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Reactions of Acetoin and Benzoin with Malononitrile

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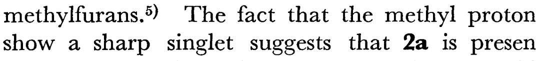
Although the Knoevenagel reactions of aldehydes and ketones have been investigated by numerous workers,[1] little is known about the reactions involving acyloins and benzoins. The only reported examples involve the reaction of ethyl cyanoacetate with benzoin[2] and acetoins[3] in the presence of sodium 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 Cope[4] 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.



1a, R=Me
1b, R=Ph

2a, R=Me
2b, R=Ph

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 m*l* 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 m*l* of acetic acid, snd 60 m*l* 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 $C_7H_8N_2O$: C, 61.75; H, 5.92; N, 20.58%.

IR ($CHCl_3$) 3488 (m, NH), 3400 (m, NH), 2200 (s, C≡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 m*l* of acetic acid in 60 m*l* 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 $C_{17}H_{12}N_2O$: C, 78.44; H, 4.65; N, 10.76%.

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

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