about thirty minutes. After forty-eight hours, the orange solid was separated by filtration, washed with ether and dried at room temperature. The salt was hydrolyzed by boiling with 1200 ml. of 4 *N* hydrochloric acid. The solution was cooled and the solid was separated by filtration, washed with water and air-dried. The crude aldehyde, weighing 78 g., was dissolved in 400 ml. of boiling glacial acetic acid, treated with charcoal and allowed to crystallize slowly. The light colored product obtained in this manner was separated by filtration and air-dried; yield 70 g. (68%); m. p. 128-129°.

N-Phenylbenzimidyl Chloride.—Benzophenone oxime, 45.5 g. (0.23 mole), was dissolved in 100 ml. of benzene and treated with 60 g. (0.29 mole) of phosphorus pentachloride in a manner similar to that described for the preparation of 1,2,3,4-tetrahydrophenanthrene-9-aldehyde from the oxime. The reaction mixture was transferred to a 250-ml. Claisen flask and the benzene was removed at atmospheric pressure in a metal bath heated slowly to 125°. The phosphorus oxychloride and the imidyl chloride were separated by distillation at the pressure of a water suction pump. The product distilled at 175-178° (14-15 mm.). The yield of light yellow product was 47 g. (95%). After recrystallization from ligroin, it melted at 40-41°.

A mixed melting point with an authentic sample prepared from benzanilide by the method of Wallach and Hoffman[3] showed no depression.

Imidyl chlorides react readily with water, 95% alcohol, or alkalies. To determine the ionizable chlorine, a sample (*ca.* 0.3 g.) of the imidyl chloride was dissolved in 20 ml. of 0.1 *N* alcoholic sodium hydroxide and the excess sodium hydroxide was back-titrated with 0.1 *N* hydrochloric acid. Nitrogen was determined by the Kjeldahl method.

Anal. Calcd. for $C_{13}H_{10}NCl$: ionizable Cl, 16.47; N, 6.5. Found: ionizable Cl, 16.23; N, 6.45.

Benzaldehyde. A. From Benzophenone Oxime.—The procedure followed in this preparation was very similar to the one employed in the preparation of 1,2,3,4-tetrahydrophenanthrene-9-aldehyde from the corresponding oxime. Benzophenone oxime, 91 g. (0.46 mole), was dissolved in 200 ml. of benzene and treated with 120 g. (0.58 mole) of phosphorus pentachloride. After completion of the reaction and removal of benzene and phosphorus oxychloride, the residue was dissolved in 125 ml. of ethylene chloride and treated with 390 g. of anhydrous stannous chloride in 900 ml. of absolute ether saturated with dry hydrogen chloride. The yellow salt obtained by this treatment was hydrolyzed with 1250 ml. of 4 *N* hydrochloric acid. Benzaldehyde was removed from the acid solution by steam distillation. The aldehyde was separated from the water and the water extracted with ether. The ether solutions were combined with the aldehyde and were washed with sodium bicarbonate solution, then with water and dried over calcium chloride. The ether was removed by distillation and benzaldehyde distilled in a 125-ml. Claisen flask; yield 41 g. (84.5%); b. p. 87-88° (40 mm.).

The aldehyde was identified by oxidation to benzoic acid and by the preparation of dibenzalacetone.

The acid solution from which benzaldehyde had been removed was neutralized with sodium hydroxide and the aniline isolated in the usual manner; yield 34 g. (80%).

B. From N-Phenylbenzimidyl Chloride.—Forty grams (0.186 mole) of the imidyl chloride was dissolved in 80 ml. of ethylene chloride and treated with a solution of 145 g. of anhydrous stannous chloride in 500 ml. of absolute ether saturated with dry hydrogen chloride. A yellow salt was isolated from which 14.6 g. (76%) of benzaldehyde and 13.5 g. (80%) of aniline were obtained.

Isolation of Benzalaniline from Its Double Salt.—A sample (2 g.) of the double salt obtained from benzophenone oxime by the procedure previously described was suspended in 20 ml. of chloroform and anhydrous ammonia bubbled into the mixture. The mixture was filtered and the chloroform solution allowed to evaporate at room temperature. The oily residue solidified and was recrystallized from 95% alcohol; m. p. 50-51°. A mixed melting point with benzalaniline prepared from benzaldehyde and aniline showed no depression.

