[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF KITASATO INSTITUTE]

# THE BECKMANN REARRANGEMENT WITH QUINOLINE COMPOUNDS

BY KONOMU MATSUMURA AND CHUSABURO SONE

RECEIVED DECEMBER 16, 1930 PUBLISHED APRIL 6, 1931

Schroeter, in an earlier research, found that the Beckmann rearrangement with pivalophenone oxime may be able to proceed in two opposite directions in accordance with the type of reagent used.[1] This paper represents a similar instance in the quinoline series. In the previous paper[2] it was definitely established that 5-acetyl- and 5-benzoyl-8-hydroxyquinoline oximes in the Beckmann rearrangement with hydrogen chloride, glacial acetic acid and acetic anhydride, give 5-acetamino- and 5-benzoylamino-8-hydroxyquinoline (I and II), respectively.

$CH_3CONHC_9H_6ON$ (I) $C_6H_5CONHC_9H_6ON$ (II) $C_6H_5NHCOC_9H_6ON$ (III)

In a subsequent investigation it was found that 5-benzoyl-8-hydroxyquinoline oxime, on treatment with thionyl chloride, gave an anilide of 8-hydroxyquinoline-5-carboxylic acid (III), and on hydrolysis with hydrochloric acid, the latter gave 8-hydroxyquinoline-5-carboxylic acid [m. p. 273° (dec.)]. On treating 8-hydroxyquinoline with carbon tetrachloride and potassium hydroxide in alcohol solution, Lippmann and Fleissner obtained an 8-hydroxyquinoline-carboxylic acid [m. p. 280° (dec.)] which gave quinolinic acid on oxidation with potassium permanganate and dibromo-8-hydroxyquinoline (m. p. 193°) on bromination.[3] The experimental data given by these authors make it seem likely that the compound which they obtained would be 8-hydroxyquinoline-5-carboxylic acid, identical with what we have now obtained, but some inconformities in their properties are noticed between them (on pouring in water, the hydrochloride of the authors' compound separates free base, while that of Lippmann and Fleissner is stated to be easily soluble). In order to clear up this matter, the experimental work of Lippmann and Fleissner was repeated and the identity was definitely established. To return to the oxime rearrangement, 5-benzoyl-8-hydroxyquinoline oxime, on treatment with concd. sulfuric acid, is found to give a sulfonated 8-hydroxyquinoline-5-carboxylic acid anilide, and on hydrolysis with hydrochloric acid (20%), the latter gives 8-hydroxyquinoline-5-carboxylic acid. Concerning the position of the sulfonic acid group, no definite proof can be obtained, but the sulfonated compound gives a red color reaction with diazotized sulfanilic acid in alkaline solution. This seems to indicate that the position ortho to the hydroxyl group is not occupied.

[1] Schroeter, *Ber.*, **44**, 1201 (1911).

[2] Matsumura, THIS JOURNAL, **52**, 4433 (1930).

[3] Lippmann and Fleissner, *Ber.*, **19**, 2467 (1886); *Monatsh.*, **8**, 311 (1887).

Moreover, 5-acetyl-8-hydroxyquinoline oxime, in a similar treatment, does not give rise to sulfonation. These facts seem to favor the opinion that the sulfonic acid group might perhaps be in the aniline molecule and then probably in the para position to the amino group.

5-Acetyl-8-hydroxyquinoline oxime, on the other hand, on treating either with thionyl chloride or with sulfuric acid, gives, in either case, 5-acetamino-8-hydroxyquinoline, the same product that is obtainable on treatment with hydrogen chloride, glacial acetic acid and acetic anhydride.

## Experimental

**8-Hydroxyquinoline-5-carboxylic Acid Anilide.**—Thionyl chloride (10 cc.) is added to the cooled solution (0°) of 5-benzoyl-8-hydroxyquinoline oxime (1 g.) in dry ether (150 cc.) with stirring. The resulting yellow precipitate is filtered, after standing for three hours at room temperature (25°), and washed with ether.

On dissolving the precipitate in cold water and making alkaline with sodium carbonate, colorless crystals separated; yield, 1 g. It gives yellowish-white thin plates with a silky luster from alcohol, m. p. 211–212°. It is easily soluble in alcohol, fairly soluble in hot benzene and chloroform, sparingly in ether and insoluble in water.

In this reaction, on using chloroform instead of ether as solvent, the same reaction product can be obtained in a far inferior yield.

*Anal.* Subs., 4.145 mg.: $N_2$, 0.376 cc. (23°, 769 mm.). Calcd. for $C_{16}H_{12}O_2N_2$: N, 10.60. Found: N, 10.28.

