HYDRATION OF THE 2-MONOANIL OF 1,3-DIPHENYLPROPANE-1,2,3-TRIONE. REVISED STRUCTURE OF THE HYDRATION PRODUCT.

> J. P. Freeman^{*} Department of Chemistry, University of Notre Dame Notre Dame, Indiana 46556

M. J. Haddadin Department of Chemistry, American University of Beirut Beirut, Lebanon

W. H. Rastetter^{*}, T. Chancellor Department of Chemistry, Massachusetts Institute of Technology Cambridge, Massachusetts 02139

Abstract: The base-catalyzed hydration of anil 1 affords O-benzoylmandelanilide (7) rather than hydroxylamine 2 as was previously reported.

The report¹ of the abnormal² hydration of anil <u>1</u> (<u>1</u> + <u>2</u>, Scheme 1) prompted the study of the hydration as a model for N(5)-adduct formation in the flavin coenzyme series.³ Two of us (J. P. F. and M. J. H.),⁴ however, have assigned a revised structure to the presumed anil (<u>1</u>) used in the original hydration study.¹ Scheinbaum's hydration¹ is now understood⁴ not to be of anil <u>1</u>, but of the meso-ionic compound <u>8</u> to O-benzoylmandelanilide (<u>7</u>). Herein we report that authentic anil <u>1</u>⁵ also affords <u>7</u> upon hydration rather than hydroxylamine <u>2</u> as was previously reported.¹

Authentic anil $\underline{1}$, 5^{5} prepared by condensation of dibenzoylmethane and nitrosobenzene, undergoes hydration in moist acetonitrile containing tertiary amine, tertiary amine N-oxide or potassium phenolate catalysts.³ The hydration product, O-benzoylmandelanilide, ($\underline{7}$) is evident by TLC within minutes and is the major product after 15 hours.⁶ O-Benzoylmandelanilide formed by hydration of $\underline{1}$ is indistinguishable (TLC, high field ¹H and ¹³C NMR, IR, electron impact MS and mixture mp) from authentic $\underline{7}$ made by benzoylation of mandelanilide ($\underline{9}$).⁷ A reaction performed in CD₃CN with N-methylpyrrolidine N-oxide as catalyst and monitored by ¹H NMR (270 MHz) showed the conversion of $\underline{1}$ into $\underline{7}$ without the accumulation of intermediates.

Scheme 1 shows the probable mechanism for the hydration of anil <u>1</u>. The hydration likely gives the normal Schiff's base hydration product $(\underline{3})^2$ as the initial intermediate. The rearrangement via aziridine <u>4</u> is precedented by the rearrangement of the adduct of anil <u>1</u> with thiols.⁵ Also, the conversion <u>4</u> + <u>5</u> is paralleled in the reaction of enolic <u>B</u>-diketones with N-aminophthalimide and Pb(OAc)₄,⁸ which is thought to proceed via similar hydroxy-substituted aziridines (see <u>4</u>). Finally, intermediate <u>6</u> in the N to O acyl shift (<u>5</u> + <u>7</u>) is also the likely

intermediate formed from meso-ionic compound 8 during the hydrolysis 8 + 7.4



References and Notes

(1) M. L. Scheinbaum, Tetrahedron Lett. 1969, 4221.

(2) The normal hydration of Schiff's bases yields aminals (see <u>3</u>) rather than hydroxylamines.
(3) J. W. Frost, W. H. Rastetter, <u>J. Am. Chem. Soc.</u> 1980, <u>102</u>, 7157. Authentic anil <u>1</u> (ref. 5) was used in this study. The conclusions reached remain sound despite the revised structure for the hydration product (7) reported herein.

(4) J. P. Freeman, M. J. Haddadin, A. M. Kattan, J. Org. Chem., in press.

(5) J. Mirek, J. Moskal, A. Moskal, Tetrahedron 1975, 31, 2145.

(6) A reaction catalyzed by N-methylpyrrolidine N-oxide and allowed to proceed for 24 hours afforded after recrystallization 53% of white O-benzoylmandelanilide (mp 178-179.5°C); see J. W. Frost, Ph.D. Thesis, Massachusetts Institute of Technology, 1981.
(7) Prepared by fusion of mandelic acid and aniline according to the procedure of C. A. Bischoff, P. Walden J. Liebig's Ann. Chem. 1894, 279, 128-129.
(8) H. Person, K. Luanglath, A. Foucaud, Tetrahedron Lett. 1977, 221.

(Received in USA 7 December 1981)