***syn-p*-Chlorophenyl Phenyl Ketoxime.**—This compound was prepared from *p*-chlorobenzophenone by the method of Demuth[4] with minor modifications. Both the stable *syn-p*-chlorophenyl phenyl ketoxime and the unstable, *anti-p*-chlorophenyl phenyl ketoxime were formed and were separated by fractional crystallization from dilute alcohol. From 100 g. of *p*-chlorobenzophenone there was obtained in the first fractionation 45 g. of the stable *syn* compound, m. p. 143-145°; aud 27 g. of the unstable *anti* compound, m. p. 91-95°. By repeated crystallization the two isomers were obtained in pure form. *syn-p*-Chlorophenyl phenyl ketoxime, the stable isomer, melted at 155-157° and the *anti* or unstable isomer melted at 92-94°.

A more convenient method for the preparation of the stable isomer, in which very little of the unstable isomer is formed, is that described for the benzophenone oxime.[5]

N-Phenyl-*p*-chlorobenzimidyl Chloride.—*syn-p*-Chlorophenyl phenyl ketoxime, 33 g. (0.143 mole), was treated with 36 g. (0.172 mole) of phosphorus pentachloride. After the benzene and phosphorus oxychloride were removed, the imidyl chloride solidified. The yield of crude product was 36 g. (nearly quantitative). After crystallization from ligroin, the imidyl chloride melted at 66-67°.

A mixed melting point with an authentic sample prepared from *p*-chlorobenzanilide by the method of Ley[6] showed no depression.

Anal. Calcd. for $C_{13}H_9NCl_2$: ionizable Cl, 14.2. Found: ionizable Cl, 14.04.

***p*-Chlorobenzaldehyde. A. From *syn-p*-Chlorophenyl Phenyl Ketoxime.**—This aldehyde was prepared in the same manner as benzaldehyde from benzophenone oxime. The oxime, 34.5 g. (0.15 mole), was treated with 38 g. (0.182 mole), of phosphorus pentachloride. The residue, after removal of benzene and phosphorus oxychloride, was dissolved in 50 ml. of ethylene chloride and treated with 155 g. of anhydrous stannous chloride in 400 ml. of absolute ether saturated with hydrogen chloride. The double salt was hydrolyzed by boiling with 4 *N* hydrochloric acid and the aldehyde removed by steam distillation. On cooling,

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[3] Wallach and Hoffman, *Ann.*, **184**, 79 (1877).

[4] Demuth, *Ber.*, **23**, 3610 (1890).

[5] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, New York, N. Y., 1943, p. 70.

[6] Ley, *Ber.*, **31**, 241 (1898).

the oily aldehyde layer crystallized and was separated from the water by filtration. The yield of aldehyde after air-drying was 17 g. (81%); m. p. 46–47°. The yield of aniline was 11 g. (79%).

B. From N-Phenyl-*p*-chlorobenzimidyl Chloride.—The imidyl chloride, 37.5 g. (0.15 mole), was dissolved in 100 ml. of ethylene chloride and treated with 125 g. of stannous chloride in 450 ml. of absolute ether saturated with hydrogen chloride. The *p*-chlorobenzaldehyde was isolated by the method employed in the preparation from the oxime: yield 16 g. (78%); m. p. 46–47°. The yield of aniline was 10.8 g. (80%).

Isolation of *p*-Chlorobenzalaniline from Its Double Salt.—The isolation was made by a procedure similar to the isolation of benzalaniline from the corresponding double salt. After recrystallization from 95% alcohol, the compound melted at 57–58°. A mixed melting point with *p*-chlorobenzalaniline prepared from *p*-chlorobenzaldehyde and aniline showed no depression.

Summary

A procedure has been developed for the preparation of aromatic aldehydes directly from ketoximes. This involves a Beckmann rearrangement but not the formation of the substituted amide. Evidence for a suggested mechanism is given.

