there is formed an equimolar mixture of sodium trimethyl stannide and sodium dimethyl vinyl stannide, along with methane and sodium amide. On adding methyl iodide to this mixture there is produced a mixture of tetramethyl tin and trimethyl vinyl tin. Trimethyl vinyl tin has not as yet been obtained in the pure state.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF KITASATO INSTITUTE]

THE FRIEDEL AND CRAFTS REACTION WITH 8-HYDROXYQUINOLINE

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RECEIVED JULY 14, 1930 PUBLISHED NOVEMBER 5, 1930

On adopting the method of Behn and Rosenmund,[1] the Friedel and Crafts reaction was found to be applicable to 8-hydroxyquinoline and this paper deals with the preparation of 5-acetyl-, 5-benzoyl- and 5-chloro-acetyl-8-hydroxyquinoline. That the acyl radicals which have been introduced occupied position 5 could be ascertained by converting these compounds into the known substances either by a Beckmann rearrangement of their oximes or by reduction, respectively.

Experimental

5-Acetyl-8-hydroxyquinoline.—On introducing acetyl chloride (25 g.) into the solution of 8-hydroxyquinoline (43.5 g.) in nitrobenzene (400 g.), yellow precipitates separated. On the addition of aluminum chloride to it 100 g. at a time under shaking, the precipitates disappeared and a clear solution resulted. It was kept at 70° for twelve hours in a flask fitted with a calcium chloride tube. On cooling, some crushed ice and 100 cc. of hydrochloric acid (10%) were added to it and the separated nitrobenzene was driven off with steam. On standing overnight, the separated hydrochloride of 5-acetyl-8-hydroxyquinoline was filtered. It was dissolved in water and on the addition of sodium acetate to it, the free base separated out. It was recrystallized from hot water; yield, 25.5 g. (45% of the theoretical) after recrystallization.

It forms in colorless hair-like needles from hot water, m. p. 112–112.5°. It is fairly easily soluble in the usual organic solvents, dilute mineral acid or alkali. It gives a green color with ferric chloride and a deep red color with diazotized sulfanilic acid and alkali.

Anal. Subs., 5.043 mg.: CO_2, 13.029; H_2O, 2.111. Subs., 6.715: N_2, 0.421 (15°, 769 mm.). Calcd. for $C_{11}H_9O_2N$: C, 70.59; H, 4.81; N, 7.49. Found: C, 70.46; H, 4.65; N, 7.42.

Beckmann Rearrangement of its Oxime.—A mixture of the oxime (0.2 g.), glacial acetic acid (1.6 g.) and acetic anhydride (0.4 g.) was saturated with hydrogen chloride gas in the cold and was kept at 100° for three hours in a sealed tube. On cooling, the contents were made alkaline with sodium carbonate and shaken with chloroform. On concentrating the solvent, colorless crystals were obtained; yield, 0.18 g. It formed in colorless flat needles from chloroform, m. p. 216–217.5°. The mixed melting point with an authentic specimen of 5-acetamino-8-hydroxyquinoline (m. p. 217–218°) which had

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[1] Behn, German Patent 95,901 (1897); Rosenmund and Schulz, *Arch. Pharm.*, **265**, 308 (1927).

been prepared by acetylation of the 5-amino-8-hydroxyquinoline of Kostanecki[2] gave 217–218°.

Anal. Subs., 2.681: N_2, 0.324 (24.5°, 761.8 mm.). Calcd. for $C_{11}H_{10}O_2N_2$: N, 13.86. Found: N, 13.50.

Acid sulfate gave yellow stout needles from alcohol, m. p. 263° (decomp.).

5-ω-Chloro-acetyl-8-hydroxyquinoline.—This compound was obtained in the same manner as that described for acetylhydroxyquinoline using chloro-acetyl chloride, except that the reaction temperature was kept at 90–95° for seven hours and that the recrystallization was effected by means of warm benzene; yield, 36% of the theoretical. It forms in colorless glistening needles from benzene, m. p. 158–159°. It is fairly easily soluble in the usual organic solvents, dilute mineral acid or caustic soda and moderately soluble in hot water. It gives a green color with ferric chloride and a deep red color with diazotized sulfanilic acid and alkali.

Anal. Subs., 4.984: CO_2, 10.875; H_2O, 1.676. Subs., 4.791: N_2, 0.270 (23.5°, 753 mm.). Calcd. for $C_{11}H_8O_2NCl$: C, 59.59; H, 3.61; N, 6.32. Found: C, 59.51; H, 3.73; N, 6.24.

