FORMATION OF 2-ALKYLTHIO-SUBSTITUTED 2H-PYRANS IN THE REACTION OF CYCLIC 1,3-DIKETONES WITH ALKYLTHIODIPHENYLCYCLOPROPENIUM IONS

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The reaction of methylthio-, ethylthio-, and benzylthiodiphenylcyclopropenium salts (1) with 5- and 6-membered cyclic 1,3-diketones to give either 2-alkylthio-2H-pyrans or dienone derivatives was studied.

Treatment of (1) with cyclic 1,3-diketones (2) in the presence of triethylamine afforded colorless crystals of 2-alkylthio-2H-pyrans (3). (3a) from (1a) and (2a) in 84%, (3b) from (1a) and (2b) in 74%, (3c) from (1a) and (2c) in 89%, (3d) from (1b) and (2a) in 58%, and (3e) from (1c) and (2a) in 67% yield. The structure of (3) was elucidated on the basis of their elemental analyses, IR, ^{1}H- and ^{13}C-NMR and mass spectroscopic data as well as chemical transformations described below.

2-Alkylthio-2H-pyrans (3) with mercury (II) chloride in an alcohol (ROH) underwent conversion to the corresponding 2-alkoxy-2H-pyrans (4), while treatment of (3a,d) with mercury (II) acetate in acetic acid yielded 2-hydroxy-2H-pyran (5). Oxidation of (5) follwed by hydrolysis produced known 2-benzoyl-5,5-dimethyl-cyclohexane-1,3-dione (6). The ^{1}H- and ^{13}C-NMR data of (3), (4), and (5) clearly show that the equilibrium lies completely on the side of the 2H-pyran.

In contrast, the reaction of (1) with 1,3-indandione yielded the ring-opened dienone derivatives (7) as a mixture of E and Z isomers. Desulfurization of (7) afforded (8) in good yield.