

bubbled through a benzene solution of the crude chloride to give an 80% yield of the amide, recrystallized from alcohol, m. p. 187–188°.

Anal. Calcd. for $C_{18}H_{24}O_2N_2$: N, 9.33. Found: N, 9.33.

Hydrolysis of the Condensation Product (VII).—A number of attempts to hydrolyze the acid and its dihydro derivative by boiling with acids and bases were unsuccessful; the starting materials were recovered even after boiling for ten days with 10% sodium hydroxide.

To a solution of 20 g. of potassium hydroxide in 20 cc. of water in a nickel crucible was added 20 g. of (VII). The crucible was heated over a free flame while the mixture was carefully stirred. As water was driven off the mixture solidified; it then melted again and evolved aniline (identified as the benzoyl derivative from a run carried out in glass apparatus). When the evolution of aniline had stopped the hot mixture again solidified. It was dissolved in water and boiled with charcoal. The filtrate, on acidification, gave a yellow solid. This was dried and extracted with three 25-cc. portions of hot chloroform. The residue from evaporation of the chloroform was decolorized in methyl alcohol; after three recrystallizations from dilute methyl alcohol the product, 3,5-diethylbenzoic acid (X), melting at 133°, weighed 2.5 g.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.20; H, 7.87; neut. equiv., 178. Found: C, 74.05; H, 8.04; neut. equiv., 174.

Trimesic Acid (XI).—To a solution of 1 g. of 3,5-diethylbenzoic acid and 1 g. of potassium carbonate in about 50 cc. of water was added 7.0 g. of potassium permanganate.

The mixture was heated until a vigorous reaction occurred; when the reaction subsided the mixture was heated for about ten minutes longer. The clear solution obtained after treatment with sulfur dioxide was acidified with hydrochloric acid and cooled in ice-salt. The white solid was collected, dissolved in aqueous potassium carbonate, precipitated with hydrochloric acid and dried. It did not melt at 300°. One-half gram of the acid was converted to the methyl ester by treatment with phosphorus pentachloride and methyl alcohol. After three crystallizations from methyl alcohol the ester melted at 146–147°. A sample prepared from authentic trimesic acid melted at 146–147°; mixtures of the two samples melted at 146–147°.

Anal. Calcd. for $C_{12}H_{12}O_6$: C, 57.1; H, 4.76. Found: C, 57.0; H, 4.87.

Summary

2-Ethyl-2-hexenal aniline and maleic anhydride give 75–80% yields of 5,7-diethyl-2-phenyl-2-azabicyclo-(2,3,1)-oct-6-ene-3-one-8-carboxylic acid. The structure of this product has been proved by reduction to the dihydro derivative, and by degradation to 3,5-diethylbenzoic acid which was oxidized to trimesic acid.

The reaction has been shown to occur through tautomerization of the anil and addition of maleic anhydride to the diene system of the resulting enamine.

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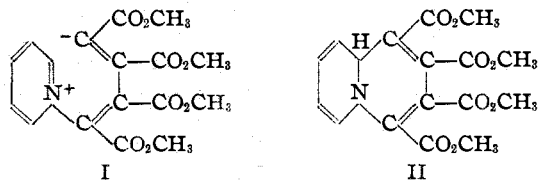
RECEIVED JULY 12, 1939

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Reactions of Anils. IV.¹ The Reactions of Benzalaniline and Cinnamalaniline with Methyl Acetylenedicarboxylate

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The behavior of simple anils toward methyl acetylenedicarboxylate is of interest in connection with the novel structure (I) assigned by Diels and Alder² to the labile isomer obtained from pyridine and this reagent. Since only the carbon-nitrogen double bond appears to be involved in the formation of this substance and its stable isomer (II), other compounds containing this linkage might be expected to give similar products.



(1) For the third communication in this series see *THIS JOURNAL*, **61**, 3568 (1939).

(2) Diels and Alder, *Ann.*, **510**, 87 (1934).

It has been found that benzalaniline and the acetylenic ester, reacting in commercial ether, give low yields of a substance (VI) having the composition corresponding to the addition of one molecule of the anil to one of the ester. However, the fact that the yields were greatly improved by the presence of a small amount of water suggested that the reaction involved hydrolysis of the anil. Addition of the liberated aniline to the acetylenic bond of the ester would give (IV), which by tautomerization ($IV \rightleftharpoons V$) and condensation with benzaldehyde would give (VI).

That the compound obtained has the structure (VI) was shown by its formation from methyl oxalacetate, benzaldehyde and aniline. It also could be obtained from methyl oxalacetate and benzalaniline in the presence of a trace of water, and from benzaldehyde, aniline and methyl acetyl-

