[Contribution from the Department of Chemistry of the University of Colorado]

THE ACTION OF ACETIC ANHYDRIDE UPON SOME FURFURYLIDENE ANTHRANILIC ACIDS

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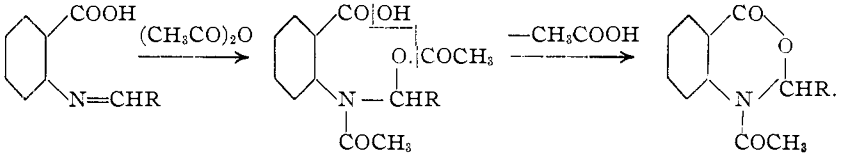
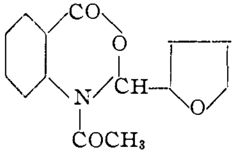
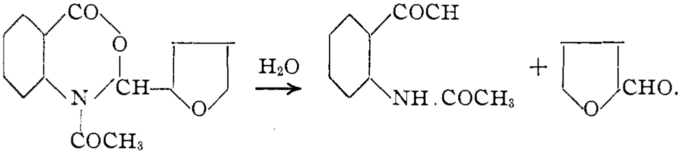
The action of acetic anhydride upon furfurylidene anthranilic acid might be inferred from its action upon benzylidene anthranilic acids,[1] in which case aceto-ketodihydro-benzometoxazines are formed, thus

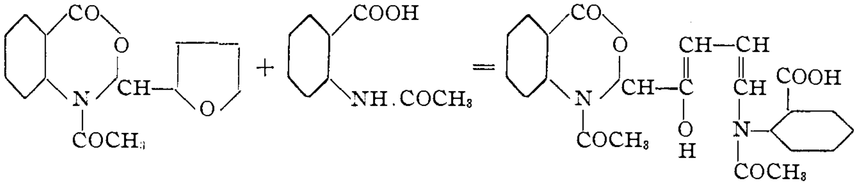


It is probable that the corresponding furfuryl compound is formed,  , but suffers a partial decomposition by the acetic acid set free in the reaction, resulting in the formation of aceto-anthranilic acid and furfurol.



This decomposition is similar to that of the oxazine derivatives obtained from benzylidene anthranilic acids which decompose into aceto-anthranilic acid and the original aldehyde on boiling with conc. hydrochloric acid.

The aceto-anthranilic acid thus set free then reacts with the remaining furfuryl oxazine derivative and in the acid solution the furan ring is broken, thus



This is analogous to the well-known reaction of furfurol with amines in acid solution.

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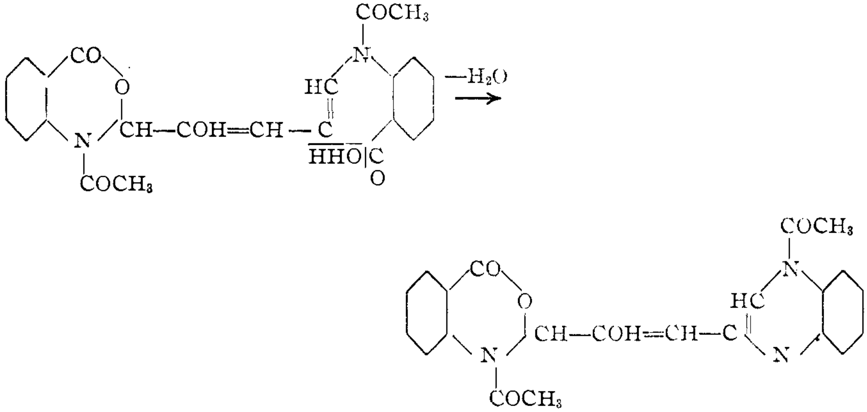
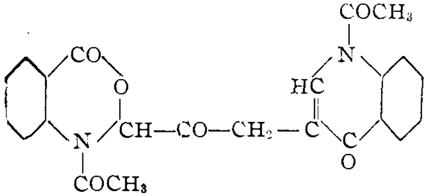
[1] This Journal, **34,** 161 (1912); **35,** 282 (1913); **36,** 603 (1914); **37,** 582 (1915); **44,** 1756 (1922).

