SYNTHESES 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 potssium 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.

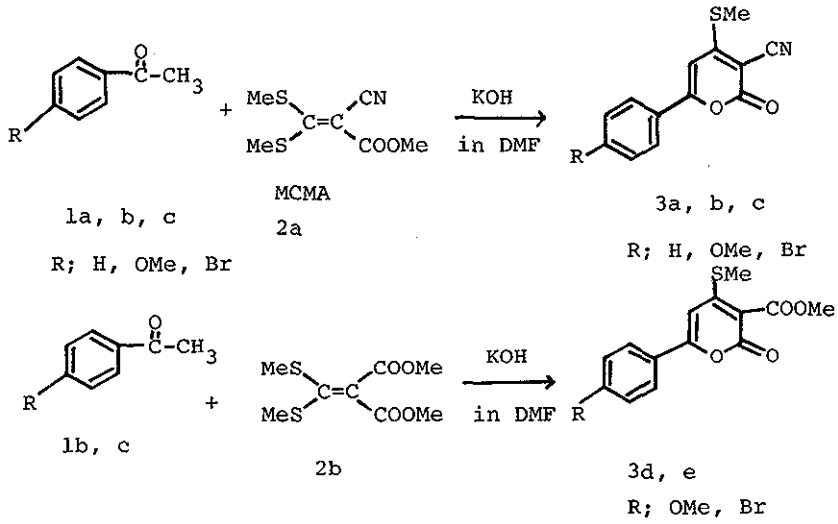

Chart 1

No.	R	mp (°C)	Yield (%)	IR(KBr) cm^{-1}	UV λ_{max}^{EtOH} nm(logε)
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.

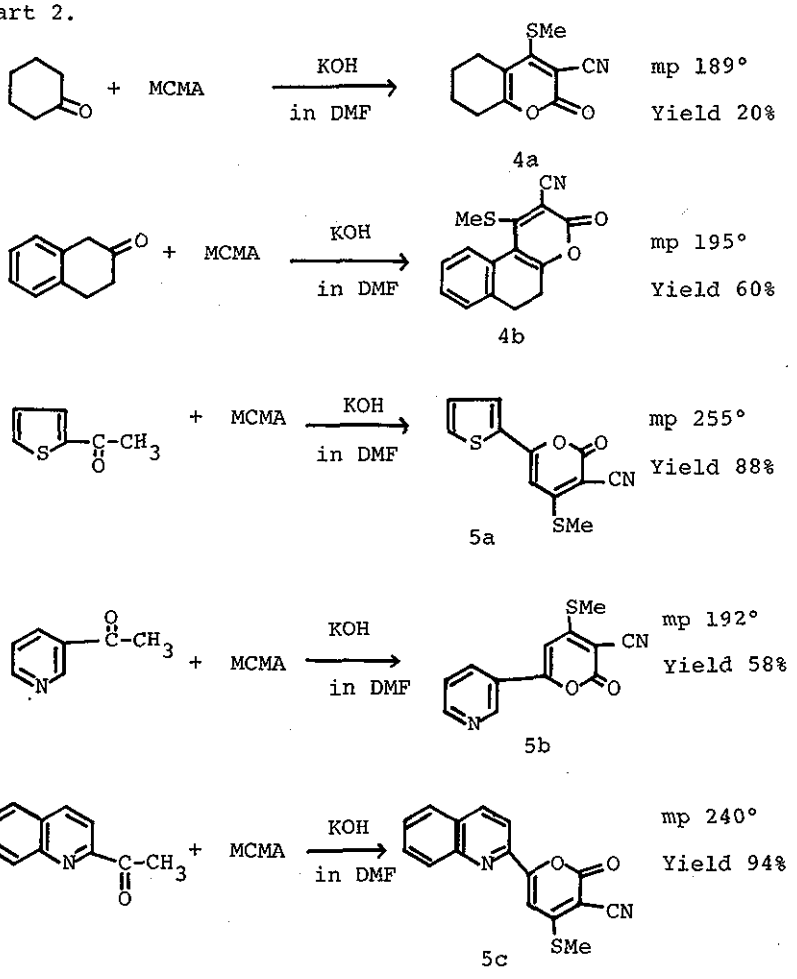

Chart 2

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 synthsis of natural 2-pyrone derivatives such as aloenin,[7] yangonin,[8] auroventin,[9] and nectriapyrone.[10]

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