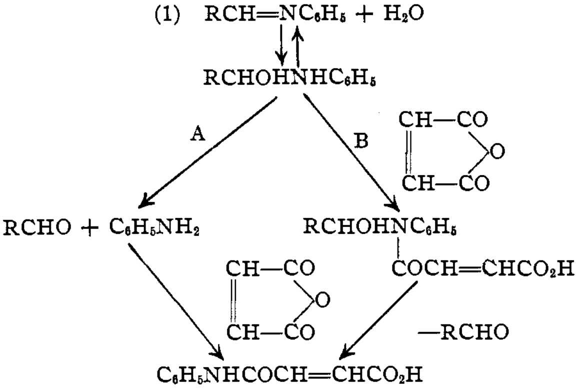
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

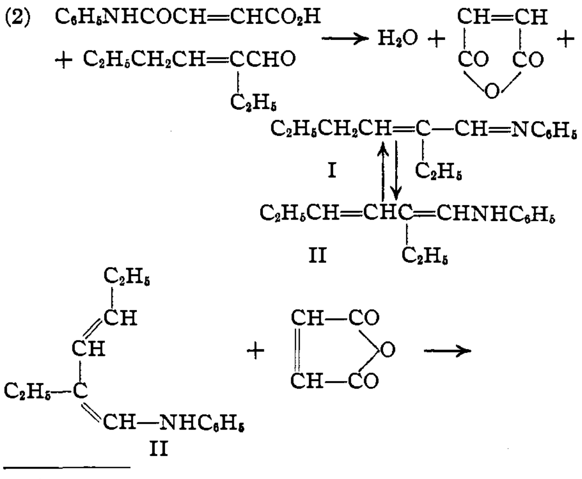
Reactions of Anils. V. The Reversibility of the Reaction with Acid Anhydrides

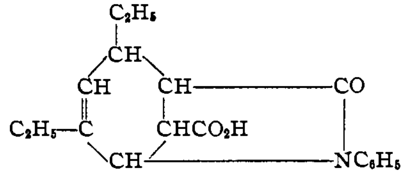
BY H. R. SNYDER AND JOHN C. ROBINSON, JR.

Anils react with maleic andydride in the presence of water to form maleanilic acid and aldehydes.[1,2] On the basis of evidence now available,[3] the reaction may be formulated as shown. Formation of the final products may involve decomposition of the product of hydration followed by acylation (A), or these two steps may occur in the alternate order (B).



The recently discovered Diels–Alder reaction between maleic anhydride and the enamine form of 2-ethyl-2-hexenalaniline (II)[2] offers a unique opportunity for investigating the reversibility of reactions of the above type. If maleanilic acid and 2-ethyl-2-hexenal undergo the reverse reaction (2) to give maleic anhydride and the anil (I), then these should combine to form the bicyclic amido acid (III).





III

The reverse reaction has been found to occur readily. When mixtures of maleanilic acid and 2-ethyl-2-hexenal were heated on the steam-bath, the condensation product, III, was obtained in good yields. Similarly, 2-methyl-2-pentenal was converted to the dimethyl analog of III. The occurrence of the reverse reaction is of practical interest, because this method of synthesis is more convenient than that involving the preparation of the anils.

It is probable that the formation of the condensation product from maleanilic acid and an unsaturated aldehyde involves interaction of the two substances to form an addition product, perhaps that indicated in path B of equation 1. It is unlikely that the maleanilic acid reverts to maleic anhydride and aniline, for no condensation product was obtained when 2,3-dimethylbutadiene was substituted for the unsaturated aldehyde. Another possible path is that depending on the participation of water. Maleanilic acid might be hydrolyzed, yielding maleic acid and aniline. The latter would react with the aldehyde to form the anil and water and the maleic acid would be in equilibrium with maleic anhydride and water. Only a trace of water would be required to initiate the process, since more is formed in the later steps. However, if the reaction proceeds according to this scheme, it should be incapable of starting in the presence of a strong dehydrating agent. Actually, the addition of phenyl isocyanate to the reaction mixture only reduced the yield. N-Phenylmaleimide, which is known to form when maleanilic acid is heated, was found by trial not to be a precursor of the condensation product.

Experimental

Maleanilic Acid and Unsaturated Aldehydes. (1).—A mixture of 14 g. of maleanilic acid and 10 g. of 2-ethyl-2-hexenal was refluxed on a steam-bath for twenty-four

---

[1] Bergman, THIS JOURNAL, **60**, 2811 (1938).

[2] Snyder, Hasbrouck and Richardson, *ibid.*, **61**, 3558 (1939).

