

A Facile Conversion of α -Keto Acid Anils to Anilides

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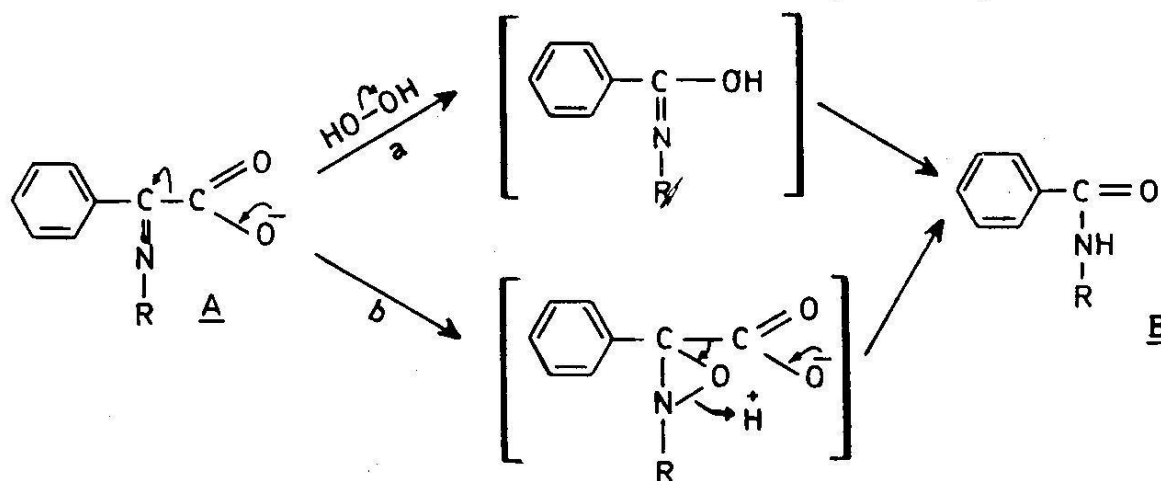
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The conversion of an α -keto acid anil to the corresponding anilide was shown to occur in aqueous solution by using hydrogen peroxide as an oxidising agent under neutral or slightly alkaline conditions. The generality of this reaction has been established. A number of α -keto acid anils were prepared and shown to undergo this change by oxidative decarboxylation giving good yields of the corresponding anilides under the same reaction conditions. The reaction is generally complete in one hour at room temperature. Optimum pH for this reaction is 8.5.

Experimental*Synthesis of Phenylglyoxylic Acid Anil*

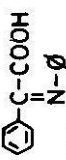
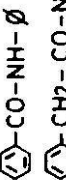















Phenylglyoxylic acid (7.5 g, 0.05 mole) in dry methanol (30 ml) was treated with stirring at room temperature with aniline (4.65g, 0.05 mole) in dry methanol (20 ml). Immediately phenylglyoxylic acid anil started to precipitate. The solution was stirred for one hour at room temperature, cooled and filtered. The anil was washed with cold methanol and dried under vacuum (7.87 g, 70%) and melted at 152° (decomp.). Analysis: Found:



It has also been observed that the same reactions can be realized by replacing hydrogen peroxide with other oxidising agents such as alkaline KMnO_4 or $\text{K}_3\text{Fe}(\text{CN})_6$ giving lower yields of the anilides. Oxidation using Fenton's reagent [1] failed to give this reaction indicating that this reaction does not involve free radical mechanism.

C = 74.47, H = 4.97, N = 6.23%;
calculated for $\text{C}_{14}\text{H}_{11}\text{NO}_2$: C = 74.65,
H = 4.92, N = 6.22%; Infrared absorption
frequencies in nujol mull (cm^{-1}):
485 (m), 670 (m), 680 (s), 700 (m),
743 (s), 780(w), 835 (w), 995 (s),
1023 (w), 1255(m), 1315 (s), 1340(s),
1430(s), 1450(s), 1578(m), 1585 (m)
and 1620 (s).

TABLE: PREPARATION OF ANILIDES **B** FROM α -KETO-ACID ANILS **A**

A	Anils ^a 	ϕ	%Yields	m.p.	%N		m.p.	%Yields	Anilide	
					Found	Calculated			B 	B' 
A1			30	152 ^b	6.31	6.22	87	163 ^c	6.95	7.10
A2		HOOC-	23	166	5.17	5.20	53	251	5.83	5.80
A3		O ₂ N-	10	260	10.58	10.37	48	216	11.52	11.57
A4		Cl-	38	86	5.45	5.39	38	192	6.10	6.04
A5		Br-	45	101	4.71	4.60	35	167	5.13	5.07
A6			6	224	4.92	5.09	13	159 ^d	5.61	5.66
A1'			40	125 ^e	5.61	5.85	90	117 ^f	6.59	6.63
A2'		HOOC-	38	172	4.93	4.95	61	240	5.51	5.49
A3'		O ₂ N-	8	202	9.76	9.86	47	114	10.87	10.93
A4'		Cl-	47	180	5.02	5.12	43	136	5.73	5.70
A5'		Br-	60	278	4.37	4.40	48	146	4.85	4.83
A6'			9	202	4.93	4.84	39	154	5.41	5.36

a. Some anils can also be prepared from their anilinium salts by sublimation under vacuum (10^{-3} mm). They all melted with decomposition.

b. reported m.p. 151-52^{o2}; c. reported m.p. 163^{o3}; d. reported m.p. 159-60^{o4}; e. reported m.p. 131-32^{o5}

f. reported m.p. 117-18^{o6}.

*Oxidation of Phenylglyoxylic Acid Anil
With Hydrogen Peroxide*

To a solution of phenylglyoxylic acid anil (0.225 g, 0.001 mole) in 0.1M aqueous sodium hydroxide (pH adjusted at 8.5) was added hydrogen peroxide (15%, 0.5 ml) with stirring at room temperature. After 15 minutes the precipitated benzanilide was extracted into ether. The ethereal solution washed with a little cold water and dried over anhydrous sodium sulphate before evaporating to dryness. The crude product so obtained was sublimed at 90°C (10⁻³ mm) to give benzanilide (0.177 g, 90%) melting at 115-116°C, and was identical in infra-red absorption with authentic specimen*. Infra-red absorption frequencies in nujol mull (cm⁻¹): 690(m), 722 (s), 755(m), 840(w), 897(w),

975(w), 1030(w), 1075(w), 1165 (m), 1260 (w), 1375 (s), 1460 (s), 1150 (w), 1600 (m), 1650 (s) and 3230 (weak and broad).

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* Authentic specimens of anilides were obtained by treating equimolar quantities of the corresponding acids with appropriate amino compounds and N,N-dicyclohexylcarbodiimide in redistilled tetrahydrofuran. Dicyclohexylurea was removed and anilides purified by recrystallization followed by sublimation under vacuum