SYNTHESIS OF 2-PYRONE DERIVATIVES USING KETENETHIOACETAL(3)

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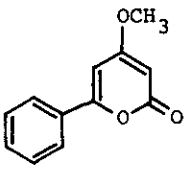
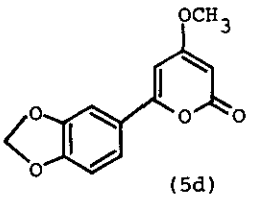
Ketenethioacetals appropriatly functionalized (cyano, ester carbonyl, ketone carbonyl, sulfonyl groups and etc.) are very usefull reagents for the synthesis of heterocyclic compounds. We now wish to report the synthesis of 2-pyrone derivatives using dimethyl bis(methylthio)methylenemalonate (1).

The reaction of compound 1 with the acetyl compounds (acetophenone, p-methoxyacetophenone, 3,4-dimethoxyacetophenone, 3,4-methylenedioxyacetophenone, p-bromoacetophenone, and 3-acetylpyridine) in the presence of powdered potassium hydroxide as a base in dimethyl sulfoxide gave the corresponding 6-substituted 3-methoxycarbonyl-4-methylthio-2-pyrone derivatives(3a, b, c, d, e, and f) in good yields. Similarly, p-methoxybenzalacetone and 3,4-methylenedioxybenzalacetone were allowed to react with 1 to yield the corresponding 6-substituted styryl-3-methoxycarbonyl-4-methylthio-2-pyrones (4a and b) in 15% and 17% yields,respectively.

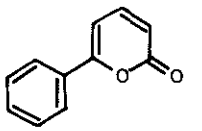
Compounds 3 (a: 6-phenyl, b: 6-(p-methoxy)phenyl, c: 6-(3,4-dimethoxy)phenyl, d: 6-(3,4-methylenedioxy)phenyl) were treated with sodium methylate in methanol to give the corresponding 6-substituted phenyl-4-methoxypyrones (5a: 4-methoxyphenylcoumalin, 5b, 5c, and 5d: 4-methoxyparacotoin) in good yields. Phenylcoumalin (6-phenyl-2-pyrone)(7a) and paracotoin (6-(3,4-methylenedioxy)phenyl-2-pyrone)(7b) were obtained by the desulfurisation of 4-methylthio-6-phenyl-2-pyrone(6a) and 6-(3,4-methylenedioxy)phenyl-4-methylthio-2-pyrone (6b) which were prepared by the decarboxylation with polyphosphoric acid in good yields.



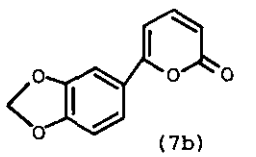
(5a)



(5d)



(7a)



(7b)