Reduction of 5-Chloro-acetyl-8-hydroxyquinoline.—A mixture of 0.15 g. of 5-chloro-acetyl-8-hydroxyquinoline, 1 g. of iron powder and 25 g. of alcohol (80%) with the addition of two drops of hydrochloric acid (10%) was refluxed for three hours. The reaction fluid, after filtration while hot, was evaporated to dryness. On the addition of hydrochloric acid (10%) and trituration, yellowish-white crystals separated out. It was filtered and dissolved in hot water. On addition of sodium acetate to it, colorless flocculent needles separated. These were recrystallized from hot water into colorless needles; m. p. 110–111°; yield, 0.05 g. The mixed melting point with 5-acetyl-8-hydroxyquinoline (m. p. 112–112.5°) gave m. p. 110–112°.

Anal. Subs., 4.022: N_2, 0.269 (22.6°, 758.4 mm.). Calcd. for $C_{11}H_9O_2N$: N, 7.49. Found: N, 7.48.

5-Benzoyl-8-hydroxyquinoline.—Benzoyl chloride (9 g.), 8-hydroxyquinoline (8.7 g.) and aluminum chloride (20 g.) were dissolved in nitrobenzene (80 g.) in the same manner that was described in the previous case. The solution was kept at 110–120° for seven and one-half hours. On cooling, after the addition of ice and hydrochloric acid, the separated nitrobenzene was distilled with steam. Then the separated crystalline mass was filtered, after standing overnight, and washed with hydrochloric acid (10%) until the filtrate became colorless.

It was recrystallized from dilute hydrochloric acid and then the free base was isolated by means of sodium acetate; yield, 11.5 g. (77% of the theoretical). It forms in colorless needles from hot alcohol; m. p. 118–119°. It is fairly easily soluble in the usual organic solvents or in dilute mineral acid, moderately soluble in hot water but difficultly in dilute caustic soda. It gives a green color with ferric chloride and a red color with diazotized sulfanilic acid and alkali.

Anal. Subs., 5.181: CO_2, 14.691; H_2O, 1.967. Subs., 5.152: N_2, 0.261 (21°, 757.7 mm.). Calcd. for $C_{16}H_{11}O_2N$: C, 77.11; H, 4.42; N, 5.62. Found: C, 77.33; H, 4.22; N, 5.73.

Beckmann Rearrangement of its Oxime.—Two-tenths gram of the oxime was treated in exactly the same manner as that described for the rearrangement of the oxime of 5-acetyl-8-hydroxyquinoline; yield, 0.2 g. It forms in yellowish-white small plates from chloroform; m. p. 237–238°. The mixed melting point with an authentic specimen of 5-benzoylamino-8-hydroxyquinoline (m. p. 237–238°) which had been pre-

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[2] Kostanecki, *Ber.*, **24**, 152 (1891).

TABLE I

DERIVATIVES OF 5-ACETYL-8-HYDROXYQUINOLINE

Derivative	M. p., °C.	Properties	Formula	Analyses, % Calcd.	Found	Calcd.	Found
Hydrochloride	284–285 (dec.)	Yellow cols. from dil. HCl. Hydrolyzes in water	$C_{11}H_9O_2N\cdot HCl\cdot 3H_2O$	HCl 16.33	16.28	H_2O 19.46	19.41
Acid sulfate	248 (dec.)	Yellow needles from alc. Easily sol. in water	$C_{11}H_9O_2N\cdot H_2SO_4$	H_2SO_4 34.39	34.48		
Picrate	188–189	Yellow needles from hot water	$C_{11}H_9O_2N\cdot C_6H_3O_7N_3\cdot H_2O$	N 13.46	13.50	H_2O 4.14	4.81
Chloroplatinate	275 (dec.)	Yellow needles from dil. HCl	$(C_{11}H_9O_2N\cdot HCl)_2\cdot PtCl_4$	Pt 24.89	24.85		
Methyl iodide	210 (dec.)	Yellow needles from hot water. Fairly sol. in alcohol or water	$C_{11}H_9O_2N\cdot CH_3I\cdot H_2O$	I 38.60	38.27	H_2O 5.19	5.44
Oxime	193	Colorless needles from alc. Fairly sol. in usual organic solvents	$C_{11}H_{10}O_2N_2$	N 13.86	13.89		

