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

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Abstract-- The reaction of methylthio-, ethylthio-, and benzylthiodiphenylcyclopropenium salts with 5- and 6-membered cyclic 1,3-diketones giving 2-alkylthio-2H-pyrans in good yields is reported.

2H-Pyrans are apparently not well known.[1] Electrocyclic ring openings of 2H-pyrans and ring closures of dienones have been of considerable interest in view of the yet unresolved question how the presence of heteroatoms in a conjugated chain has their influence on the electrocyclic process.[2] Although some synthetic routes to the stable 2H-pyrans like halogen-substituted 2H-pyrans have been developed,[2] no physical as well as chemical properties of sulfur containing 2H-pyrans has been reported. Quite recently, we have communicated[3] the reaction of alkylthiodiphenylcyclopropenium salts (1) with acyclic 1,3-diketones to give the cyclopentadienol derivatives. Here we describe a novel cyclization reaction of (1) with cyclic 1,3-diketones to produce 2-alkylthio-substituted 2H-pyrans (3).

A mixture of alkylthiodiphenylcyclopropenium salt (1), cyclic 1,3-diketone (2), and triethylamine in a molar ratio of 1:1:2 was stirred in benzene at room temperature for 15 min. Column chromatography of the reaction product on silica gel afforded colorless crystals of the alkylthio-2H-pyran (3)(Table 1).[4] 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.

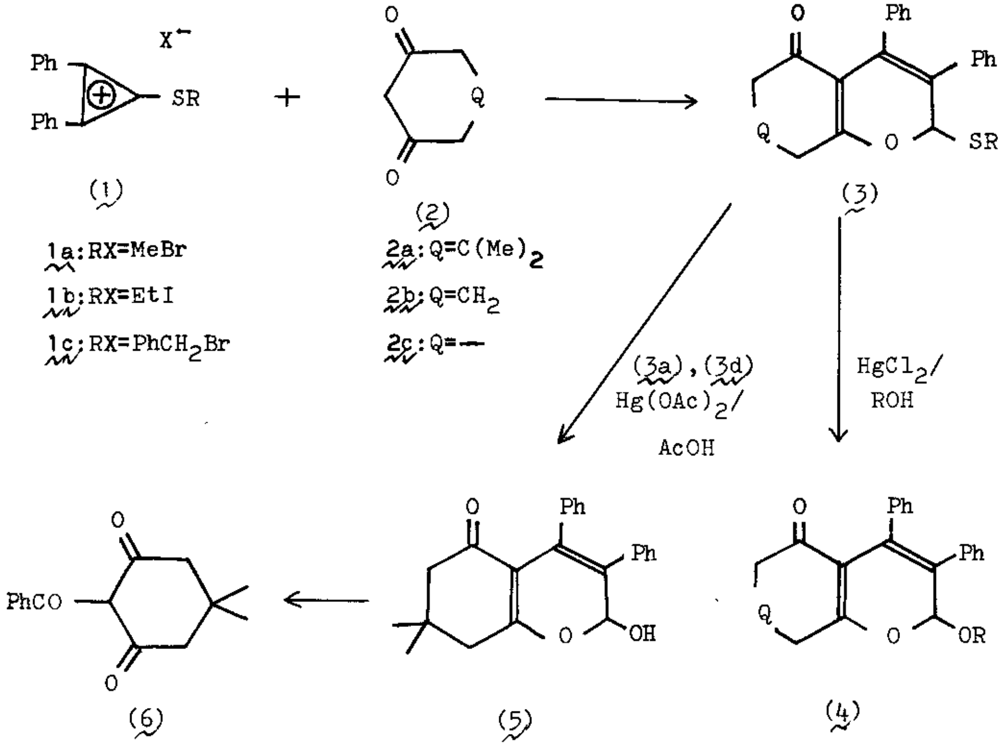


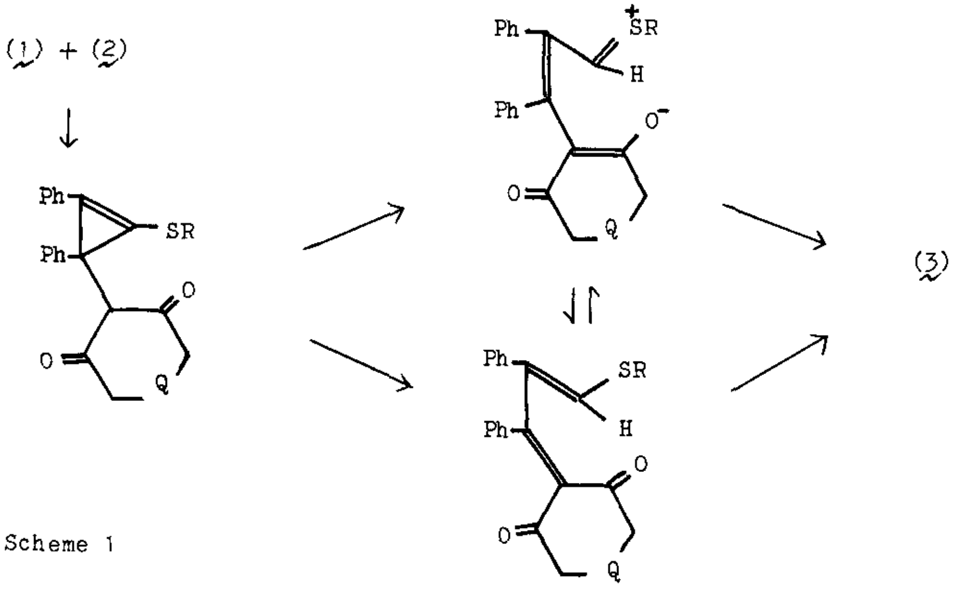
Table 1. Alkylthio- and Alkoxyl-substituted 2H-Pyrans (**3**) and (**4**).

