

Reactions of Acetoin and Benzoin with Malononitrile

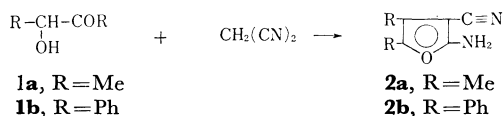
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Although the Knoevenagel reactions of aldehydes and ketones have been investigated by numerous workers,¹⁾ little is known about the reactions involving acyloins and benzoin. The only reported examples involve the reaction of ethyl cyanoacetate with benzoin²⁾ and acetoin³⁾ in the presence of sodium ethoxide to give α,β -disubstituted γ -lactones.

The present paper deals with the reactions of malononitrile with acetoin (**1a**) and benzoin (**1b**) under the conditions used by Cope⁴⁾ to give 2-amino-3-cyano-4,5-disubstituted furans (**2**) in good yield. The structure of **2a** was inferred from elementary analysis and spectral studies. The NH_2 stretching



bands appeared at 3488 and 3400 cm^{-1} , and the conjugated CN group occurred at 2200 cm^{-1} . The NMR spectrum (CDCl_3) showed the broad NH_2 signal at 4.68 ppm and the two methyl at 1.92 and 2.07 ppm, which are just in the range expected for methylfurans.⁵⁾ The fact that the methyl protons show a sharp singlet suggests that **2a** is present almost completely in the amino form shown. This conclusion may be supported by the fact that the IR spectrum shows no imino absorption.

Recently, 2-amino-3-cyano-4,5-diphenylfuran (**2b**) has been synthesized by Russian workers from desyl chloride and malononitrile in the presence of sodium ethoxide.⁶⁾ The melting point of **2b**

obtained in the present investigation agreed with that reported. The IR and NMR spectra suggest that **2b** is also present in the amino form.

Experimental

NMR spectra were obtained on a JNM-C-60 high-resolution NMR spectrometer at 19–20°C. Tetramethylsilane was used as an internal standard. IR spectra were determined in the chloroform solution using a Perkin-Elmer 521 spectrophotometer.

Reaction of Acetoin (1a) with Malononitrile. In a 200 ml round bottomed flask attached to a constant water separator,⁴⁾ were placed 11.4 g (0.12 mol) of acetoin, 6.6 g of malononitrile, 3.0 g of ammonium acetate, 2.0 ml of acetic acid, and 60 ml of benzene. The solution was refluxed at 120°C in an oil bath till the formation of water ceased. After the solution had been cooled to room temperature, deposited crystals were recrystallized from ethanol-benzene. The yield of **2a**, melting at 167.5–168.5°C, was 7.4 g (54.4% based on malononitrile).

Found: C, 61.87; H, 6.08; N, 20.20%. Calcd for $\text{C}_7\text{H}_8\text{N}_2\text{O}$: C, 61.75; H, 5.92; N, 20.58%.

IR (CHCl_3) 3488 (m, NH), 3400 (m, NH), 2200 (s, $\text{C}\equiv\text{N}$), 1640 cm^{-1} (s, δNH_2); NMR (CDCl_3) 1.92 (s, CH_3), 2.07 (s, CH_3), and 4.68 ppm (broad, NH_2).

Reaction of Benzoin (1b) with Malononitrile. A mixture of 11.0 g of benzoin, 4.5 g of malononitrile, 3.0 g of ammonium acetate, and 2.0 ml of acetic acid in 60 ml of benzene was refluxed for 5 hr in an apparatus of the same type as used above. After the solvent had been removed, solid product was recrystallized from toluene and then from ethanol, giving 5.0 g of pale yellow needles (**2b**), melting at 205–206°C (uncor., lit.⁶⁾ 207–208°C), yield, 28% based on malononitrile.

Found: C, 78.28; H, 4.65; N, 10.79%. Calcd for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}$: C, 78.44; H, 4.65; N, 10.76%.

IR (CHCl_3) 3490 (m, NH), 3400 (m, NH), 2200 (s, $\text{C}\equiv\text{N}$), and 1638 cm^{-1} (s, δNH_2); NMR ($\text{DMSO}-d_6$) 7.25 (s, Ph), 7.44 (s, Ph), and 7.79 (broad, NH_2).

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