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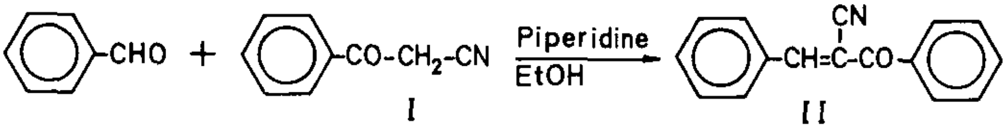
# A NEW COMPOUND FROM AN OLD REACTION: THE CONDENSATION OF ω-CYANOACETOPHENONE WITH BENZALDEHYDE.

José L. Soto*, Carmen Aparicio, Carlos Seoane and José A. Valdés
Departamento de Química Orgánica. Facultad de Química. Universidad Complutense. Madrid-3. Spain

Abstract - The reaction of ω-cyanoacetophenone with benzaldehyde affords a 4H-pyran together with the normal condensation product.

The Knoevenagel condensation of ω-cyanoacetophenone (I) with benzaldehyde has been known for more than sixty years since it was reported by Kauffmann in 1917 [1] (Scheme 1).



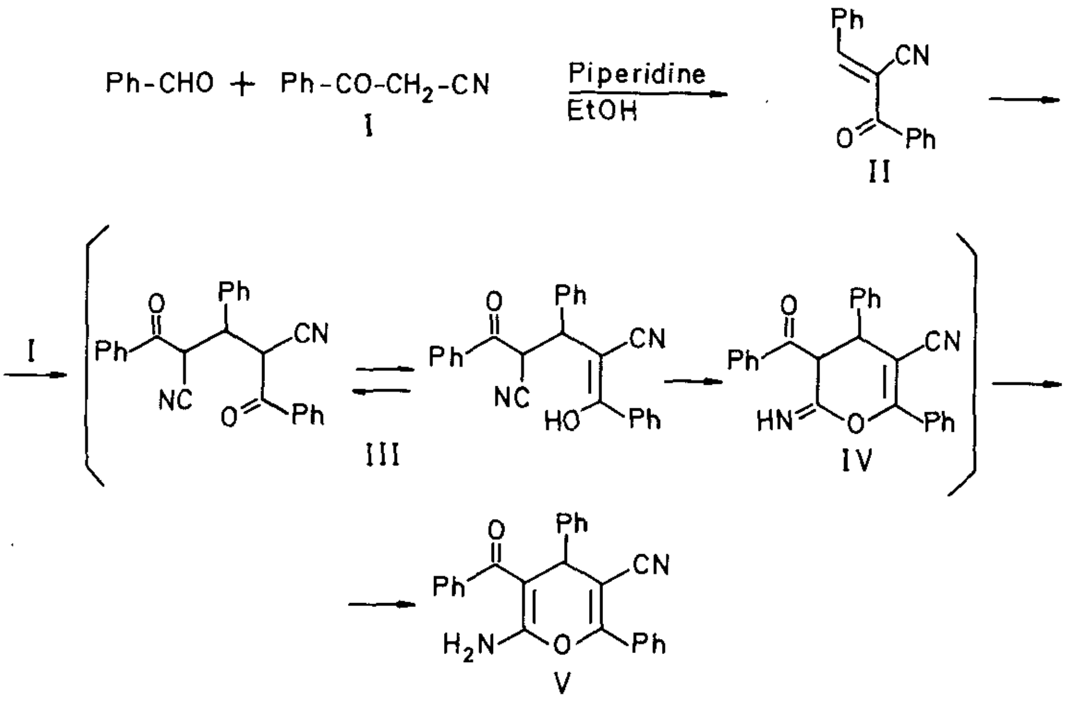
Scheme 1

This reaction was apparently not used again until 1950 [2]. Since then, the reaction was used many times to prepare α-benzoylcinnamonitrile (II) [3-19] with a good yield of this compound, and no side reactions were reported.

In connection with a project now underway, we used the above mentioned reaction to prepare II. This compound was actually obtained in yields ranging from 62% to 80% by carrying out the reaction at either room temperature or reflux temperature. In either case, II crystallizes nicely from the reaction medium. However, chromatographic examination of the reaction mixture showed the presence of another product in sizeable quantity. This compound could be isolated in a pure state from the mother liquors after separating II. (In a typical experiment, after reflux for 4 hours 1.6 g. of this compound and 15.7 g. of II were obtained).

The *microanalytical and mass spectral data* (C, 79.25%; H, 4.90%; N, 7.57%; $M^+$, 378) are in agreement with the molecular formula $C_{25}H_{18}N_2O_2$.

Spectroscopic data of this compound lead to a structure of 2-amino-4H-pyran (V). The IR-spectrum (potassium bromide pellet) shows a strong conjugated carbonyl stretching band at 1640 $cm^{-1}$ and a cyano stretching band at 2215 $cm^{-1}$. This group also gives rise to a broad singlet at 9.1 ppm in the $^1H$-NMR spectrum (in DMSO-$d_6$ at 60 $MH_z$). The 15 hydrogens of the three aromatic rings appear as a *multiplet* at 6.6 - 7.9 ppm and the hydrogen atom located in position 4 of the pyran ring gives



Scheme 2

rise to a sharp singlet at 4.56 ppm, which is in good agreement with the reported values for this kind of ring[20,21]. On the other hand, the $^{13}C$ NMR spectrum of V (in DMSO-d$_6$ at 20 MH$_z$) shows, besides the aromatic carbons, a characteristic singlet of the cyano carbon at 117.64 ppm, and a carbonyl carbon at 193.63 ppm, which are in good agreement with literature data[22,23]. The $C_4$ carbon of the heterocyclic ring appears at 41.34 ppm, the $C_2$ and $C_6$ peaks appear at 156.43 and 160.70 ppm and the $C_3$ and $C_5$ carbons give rise to another pair of peaks at 92.99 and 85.42 ppm, which agree with calculated values[22].

The formation of pyran V, can be explained by a reaction sequence (Scheme 2) beginning with the Knoevenagel condensation of ω-cyanoacetophenone (I) with benzaldehyde. The resulting α-benzoylcinnamomononitrile (II) undergoes a Michael's addition of another molecule of I, to give adduct III. Cyclization of III through a nucleophilic attack by the carbonyl oxygen at the cyano group affords the 2-amino-4H-pyran ring.

This result, which amounts to cyclization of a 5-oxonitrile, is in good agreement with the known behaviour of these compounds. They seem to undergo such a cyclization[24] if the enolic form of the carbonyl group is stabilized by an adequate subtituent, such a cyano, ethoxycarbonyl or phenyl group in the α-position with respect to the carbonyl group.

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