TABLE II

DERIVATIVES OF 5-CHLORO-ACETYL-8-HYDROXYQUINOLINE

Derivative	Properties	M. p., °C.	Formula	Analyses, % Calcd.	Found
Hydrochloride	Yellow needles from dil. HCl. Hydrolyzes completely in water	287 (dec.)	$C_{11}H_8O_2NCl\cdot HCl$	HCl 14.15	14.24
Acid sulfate	Yellow plates from dil. H_2SO_4. Hydrolyzes in water	263 (dec.)	$C_{11}H_8O_2NCl\cdot H_2SO_4$	H_2SO_4 30.67	30.54
Picrate	Yellow needles from alcohol	179	$C_{11}H_8O_2NCl\cdot C_6H_3O_7N_3$	N 12.43	12.35
Chloroplatinate	Yellow prisms from dil. HCl	275 (dec.)	$(C_{11}H_8O_2NCl\cdot HCl)_2PtCl_4$	Pt 22.88	22.71

TABLE III

DERIVATIVES OF 5-BENZOYL-8-HYDROXYQUINOLINE

Derivative	Properties	M. p., °C.	Formula	Analyses, % Calcd.	Found
Hydrochloride	Yellow needles from dil. HCl. Hydrolyzes in water	252–260	$C_{16}H_{11}O_2N\cdot HCl$	HCl 12.78	12.72
Acid sulfate	Yellow needles from alc. Hydrolyzes in water	219–220	$C_{16}H_{11}O_2N\cdot H_2SO_4$	H_2SO_4 28.21	28.38
Picrate	Yellow needles from alcohol	143–145	$C_{16}H_{11}O_2N\cdot C_6H_3O_7N_3$	N 11.72	11.63
Methyl iodide	Garnet-colored prisms from hot water. Fairly sol. in hot water	199.5 (dec.)	$C_{16}H_{11}O_2N\cdot CH_3I$	I 32.48	32.33
Oxime	Colorless tables from dil. alc. Easily sol. in usual organic solvents	147–148	$C_{16}H_{12}ON_2$	N 10.61	10.41

pared by benzoylation of 5-amino-8-hydroxyquinoline showed no depression. Moreover, by hydrolysis with hydrochloric acid (20%) the formation of benzoic acid could be ascertained by the mixed melting point method.

Anal. Subs., 3.066: N_2, 0.290 (24°, 766 mm.). Calcd. for $C_{16}H_{12}O_2N_2$: N, 10.61. Found: N, 10.63.

Acid sulfate gave yellow columns from alcohol; m. p. 221–222° (decomp.).

8-Benzoyloxyquinoline.—The benzoylation of 8-hydroxyquinoline with benzoyl chloride was carried out in the presence of pyridine in the cold; yield, 90% of the theoretical after recrystallization. It forms in colorless tables from alcohol; m. p. 122–122.5°.

This compound was prepared first by Bedall by the interaction of 8-hydroxyquinoline and benzoyl chloride at a high temperature; he found a melting point of 118–120° for his product.[3]

Anal. Calcd. for $C_{16}H_{11}O_2N$: N, 5.62. Found: N, 5.54.

The hydrochloride was obtained by treating an ice cold ethereal solution of the free base with dry hydrogen chloride gas. It forms in colorless needles; m. p. 124°. It is easily soluble in water.

Anal. Calcd. for $C_{16}H_{11}O_2N\cdot HCl$: HCl, 12.78. Found: HCl, 12.54.

On submitting this hydrochloride to a Friedel and Crafts reaction, benzoic acid and 8-hydroxyquinoline could be recovered and no condensation product could be isolated.

I hereby desire to express my hearty thanks to Professor Hata for the interest which he has kindly taken in this work and to Mr. C. Sone for his assistance in this investigation.

Summary

The preparation of 5-acetyl-, 5-chloro-acetyl- and 5-benzoyl-8-hydroxyquinoline has been reported.

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

THE DETERMINATION OF THE STRENGTH OF WEAK BASES AND PSEUDO BASES IN GLACIAL ACETIC ACID SOLUTIONS[1]

BY J. B. CONANT AND T. H. WERNER

RECEIVED JULY 17, 1930 PUBLISHED NOVEMBER 5, 1930

Previous papers of this series have shown that the titration of bases with strong acids in glacial acetic acid solution may be followed by means of the chloranil electrode. We have been interested in extending this study of weak bases to weak pseudo-bases of the type of triphenyl carbinol. It is only by the use of a solvent such as glacial acetic acid that these weak pseudo-bases can be studied and the oxidation–reduction systems composed of free radicals and halochromic salts can be investigated. Before continuing the study of these more strictly organic problems, it was necessary

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[3] Bedall and Fischer, *Ber.*, **14**, 1367 (1881).

[1] This is Paper 4 in a series on Superacid Solutions. For earlier papers of this series, see THIS JOURNAL. **49**, 3047, 3062 (1927); and **50**, 2367 (1928).