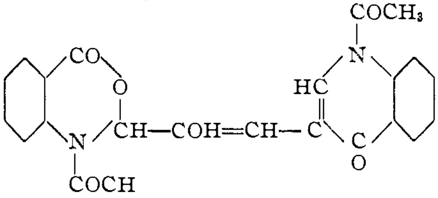
The resulting carbon chain then suffers condensation with the carboxyl of the substituted anthranilic acid thus formed so that a quinoline derivative results. This final compound yields no furfurol or aceto-anthranilic acid on boiling with acids or alkalies.



This compound should be either the keto or the enol form of an aceto-ketodihydro-quinolyl-acetyl-aceto-ketodihydro-benzometoxazine.



(keto) or



(enol)

Since experiment gave no evidence of the formation of an oxime or a phenylhydrazone, it was assumed that the compound was in the enol form.

The reaction was also tried with 2-bromomethyl-5-furfurylidene anthranilic acid, but no corresponding compound could be isolated. That the 2-bromomethyl-5-furfuryl oxazine derivative is formed during the course of the reaction is shown by the fact that the reaction products contain aceto-anthranilic acid and the aldehyde, but the succeeding complex reactions gave no product similar to that obtained from furfurylidene anthranilic acid.

Experimental

Furfurylidene Anthranilic Acid.—Molecular proportions of furfurol and anthranilic acid were dissolved in the least possible amount of alcohol at about 30°, thoroughly mixed, and then cooled to 0°. The furfurylidene anthranilic acid separated out as a bulky precipitate colored red by the furfurol dye that forms in small amounts. The substance was purified by redissolving the precipitate in fresh alcohol and allowing the alcohol to evaporate, when the dye collects upon the sides of the beaker. Similar successive treatments rendered the compound pure enough for analysis as a straw-colored powder, melting at 151° with decomposition.

Analysis. Calc. for $C_{12}H_9NO_3$: N, 6.51. Found: 6.44.

Aceto-ketodihydro-quinolyl-enol-acetyl-aceto-ketodihydro-benzometoxazine.—Furfurylidene anthranilic acid was heated in xylene with an excess of acetic anhydride. In the presence of the anhydride the furfurylidene anthranilic acid is only slightly soluble in the xylene, while the products which form are readily soluble. When the solution became a deep wine-red, the xylene was decanted from the furfurylidene anthranilic acid still unacted upon. The operation was repeated with successive portions of xylene and anhydride until the conversion into the final product was complete. The xylene liquors were united and cooled when the impure substance separated out. It was then recrystallized from xylene until light yellow, and finally from alcohol, yielding a colorless crystalline compound, melting at 208°.

Analyses. Calc. for $C_{23}H_{18}N_2O_6$: C, 66.02; H, 4.34; N, 6.70. Found: C, 65.56; H, 4.47; N, 6.58.

Mol. wt. Calc.: 418. Found (cryoscopic method): 396.

In a separate experiment aceto-anthranilic acid was isolated from the reaction mixture and furfurol was shown, by the aniline hydrochloride test, to be escaping.

2-Bromomethyl-5-furfurylidene anthranilic acid.—2-Bromomethyl-5-formylfuran was prepared from levulose by means of hydrobromic acid.[2] With anthranilic acid in molecular proportions in benzene solution at 0°, it forms the corresponding substituted furfurylidene anthranilic acid; recrystallized from benzene it yields yellow crystals, which change to olive-green on standing. At 120° the substance chars but does not melt.

Analysis. Calc. for $C_{13}H_{10}NO_3Br$: N, 4.54. Found: 4.50.

Summary

1. Furfurylidene and 2-bromomethyl-5-furfurylidene anthranilic acids have been prepared.

2. Acetic anhydride reacts with furfurylidene anthranilic acids to form as a final product a compound whose constitution is probably represented by an aceto-ketodihydro-benzometoxazine group united by means of $—COH=CH_2—$ to a similar dihydro-quinolyl group.

3. The reaction of acetic anhydride with 2-bromomethyl-5-furyfurylidene anthranilic acid yields no compound corresponding to that obtained from furfurylidene anthranilic acid.

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[2] *J. Chem. Soc. Trans.*, **79**, 361 (1901).