Heterodiene Cycloadditions of 3-Acylchromones with Ethoxyethene

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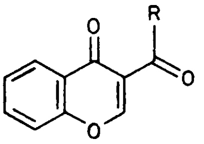
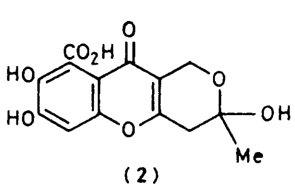
3-Acylchromones behave as heterodienes in stereoselective ($4\pi + 2\pi$) cycloadditions with ethoxyethene, the formal *endo*-addition product predominating.

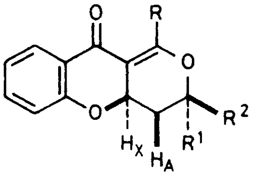
Recent results have demonstrated that the ($4\pi + 2\pi$) cycloaddition of α,β-unsaturated carbonyl compounds to enol ethers is encouraged by an acceptor group in the α-position of the heterodiene.[1] Since 3-acylchromones (**1**) incorporate this structural feature, they are potential precursors of the pyrano[4,3-*b*][1]benzopyran system, which is found intact in fulvic acid (**2**) and rearranged in other biologically active polyketide natural products.[2,3] In the absence of an alternative route to this system, the reactions of the chromones (**1**) with an enol ether have been examined.



(**1**)



(**2**)



(**3**) $R^1 = H_Y$, $R^2 = OEt$
(**4**) $R^1 = OEt$, $R^2 = H_Y$

a; R = H
b; R = Me
c; R = Ph

Treatment of 3-formylchromone (**1a**)[4] with excess of ethoxyethene in dichloromethane at room temperature resulted in the simultaneous formation of two products. The major of these was isolated by evaporation and crystallisation as

Table 1. Reaction of 3-acylchromones (**1**) with ethoxyethene.

Chromone	R	Method[a]	Reaction time /days	Products (% yields)[b]	
				(**3**)	(**4**)
(**1a**)	H	A	3	75 (74)	15
(**1a**)	H	B	1	71 (68)	24
(**1b**)	Me	A	15	— (28)	—[c]
(**1b**)	Me	B	2	72 (33)	20
(**1c**)	Ph	A	15	— (—)	—[d]
(**1c**)	Ph	B	3	64 (57)	23[e]

[a] Method A: ethoxyethene (20 equiv.), CH_2Cl_2 [4 ml per mmol of (**1**)], room temp.; method B: ethoxyethene (2.1 equiv.), CH_2Cl_2 [1.8 ml per mmol of (**1**)], sealed tube, 115 °C. [b] Yields refer to chromatographically homogeneous material, isolated by evaporation, trituration, and crystallisation, followed by medium pressure column chromatography of the mother liquors over silica gel. Yields after the crystallisation but before the chromatography are shown in parentheses. All products were characterised by elemental analysis and spectrometry (mass, n.m.r., i.r.). [c] Reaction did not go to completion. [d] Substantial amount of starting material remained. [e] Starting material (5%) also recovered.

needles, m.p. 176—177 °C (ethanol). The minor was isolated from the mother liquors by chromatography as prisms, m.p. 83—84 °C (petroleum). Microanalysis and spectroscopy indicated that they were the isomeric cycloadducts (**3a**) and (**4a**), formal *endo* and *exo* addition products, respectively. Distinguishing features were found in the 220 MHz ^{1}H n.m.r. spectra; for (**3a**) the coupling constants J_{AX} and J_{AY} are 10 and 10 Hz, consistent with the *trans* diaxial relationships indicated; for (**4a**) the corresponding values are 10.5 and 2.8 Hz, indicating *trans* diaxial and axial–equatorial relationships, respectively.

Other results are shown in Table 1. The acetyl- and benzoylchromones (**1b**)[5] and (**1c**)[5] were less reactive than (**1a**), presumably reflecting adverse steric interactions during the cycloaddition. Synthetically useful reactions were observed at higher temperatures at the expense of some stereoselectivity.

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