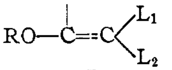
IOWA CITY, IOWA RECEIVED MAY 13, 1946

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Reduction of Amide Vinylogs

BY ROBERT H. BAKER AND ARTHUR H. SCHLESINGER[1]

The observation that hydrogen attacks ester vinylogs of the type I



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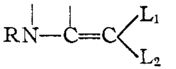
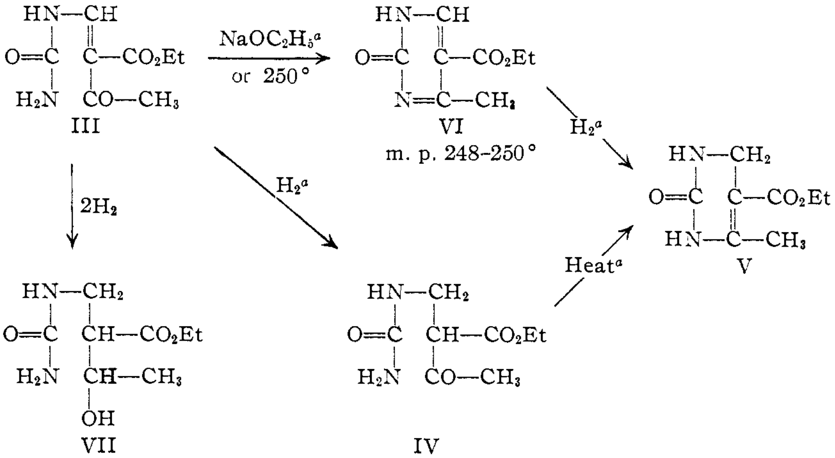


II

with preferential cleavage of the alkoxyl group[2] prompted a study of the nitrogen analogs II. In contrast to the behavior of I, which can be hydrogenated at the olefinic linkage without cleavage when only one of the L groups is an acyl, the nitrogen analog of such a compound adds hydrogen exclusively by cleavage. This is clearly demonstrated by the behavior of O-ethylbenzoylacetone from which it is possible to isolate 3-ethoxy-1-phenyl-1-butanol in 57% yield by nickel hydrogenation whereas β-anilinocrotonophenone under similar conditions yields only aniline and butyrophenone.



a See Reference 3.

Of the nitrogen compounds only those with acyl groups on the nitrogen have resisted cleavage to any extent. Acetamido-, benzamido- and ureidomethyleneacetoacetic ester have been hydrogenated to the corresponding saturated keto esters in limited yields. The latter of these compounds, III, has previously been hydrogenated by Bergmann and Johnson[3] with a limited quantity of hydrogen. Although they made no attempt to isolate the primary product it must have been the ureidomethylacetoacetic ester, IV, because heating with water converted it into 5-acetyldihydrouracil, V, which could also be obtained from the sodium ethoxide condensation product, VI, of III. In the present investigation it was customary to allow hydrogenations to run as long as hydrogen was absorbed at an appreciable rate. Over platinum oxide the ureidomethylene compound, III, took up the equivalent of 1.66 moles of hydrogen to produce mainly the saturated alcohol, VII, along with a small amount of the cleavage product, methylacetoacetic ester, and a trace of an unidentified product, m.p. 250–251°, which depresses the melting point of VI by 15°.

It is of interest to note that the aminomethylene derivatives of the ketones are cleaved with preservation of the keto groups, in spite of the fact that no attempts were made to stop the reduction short of saturation. Since considerable quantities of starting material could usually be isolated it is evident that some product of the reduction, probably the amine, hinders the reduction of the carbonyl group.[4]

It is difficult to correlate the effects of structure

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(1) Wade Fetzer Fellow 1945–1946.

(2) Baker and Weiss, THIS JOURNAL, **66**, 343 (1944).

(3) Bergmann and Johnson, *Ber.*, **66**, 1492 (1933).

(4) Weizmann, U. S. Patent 2,367,078; *C. A.*, **39**, 2293 (1945), used amine hydrochlorides and nickel to produce saturated ketones from unsaturated ones.