

SYNTHESIS OF 2-PYRONE DERIVATIVES

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2-Pyrone derivatives were synthesized by the reaction of monoketone compounds with ketenethioacetals in the presence of powdered potassium hydroxide as a base.

In a continuation of our previous studies of the ketenethioacetals, we have synthesized several heterocyclic compounds using the displacement reaction of ketenethioacetals.^{1,2,3)} The present paper reports the syntheses of 2-pyrones by the reaction of ketenethioacetals with monoketone derivatives.

Reaction of ketenethioacetal, methyl 2-cyano-3,3-bis(methylthio)acrylate (MCMA) (2a), with acetophenone in the presence of powdered potassium hydroxide as a base gave 3-cyano-4-methylthio-6-phenyl-2-pyrone (3a), mp 201°, in 65% yield. In the same manner, 3-cyano-4-methylthio-6-(*p*-methoxy and *p*-bromo)phenyl-2-pyrones (3b, c) were obtained in a good yield as shown in Chart 1. Reaction of 1b and 1c with 2-methoxycarbonyl-3,3-bis(methyl-

thio)acrylate (2b) gave 3-methoxycarbonyl-4-methylthio-6-(p-methoxy and p-bromo)phenyl-2-pyrones (3d, e) in a poor yield as shown in Chart 1.

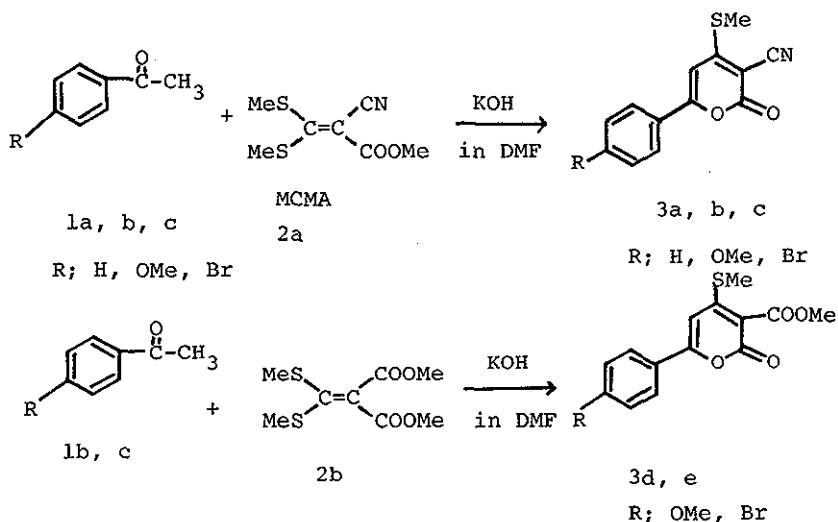


Chart 1

No.	R	mp (°C)	Yield (%)	IR(KBr) cm^{-1}	UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm(log ϵ)
3a	H	201	65	2200 (CN), 1715 (C=O)	239(3.08), 255(3.42) 330(3.50), 370(3.08)
3b	MeO	215	35	2200 (CN), 1715 (C=O)	250(3.42), 342(3.42) 395(3.83)
3c	Br	240	42	2200 (CN), 1725 (C=O)	245(*), 262(*), 338(*), 375(*)
3d	MeO	181	4	1705 (C=O), 1670 (C=O)	245(3.96), 340(4.02) 380(4.22)
3e	Br	229	2	1705 (C=O)	245(3.82), 338(4.08)

* Concentration is unknown because of insufficient solubility.

In a similar manner, cyclic monoketone derivatives, cyclohexanone and β -tetralone, reacted with 2a to give the condensed 2-pyrone derivatives (4a, b) in 20%, 60% yield, respectively.

Analogous to the foregoing reaction, acetyl heterocyclic compounds, 2-acetylthiophene, 3-acetylpyridine, and 2-acetylquinoline, were allowed to react with 2a to produce the corresponding 2-pyrone derivatives (5a, b, c) in a good yield as shown in Chart 2.

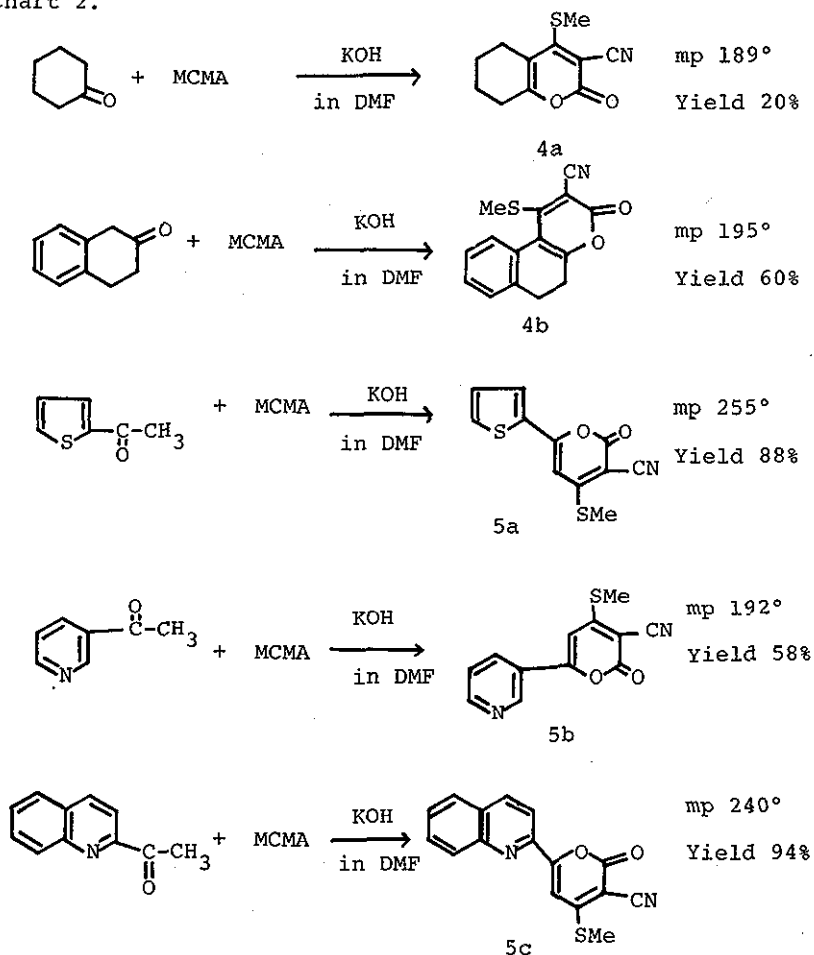


Chart 2

Since 4-methylthio-2-pyrone derivatives have an active methylthio group for nucleophilic reagents such as amines or active methylene compounds,^{4,5,6)} compounds 3, 4, and 5 would be useful as synthetic intermediates of 2-pyrone derivatives and this synthetic method may offer a useful information for synthesis of natural 2-pyrone derivatives such as aloenin,⁷⁾ yangonin,⁸⁾ auroventin,⁹⁾ and nectriapyrone.¹⁰⁾

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