Product	Reactants		Yield/%	Mp/^{o}C
(**3a**)	(**1a**)	(**2a**)	84	190-192
(**3b**)	(**1a**)	(**2b**)	74	174-176
(**3c**)	(**1a**)	(**2c**)	89	175
(**3d**)	(**1b**)	(**2a**)	58	152-154
(**3e**)	(**1c**)	(**2a**)	67	153-159
(**4a**) R=Me	(**3a**)		93	175-177
(**4b**) R=Et	(**3a**)		78	116-118
(**4c**) R=Me	(**3b**)		79	175-177
(**4d**) R=Me	(**3c**)		87	130-133
(**5**)	(**3a**)		57	105-107

2-Alkylthio-substituted 2H-pyrans (3) with mercury (II) chloride in an alcohol underwent conversion to the corresponding 2-alkoxy-2H-pyrans (4),[5] while treatment of (3a) with mercury (II) acetate in acetic acid yielded the 2-hydroxy-2H-pyran (5). Oxidation of (5) with sodium dichromate in acetic acid followed by hydrolysis produced known 2-benzoyl-5,5-dimethylcyclohexane-1,3-dione (6).

A reaction mechanism shown in Scheme 1 is proposed. The initial step involves a nucleophilic attack of the carbanions generated from (2) on the cyclopropene ring of (1). Subsequent elimination of the acidic methine hydrogen and ring expansion gives either a conjugated betain or a dienone intermediate, followed by intramolecular cyclization leading to the 2H-pyran (3) as depicted in the Scheme. The ^{1}H- and ^{13}C-nmr data clearly show that the equilibrium lies completely on the side of the 2H-pyran.

The marked difference in the reaction products between cyclic and acyclic 1,3-diketones is possibly ascribed to the ring strain of (2).



Scheme 1

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1. R. M. Acheson, "An Introduction to the Chemistry of Heterocyclic Compounds" 3rd ed., p.283, Wiley (1977).
2. E. N. Marvel, "Thermal Electrocyclic Reactions" pp.305-319, Academic Press (1980).
3. H. Yoshida, M. Nakajima, T. Ogata, K. Matsumoto, R. M. Acheson, and J. D. Wallis, Chem. Lett., 1983, 155.
4. e.g. (**3a**): ir(KBr) 1670, 1630 cm^{-1}; ^{1}H-nmr($CDCl_3$) 1.16(3H, s, $C\underline{H}_3$), 1.21(3H, s, $C\underline{H}_3$), 2.30(5H, s, $SC\underline{H}_3$ and $C\underline{H}_2$), 2.48(2H, s, $C\underline{H}_2$), 6.03(1H, s, $\underline{C}H$), 6.9-7.2(10H, m, 2 x Ph); ^{13}C-nmr($CDCl_3$) 13.9(q, $S\underline{C}H_3$), 27.3 and 29.4(q, 2 x $\underline{C}H_3$), 31.8(s, C-7), 42.9 and 51.7(t, C-6 and C-8), 88.3(d, C-2), 116.5(s), 123.4(s), 126.6(d), 127.0 (d), 127.4(d), 127.8(d), 129.2(d), 132.4(s), 136.9(s), 137.8(s), 168.5(s, C-8a), 193.5(s, C=O); m/e 376 (M^+).
5. e,g. (**4a**): ir(KBr) 1670, 1630 cm^{-1}; ^{1}H-nmr($CDCl_3$) 1.11(3H, s, $C\underline{H}_3$), 1.20(3H, s, $C\underline{H}_3$), 2.26(2H, $C\underline{H}_2$), 2.58(2H, $C\underline{H}_2$), 3.59(3H, $OC\underline{H}_3$), 5.56(1H, $C\underline{H}$), 6.8-7.7(10H, m, 2 x Ph); ^{13}C-nmr($CDCl_3$) 27.3 and 29.3(q, 2 x $\underline{C}H_3$), 31.7(s, C-7), 42.6 and 51.8(t, C-6 and C-8), 55.3(q, $O\underline{C}H_3$), 101.4(d, C-2), 113.9(s), 123.5(s), 126.5(d), 126.7(d), 127.7(d), 129.2(d), 129.3(d), 132.0(s), 137.1(s), 138.0(s), 167.2(s, C-8a), 193.6(s, C=O); m/e 360 (M^+).

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