**The sulfate** gives yellow needles from alcohol, decomposing at 211–215°. When water is poured in, it separates as the free base.

**Hydrolysis of 8-Hydroxyquinoline-5-carboxylic Acid Anilide.**—Two tenths gram of 8-hydroxyquinoline-5-carboxylic acid anilide and 8 g. of hydrochloric acid (20%) were refluxed for six hours. On cooling, the resulting crystals of the hydrochloride of 8-hydroxyquinoline-5-carboxylic acid were filtered. The filtrate, on being made alkaline, gave an odor specific to aniline, and a deep violet coloration when in contact with a solution of bleaching powder. The hydrochloride was dissolved in dilute ammonia and on acidification with acetic acid, yellow needles of 8-hydroxyquinoline-5-carboxylic acid separated; yield, 0.1 g. It crystallizes from alcohol to egg-yellow, stout needles, melting at 273° (uncorr.) with decomposition, after preliminary subliming in a sealed capillary. It is moderately soluble in hot alcohol and hot acetone, but difficultly so in ether, chloroform and benzene, and easily soluble in dilute mineral acid and alkali. The alcoholic solution gives a green color reaction with ferric chloride. An attempt to prepare the chloroplatinate was unsuccessful.

*Anal.* Subs., 4.977: $CO_2$, 11.608; $H_2O$, 1.770. Subs., 3.603: $N_2$, 0.245 cc. (29°, 760.5 mm.). Calcd. for $C_{10}H_7O_3N$: C, 63.49; H, 3.70; N, 7.40. Found: C, 63.61; H, 3.95; N, 7.35.

**The hydrochloride** gives colorless columns from hydrochloric acid (10%), m. p. 239° (decomp.), and separates free base on pouring in water.

*Anal.* Subs., 5.000: AgCl, 3.149. Calcd. for $C_{10}H_7O_3N\cdot HCl$: Cl, 15.74. Found: Cl, 15.58.

**The neutral barium salt** gives yellow needles from hot water. It is fairly soluble in water but insoluble in alcohol.

*Anal.* (water of crystallization). Subs., 0.0315: $H_2O$, 0.0051. Calcd. for $(C_{10}H_6O_3N)_2Ba\cdot 5.5H_2O$: $H_2O$, 16.18. Found: $H_2O$, 16.19. Subs., 5.889: $BaSO_4$, 2.651. Calcd. for $(C_{10}H_6O_3N)_2Ba$: Ba, 26.75. Found: Ba, 26.51.

**8-Acetoxyquinoline-5-carboxylic acid** gives light yellow prisms from ethyl acetate, decomposing at 312°.

*Anal.* Subs., 5.101: $CO_2$, 11.638; $H_2O$, 1.838. Subs., 5.215: $N_2$, 0.281 cc. (20°, 754.5 mm.). Calcd. for $C_{12}H_9O_4N$: C, 62.33; H, 3.90; N, 6.05. Found: C, 62.22; H, 4.00; N, 6.09.

**8-Methoxyquinoline-5-carboxylic Acid.**—A methyl alcohol suspension of 8-hydroxyquinoline-5-carboxylic acid was treated with ethereal diazomethane and the resulting difficultly crystallizable dimethyl derivative was hydrolyzed with alcoholic potassium hydroxide solution. The final product was recrystallized from alcohol into small yellow crystals, m. p. 225–226° (dec.).

*Anal.* Subs., 3.634: AgI, 4.116. Calcd. for $C_{11}H_9O_3N$: $OCH_3$, 15.27. Found: $OCH_3$, 14.95.

**Sulfonated 8-Hydroxyquinoline-5-carboxylic Acid Anilide.**—A solution of 5-benzoyl-8-hydroxyquinoline oxime (0.5 g.) in concd. sulfuric acid (5 g.) was kept at 100° for an hour. On pouring onto crushed ice (20 g.), a resinous precipitate, which soon turned to a yellow crystalline mass, was formed. It was dissolved in dilute sodium carbonate, reprecipitated with dilute sulfuric acid, and repeatedly washed with cold water; yield, 0.4 g.; m. p. >300°.

It forms in yellowish-white thin plates, practically insoluble in the usual organic solvents, but easily soluble in dilute alkali, and moderately so in boiling water. It gives a green color reaction with ferric chloride, and a red color reaction with diazotized sulfanilic acid and alkali. On hydrolysis with hydrochloric acid (20%), this compound gives 8-hydroxyquinoline-5-carboxylic acid [m. p. 273° (dec.)] in a good yield. An attempt to isolate another component, perhaps sulfanilic acid, failed.

