bubbled through a benzene solution of the crude chloride to give an 80% yield of the amide, recrystallized from alcohol, m. p.  $187-188^{\circ}$ .

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  $146-147^{\circ}$ . A sample prepared from authentic trimesic acid melted at  $146-147^{\circ}$ ; mixtures of the two samples melted at  $146-147^{\circ}$ .

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-hexenalaniline and maleic anhydride give 75-80% yields of 5,7-diethyl-2-phenyl-2azabicyclo-(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 eneamine.

Urbana, Illinois

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## [CONTRIBUTION FROM THE NOVES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

# Reactions of Anils. IV.<sup>1</sup> The Reactions of Benzalaniline and Cinnamalaniline with Methyl Acetylenedicarboxylate

BY H. R. SNYDER, HARRY COHEN AND WM. J. TAPP

The behavior of simple anils toward methyl acetylenedicarboxylate is of interest in connection with the novel structure (I) assigned by Diels and Alder<sup>2</sup> 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, 3558 (1939). 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  $\gtrsim$  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-

<sup>(2)</sup> Diels and Alder, Ann., 519, 87 (1984).



enedicarboxylate. The substance has the interesting property of dissolving in warm dilute alkali, and may be recovered unchanged from such a solution by acidification. This weakly acidic property must derive from the highly unsaturated character of the molecule.

Cinnamalaniline, C<sub>6</sub>H<sub>5</sub>CH=CHCH=NC<sub>6</sub>H<sub>5</sub>, which approximates more nearly the structural features of pyridine, reacts with the acetylenic ester to give two isomeric products of the composition corresponding to the addition of two molecules of the ester to one of the anil. This is the composition to be expected by analogy to the products from pyridine. When carried out in the absence of a solvent the reaction is highly exothermic, resembling in this respect also the reaction of pyridine and the ester. These compounds have not yet been obtained in quantities great enough to permit structural studies; since the work must be interrupted for a year it is being reported in its present status.

#### Experimental

Benzalaniline and Methyl Acetylenedicarboxylate.—A mixture of 8 g. of methyl acetylenedicarboxylate, 14 g. of benzalaniline, 2 g. of water and 50 cc. of absolute ether was allowed to stand for two days at room temperature. Filtration gave 3.8 g. of white crystals; after recrystallization from toluene the product, methyl  $\alpha$ -benzal- $\alpha'$ -phenyliminosuccinate, melted at 192–193°. Similar results were obtained from aniline, benzaldehyde and methyl acetylenedicarboxylate in anhydrous ether.

Anal. Calcd. for  $C_{19}H_{17}O_4N$ : C, 70.6; H, 5.27; N, 4.34; methoxyl, 19.4; mol. wt., 323. Found: C, 70.44; H, 5.38; N, 4.34; methoxyl, 19.2; mol. wt., 353.

Benzalaniline and Methyl Oxalacetate.—A solution of 0.1 g. of methyl oxalacetate and 0.1 g. of benzalaniline in 1.0 cc. of wet ether deposited crystals after a few hours at room temperature. After two days these were removed by filtration and recrystallized from toluene; m. p. 192–

193°; this melting point was not affected by admixture of the product described above.

Benzaldehyde, Aniline and Methyl Oxalacetate.—A solution of 0.1 g. of aniline, 0.1 g. of benzaldehyde and 0.2 g. of methyl oxalacetate in 3.0 cc. of absolute ether deposited crystals after a few hours. After recrystallization from toluene the product melted at 192–193°. The melting point was not affected by admixture of the above samples.

Cinnamalaniline and Methyl Acetylenedicarboxylate.— A solution of 2.8 g. of the ester and 4.0 g. of the anil in 70 cc. of petroleum ether was heated under reflux for two days. After decantation of the solvent, the residue was washed with petroleum ether and crystallized several times from methanol. The yellow crystals weighed 1.1 g. (23%) and melted at 166–167°.

Anal. Calcd. for  $C_{27}H_{25}O_5N$ : C, 66.0; H, 5.13; N, 2.86; methoxyl, 27.7; mol. wt., 491. Found: C, 66.10; H, 5.29; N, 3.13; methoxyl, 27.4; mol. wt., 441.

The higher-melting isomer was obtained by the following procedure. A flask containing 1.4 g. of the ester was cooled in an ice-bath and 2.0 g. of the anil was added with stirring. The mixture was kept in the ice-bath for four hours and was then allowed to stand at room temperature for two weeks. After washing with petroleum ether, the residue was dissolved in 15 cc. of toluene. The yellow crystals which separated from this solution after about two hours were collected and recrystallized from methanol; m. p. 309–310°, yield 0.05 to 0.10 g.

Anal. Calcd. for  $C_{27}H_{25}O_8N$ : C, 66.0; H, 5.13; N, 2.86; mol. wt., 491. Found: C, 66.2; H, 5.17; N, 2.90; mol. wt., 436.

Addition of petroleum ether to the toluene mother liquor caused precipitation of the low-melting isomer, which after crystallization from methanol melted at  $166-167^{\circ}$ ; yield 0.5 g. (20%).

### Summary

Benzalaniline reacts with methyl acetylenedicarboxylate in the presence of water to give methyl  $\alpha$ -benzal- $\alpha'$ -phenyliminosuccinate. The same product may be obtained from benzaldehyde, aniline and methyl oxalacetate or from benzalaniline and methyl oxalacetate.

Cinnamalaniline and methyl acetylenedicarboxylate react to give two isomeric products of composition corresponding to one molecule of anil to two of the ester. The structures of these products have not been determined.

URBANA, ILLINOIS

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