REISSERT COMPOUND STUDIES. PART XXV. A NOVEL REACTION WITH 2-NITROBENZALDEHYDE AND THE ANION OF 2-ACETYL-1,2-DIHYDROISOQUINALDONITRILE[1]

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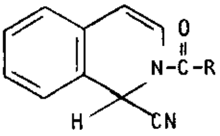
In contrast to the reaction of the anion of 2-benzoyl-1,2-dihydroisoquinaldonitrile with aldehydes, the reaction of the anion of 2-acetyl-1,2-dihydroisoquinaldonitrile with 2-Nitrobenzaldehyde involves the formation of a novel type of product (VII).

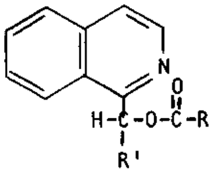
The condensation of aldehydes, including 2-nitrobenzaldehyde,[2] with the anion of 2-benzoyl-1,2-dihydroisoquinaldonitrile (I) to give, through an intramolecular rearrangement, esters of the type II is a well known reaction.[2-4] Support for the intramolecular nature of the reaction is had by the isolation of III from the reaction of the anion of IV with benzaldehyde.[5]



I R = C_6H_5

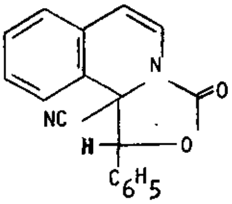
IV R = OC_2H_5

V R = CH_3



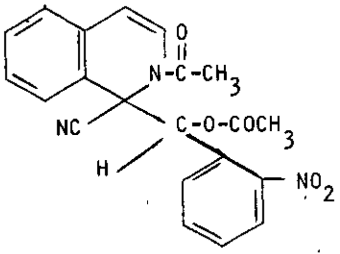
II R = C_6H_5

VI R = CH_3, R' = 2-$NO_2C_6H_4$

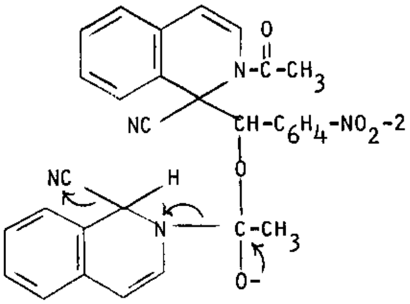


III

We now wish to report that condensation of the anion (generated by phenyl lithium in ether-dioxane) of 2-acetyl-1,2-dihydroisoquinaldonitrile (V) with 2-nitrobenzaldehyde in the usual manner[2,3] did not give rise to VI but rather gave a 48% yield of a compound, m.p. 199-201°, to which we have assigned structure VII



VII



VIII

(Found: C, 64.37, 64.28; H, 4.39, 4.43; N, 10.69, 10.65. Calcd. for $C_{21}H_{17}N_3O_5$: C, 64.44; H, 4.38; N, 10.74.) The infrared [γ (KBr): 1765, 1695, 1635, 1515, 1340 cm.$^{-1}$], nuclear magnetic resonance [($DMSO-d_6$): 1.78 (s, 3H), 1.97 (s, 3H), 5.93 (d, H), 6.70 (d, H), 6.83 (s, H), 7.00-7.83 δ (m, 8H)], and mass spectral data (Found m/e 391.1202, Calcd. 391.1168) all support Structure VII. The dominant ion in the mass spectrum of VII was the 1-cyanodihydroisoquinoline ion (m/e 155) and the fragmentation of VII generally follows the pattern previously indicated for Reissert compounds.[6]

Compound VII can only have arisen through an intermolecular attack of the alkoxide, formed by reaction of the Reissert compound anion with the carbonyl group of the aldehyde, on another molecule of the Reissert compound to give the intermediate VIII which then gives VII as indicated. Support for this was obtained by the isolation of isoquinoline, as its picrate, from the reaction mixture.

The scope of this reaction is under investigation.

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