The reaction fluid, however, on being made alkaline, gave no odor of aniline, and after treatment with nitrous acid gives a red coloration with alkaline β-naphthol.

*Anal.* Subs., 4.545: $N_2$, 0.339 cc. (28°, 760 mm.). Subs., 5.939: $BaSO_4$, 3.754. Calcd. for $C_{16}H_{11}O_5N_2S$: N, 8.16; S, 9.35. Found: N, 8.15; S, 8.68.

**The Reaction of 8-Hydroxyquinoline and Carbon Tetrachloride.**—The compound prepared from 8-hydroxyquinoline (20 g.) and carbon tetrachloride by following the method of Lippmann and Fleissner[3] for 8-hydroxyquinoline-carboxylic acid, gives yellow needles from alcohol, melting at 273° (dec.) alone or mixed with 8-hydroxyquinoline-5-carboxylic acid; yield, 3.35 g. The hydrochloride [m. p. 239° (dec.)] separates free base on pouring into water and its methyl ether and acetoxyl derivatives melt at 223–224° (dec.) and 310° (dec.), respectively.

The Beckmann rearrangement of 5-acetyl-8-hydroxyquinoline oxime either with thionyl chloride in chloroform solution or with concd. sulfuric acid gives 5-acetamino-8-hydroxyquinoline (m. p. 217–218°), identified by the mixed melting point test with an authentic specimen.

The writers, hereby, wish to express their hearty thanks to Professor Hata for the interest which he has kindly taken in this work.

## Summary

1. 5-Benzoyl-8-hydroxyquinoline oxime, on treatment with thionyl chloride, gives 8-hydroxyquinoline-5-carboxylic acid anilide and with concd. sulfuric acid gives sulfonated 8-hydroxyquinoline-5-carboxylic acid anilide. Both reaction products, on hydrolysis with hydrochloric acid, give 8-hydroxyquinoline-5-carboxylic acid.

2. 5-Acetyl-8-hydroxyquinoline oxime on treatment either with thionyl chloride or with concd. sulfuric acid gives 5-acetamino-8-hydroxyquinoline.

TOKYO, JAPAN

---

[CONTRIBUTION FROM THE CHEMICAL INSTITUTE, MARBURG A. L., GERMANY]

# THE TITRIMETRIC AND SPECTROMETRIC ANALYSIS OF KETO–ENOL MIXTURES. ALPHA-PHENYLACETOACETIC ESTER

BY KARL V. AUWERS

RECEIVED JANUARY 2, 1931 PUBLISHED APRIL 6, 1931

In a recent paper[1] on the keto–enol equilibrium in α-phenylacetoacetic ester, Post and Michalek have attempted to determine the percentage of the enolic modification, both titrimetrically and spectrometrically. Indirect titration with bromine, by the Kurt Meyer method, gave them an average value of 28.6% of enol, whereas, from its molecular refraction, they calculate the impossible value of 137.13%, which they attribute to the "anomalous" structure of the phenyl group.

These authors also mention, incidentally, that from its molecular refraction the enol content of the unsubstituted acetoacetic ester is 59.2%, whereas, according to the bromine titrations, it contains only 7.7%.

These statements make it appear that spectrochemistry would lead to entirely false results with substances of this type and would not be useful for the analysis of keto–enol mixtures.

However, these authors have overlooked the fact that this problem of the apparent contradiction between the results of the bromine titrations and those of spectrochemistry has long since been investigated and explained.[2]

It has been found that both methods in reality give results which are in sufficient agreement, if certain well-known spectrochemical regularities are correctly taken into account.

Post and Michalek[3] arrive at their values for the enol content by comparing the experimental molecular refraction with the values which they calculate, theoretically, on the basis of atomic refractions. By this procedure, however, correct values are obtained only for the keto forms; those for the enol forms are too low. The molecules of the enolic acetoacetic ester contain a conjugated system of double bonds, the exaltation of which is increased by the hydroxyl group attached to it,[4] since the partial valences

[1] Post and Michalek, THIS JOURNAL, **52**, 4358 (1930).

[2] K. v. Auwers, *Ann.*, **415**, 169 (1918); K. v. Auwers and H. Jacobsen, *ibid.*, **426**, 161 (1921).

[3] Post and Michalek state erroneously that their values have been calculated with the old Brühl refraction equivalents, whereas they have actually used the new Eisenlohr values. It may be mentioned, incidentally, that the accompanying reference number 9, as well as numbers 5 and 7 are not apropos.

[4] K. v. Auwers, *Ber.*, **44**, 3514 (1911).