Thermal Rearrangement of 4-Cyano-2,3-dihydro-5-ethoxy-3-methyl-3-(4-oxo-4*H*-1-benzopyran-3-yl)furans: a Reversed Alkoxycarbonylcyclopropane → 5-Alkoxy-2,3-dihydrofuran Transformation

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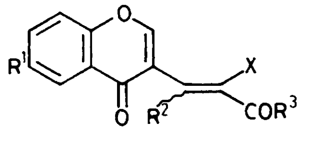
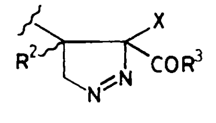
The title dihydrofurans (**3f**, R^1 = H, Me, and Cl), prepared from the α-cyano-ester (**1e**) and diazomethane, thermally rearrange to the cyclopropanes (**4f**) in predominantly *Z*-isomeric form.

The formation of the dihydrofuran (**3a**) from the 1-benzopyran derivative (**1a**) and diazomethane[1] involves a formal [1,5] sigmatropic rearrangement of the initially formed dihydropyrazole adduct (**2a**) (non-isolable) with nitrogen extrusion[2] and an acyl oxygen participation. The conversion (**2a**)→(**3a**) *via* the cyclopropane (**4a**) is ruled out as the [1,3] sigmatropic rearrangement of an acylcyclopropane such as (**4a**) is likely to involve the cleavage of the more substituted bond[3,4] so as to produce the dihydrofuran (**5**). The α-acetylacrylic ester (**1b**) with diazomethane similarly gives the dihydrofuran (**3b**). However, the methylenemalonic ester (**1c**) and diazomethane form the dihydropyrazole (**2c**) which on heating produces the *C*-methylated product (**1d**), the apparent failure of the ester carbonyl oxygen to participate in the [1,5] sigmatropic rearrangement of the diazocompound (**2c**) precluding the formation of the dihydrofuran (**3c**).

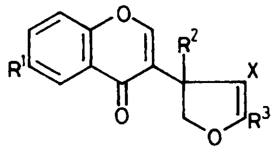
Surprisingly, we have now found that the α-cyanoester (**1e**) with diazomethane formed a complex mixture which on chromatography over alumina gave the title dihydrofuran (**3f**) (~25%) and the cyclopropane (**4f**) (~10%); the interconversion of these two products (**3f**) and (**4f**) could not be affected by alumina. Instantaneous loss of nitrogen associated with formation of a dihydropyrazole from the exocyclic alkenic bond (most likely of *E*-configuration[5]) of compound (**1e**) with diazomethane would give the α-cyano-β-methylacrylic ester (**1f**),[6] probably having the same configuration[7] as its precursor (**1e**), which would react further with diazomethane producing the dihydrofuran (**3f**),† presumably *via* the extremely unstable (**2f**). Here (**2f**), unlike several other analogues,[8,9] undergoes a formal [1,5] sigmatropic rearrangement involving the ester carbonyl oxygen with concomitant nitrogen extrusion yielding the dihydrofuran (**3f**). Intervention of the ionic intermediate (**6**) in the above transformation is ruled out as it would have given predominantly a mixture of unsaturated ester isomers.[9]



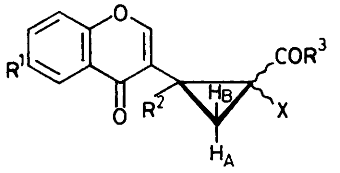
(**1**)



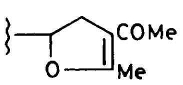
(**2**)



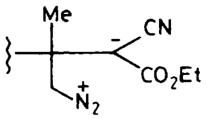
(**3**)



(**4**)



(**5**)



(**6**)

	R^2	R^3	X
a	H	Me	COMe
b	H	Me	CO_2Et
c	H	OEt	CO_2Et
d	Me	OEt	CO_2Et
e	H	OEt	CN
f	Me	OEt	CN

R^1 = H, Me, and Cl

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† All new compounds gave satisfactory microanalytical and spectral data.

The dihydrofuran (**3f**) does not arise *via* the cyclopropane (**4f**). In fact, heating (**3f**, $R^1 = H$) at 180 °C afforded (**4f**, $R^1 = H$) in nearly quantitative yield as a 3:1 mixture of *Z*- and *E*-isomers; similar thermal rearrangement of (**3f**, R^1 = Me or Cl) gave the (*Z*)-isomer of (**4f**, R^1 = Me), m.p. 144 °C, and (**4f**, R^1 = Cl), m.p. 180 °C. In contrast the 5-alkyl-2,3-dihydrofurans (**3a**) and (**3b**) were thermally stable to 200 °C. Unlike the amply demonstrated acylcyclopropane → dihydrofuran transformation and the reverse,[10] the conversion of alkoxycarbonyl-cyclopropanes[11] or -cyclopropenes[12] to 5-alkoxyfuran derivatives is rare and the reverse process was hitherto unknown. The thermal rearrangement of the title compound is thus the first example of a 5-alkoxy-2,3-dihydrofuran → alkoxycarbonyl-cyclopropane transformation.

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