[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF LOUISVILLE]

# THE REACTION OF ANILS WITH 8-QUINOLINOL

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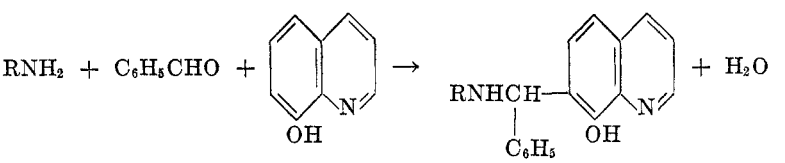
The reaction of aniline plus benzaldehyde with 8-quinolinol has been reported to yield 7-(α-anilinobenzyl)-8-quinolinol (1). The extension of this reaction to other aromatic amines and substituted benzaldehydes (2) has given chelating compounds of interest for their potential usefulness as analytical reagents and for possible amebicidal activity. In continuation of this work the products from a number of heterocyclic primary amines, benzaldehyde, and 8-quinolinol are here reported.

These products are presumed to be 7-aminobenzyl-8-quinolinols with the structures represented by formula A in the following equation:




A

Since the addition of anils to active methylene groups in other types of compounds is well known (3), it is probable that the 8-quinolinol reacts in its keto form in which there is a methylene group at the 7-position.

Nine representative heterocyclic amines gave products (Table I), as did anthranilic acid. 2,6-Diaminopyridine appeared to react at only one amino group. The anthranilic acid derivative is of particular interest because it contains in one molecule the chelating groups of anthranilic acid and 8-quinolinol both of which are useful precipitants for metal ions.

All the compounds gave a red color with concentrated sulfuric acid, a yellow color with concentrated nitric acid, and a green color with ferric chloride. These tests appear to be fairly characteristic.

The absorption spectra (Table II) generally are similar to the spectrum of 8-quinolinol in ethanol; this result was expected since the spectra may be regarded as roughly the sum of the 8-quinolinol spectrum and that of the side chain.

The times required for a product to be precipitated when equimolar amounts of benzaldehyde, amine, and 8-quinolinol were mixed (in a volume of ethanol sufficient to keep the Schiff's base in solution) ranged from one hour to eighteen days; in general the reactions were slightly faster with these heterocyclic amines than with the substituted anilines used before (2). However, the time needed for precipitation is not highly significant since seeding the solution greatly hastened the appearance of a precipitate. Speeding the reaction by refluxing was not tried because of a lack of success with this procedure in previous work.

TABLE I

ANALYSES OF 7-AMINOBENZYL-8-QUINOLINOLS

| NO. | AMINE USED | EMPIRICAL FORMULA | NITROGEN | |
|---|---|---|---|---|
| | | | Calc'd | Found |
| I | 2-Amino-3-methylpyridine | $C_{22}H_{19}N_3O$ | 12.31 | 12.04 |
| II | 2-Amino-4-methylpyridine | $C_{22}H_{19}N_3O$ | 12.31 | 11.95 |
| III | 2-Amino-5-methylpyridine | $C_{22}H_{19}N_3O$ | 12.31 | 12.24 |
| IV | 2-Amino-6-methylpyridine | $C_{22}H_{19}N_3O$ | 12.31 | 12.30 |
| V | 2,6-Diaminopyridine | $C_{21}H_{18}N_4O$ | 16.36 | 16.70 |
| VI | 2-Aminobenzothiazole | $C_{23}H_{17}N_3OS$ | 10.96 | 10.80 |
| VII | 2-Aminothiazole | $C_{19}H_{15}N_3OS$ | 12.61 | 12.78 |
| VIII | 2-Aminobenzimidazole | $C_{23}H_{18}N_4O$ | 15.29 | 15.86 |
| IX | 3-Aminoquinoline | $C_{25}H_{19}N_3O$ | 11.13 | 11.67 |
| X | Anthranilic acid | $C_{23}H_{18}N_2O_3$ | 7.56 | 7.36 |

TABLE II

ABSORPTION SPECTRA AND PROPERTIES OF 7-AMINOBENZYL-8-QUINOLINOLS

| CPD. | M.P., °C. | YIELD, % | TIME, DAYS[a] | ABSORPTION MAXIMA, mμ |
|---|---|---|---|---|
| I | 159 | 36 | 18 | 248 (59,000), 300 (9,700)[b] |
| II | 158 | 87 | 1 | 249 (42,000), 300 (6,800) |
| III | 200 | 85 | 0.3 | 248 (54,000), 310 (7,500) |
| IV | 201 | 80 | 0.2 | 247 (52,000), 305 (8,800) |
| V[c] | 270 | 55 | 0.05 | |
| VI[c] | 219 | 30 | 7 | |
| VII[c] | 212 | 43 | 1 | |
| VIII | 202 | 28 | 0.1 | 246 (34,000), 284 (14,000) |
| IX | 200 | 36 | 11 | 246 (68,000), 350 (4,800) |
| X | 206 | 45 | 7 | 247 (49,000), 340 (6,400) |

[a] Time required for precipitation to begin. [b] Molar absorbancy index in parentheses. [c] Not sufficiently soluble in ethanol to permit recording its spectrum.

## EXPERIMENTAL

*Preparation of compounds.* To 50 ml. of 95% ethanol were added 0.02 mole of benzaldehyde and 0.02 mole of amine. If precipitation of the anil occurred, more ethanol was added. Then 0.02 mole of 8-quinolinol (2.9 g.) was added, and the mixture was stoppered and left to stand at room temperature for three weeks. The precipitated product was removed by filtration and recrystallized from a 1:1 mixture of ethanol and acetone.

Spot tests with sulfuric and nitric acids and ferric chloride were performed as previously described (2). Absorption spectra were measured with a Beckman DU spectrophotometer using 1.00-cm. silica cells. The solvent was 95% ethanol.

In one preparation of the anthranilic acid product precipitation was obtained in less than one day by seeding the solution.

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SUMMARY

A series of 7-aminobenzyl-8-quinolinols has been prepared by the reaction of representative heterocyclic primary amines with benzaldehyde plus 8-quinolinol. Spot tests were performed on these compounds, and the absorption spectra of the compounds were measured.

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## REFERENCES

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