[3] Snyder, Levin and Wiley, *ibid.*, **60**, 2025 (1938).

hours. The red, viscous liquid, extracted with the minimum quantity of boiling benzene, was separated from the water layer. The crystals deposited from the benzene solution after two hours were dissolved in aqueous sodium bicarbonate and the solution decolorized. The solid precipitated upon acidification was recrystallized from aqueous alcohol; m. p. 143–144°; melting point of mixture with authentic 5,7-diethyl-2-phenyl-2-azobicyclo-(2,3,1)-oct-6-ene-3-one-8-carboxylic acid[2] 143–144°; yield, 14–16.5 g. (60–70%).

(2) Similar yields of 5,7-dimethyl-2-phenyl-2-azabicyclo-(2,3,1)-oct-6-ene-3-one-8-carboxylic acid, m. p. 157–158°, were obtained by the use of 2-methyl-2-pentenal.[4]

Anal. Calcd. for $C_{16}H_{17}O_3N$: N, 5.17. Found: N, 5.06.

This product also was prepared by the reaction of the corresponding anil with maleic anhydride. 2-Methyl-2-pentenalaniline was prepared by the method described[2] for 2-ethyl-2-hexenalaniline; b. p. 131–132° (10 mm.). The anil was treated with maleic anhydride as previously described.[2] The condensation product was obtained in 60% yield; m. p. 157.5–158°; a mixed m. p. with a sample prepared from maleanilic acid showed no depression.

Degradation with concentrated sodium hydroxide[2] gave 3,5-dimethylbenzoic acid, m. p. 166–167°; a mixed m. p. with an authentic sample showed no depression.

(3) When N-phenylmaleimide[5] was substituted for maleanilic acid in (1), no product soluble in aqueous sodium bicarbonate was formed.

(4) Repetition of (1) with 10 g. of maleanilic acid, 7 g. of 2-ethyl-2-hexenal, and 1 g. of phenyl isocyanate gave 7 g. (45%) of III, m. p. 141–143°.

(5) When 52 g. of 2,3-dimethylbutadiene was substituted for 2-ethyl-2-hexenal in (1), no reaction was observed and maleanilic acid was recovered.

Summary

The condensation product previously obtained from maleic anhydride and 2-ethyl-2-hexenalaniline is more conveniently obtained by heating a mixture of maleanilic acid and 2-ethyl-2-hexenal. The occurrence of this reaction is considered as evidence that the formation of maleanilic acid and an aldehyde from an anil, maleic anhydride, and water is a reversible process.

---

(4) Doebner and Weissenborn, *Ber.*, **35**, 1144 (1902).

(5) Anschütz and Wirtz, *Ann.*, **239**, 142 (1887).

URBANA, ILLINOIS RECEIVED AUGUST 11, 1941

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

The Synthesis of 3,5-Diethylbenzoic Acid

BY H. R. SNYDER, ROBERT R. ADAMS AND A. V. MCINTOSH, JR.

An authentic sample of 3,5-diethylbenzoic acid was sought for comparison with that obtained by degradation of the product of condensation of maleic anhydride with 2-ethyl-2-hexenalaniline.[1] Such comparison was desirable in order to eliminate the possibility that the material in hand might be a methylpropylbenzoic acid.

Several methods for the synthesis of 3,5-diethylbenzoic acid were tested. The oxidation of *sym*-triethylbenzene with nitric acid, a procedure which is reasonably satisfactory for the preparation of 3,5-dimethylbenzoic acid from mesitylene,[2] produced a mixture from which a dibasic acid and a keto acid were isolated. From the analyses and the fact that they were produced from *sym*-triethylbenzene, these substances must be 5-ethylisophthalic acid and 3-aceto-5-ethylbenzoic acid. The first was obtained as the residue from extraction of the mixed acids with benzene; the second was isolated by distillation of the methyl esters of the benzene soluble acids. 3,5-Diethylbenzoic acid was also isolated from this fraction, but in yields of only 1–2%.

The alkylation of bromobenzene with ethyl bromide and aluminum chloride was considered a possible route to a precursor of the desired acid. Berry and Reid[3] obtained products described as brominated ethylbenzenes by treatment of bromobenzene with ethylene and aluminum chloride at 70°. It is known that when bromobenzene is heated in the presence of aluminum chloride, disproportionation to benzene and dibromobenzenes occurs.[4] However, Norris and Turner[5] have concluded that in the rearrangement of the chlorotoluenes by aluminum chloride at temperatures of 100° or below, the methyl group migrates more readily than the chlorine atom. It thus appeared possible that 3,5-diethylbromobenzene might be prepared by the low temperature ethylation of bromobenzene. When the experiment

---

(1) Snyder, Hasbrouck and Richardson, THIS JOURNAL, **61**, 3558 (1939).

(2) Fittig, *Ann.*, **141**, 144 (1867).

(3) Berry and Reid, THIS JOURNAL, **49**, 3146 (1927).

(4) Copisarow, *J. Chem. Soc.*, **119**, 442 (1921).

(5) Norris and Turner, THIS JOURNAL, **61**, 2128 (1939).