Knoevenagel Reaction of Malononitrile and Its "Dimer" with β-Ketoanilides

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The reaction of benzoylacetonilides with malononitrile has been investigated. The structure of the compounds obtained (2, 3, 4) have been assigned on the basis of chemical properties and spectral data.

(Keywords: Heterocycles; Knoevenagel reaction)

Die Knoevenagel-Reaktion von Malononitril und seinem ,,Dimer" mit β-Ketoaniliden

Die Reaktion von Malononitril mit Benzoylacetoniliden wurde untersucht. Die Struktur der dabei erhaltenen Verbindungen (2—4) wurde auf Basis der chemischen und spektroskopischen Eigenschaften zugeordnet.

J. W. Ducker² has shown that under Cope-Knoevenagel reaction conditions acetoacetanilides react with malononitrile in benzene to give the dicyanomethylene compounds (a). The product (a) heating in basic (piperidine) ethanol solution produces the pyridines (b).

Scheme 1
The aim of the present study has been to investigate the condensation of benzoylacetanilides $1_\text{a,b,c,d}$ with malononitrile.

It was found that the reaction of equimolar amounts of benzoylacetanilides $1_\text{a,b,c,d}$ and malononitrile in presence of piperidine in boiling ethanol yielded two compounds ($2_\text{a,b,c,d}$ and $3_\text{a,b,c,d}$). They were separated utilizing the far greater solubility of one of them in boiling ethanol.

When the proportion of malononitrile was increased $2_\text{a,b,c,d}$ was isolated as a main product. The optimum yield of $2_\text{a,b,c,d}$ was obtained from two moles of malononitrile and one mole of benzoylacetanilide.

Attempts were made to parallel formation of $2_\text{a,b,c,d}$ or $3_\text{a,b,c,d}$ by the reaction of 4,4-dicyano-3-phenyl-N-phenyl-but-3-enamide with malononitrile in presence of piperidine in boiling ethanol but only the product $3_\text{a,b,c,d}$ was formed.

The attempt to synthesize $2_\text{a,b,c,d}$ from $3_\text{a,b,c,d}$ and malononitrile in the molecular ration $1:1$ was unsuccessful.

The analytical and IR (Table 1), MS spectral data observed for compounds $3_\text{a,b,c,d}$ show good agreement with compound (b) to which the structure of 6-anilino-2-hydroxy-4-methyl-pyridine-3-carbonitrile was assigned by Ducker$^1$.

The structure of $2_\text{a}$ was elucidated on the basis of chemical and analytical data, and IR, $^1$H-NMR, $^{13}$C-NMR, MS spectral data. Com-