The Acid-catalysed Cyclisation of Methyl 1-(3-Oxobutyl)-2-oxocyclopentanecarboxylate: *X*-Ray Analysis of the Product

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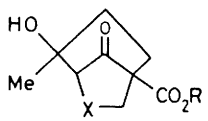
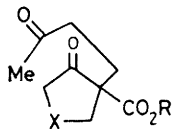
An *X*-ray analysis confirms that the acid-catalysed cyclisation of methyl 1-(3-oxobutyl)-2-oxocyclopentanecarboxylate leads to the formation of methyl 5-methyl-7-oxo-6-oxabicyclo[3.2.2]nonane-1-carboxylate *via* a rearrangement reaction.

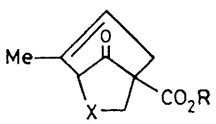
In the course of a synthetic project we have attempted to synthesise the hydroxy-ester (**1**). Since the corresponding ethyl ester (**2**) has been reported[1] to be the major product from acid catalysed cyclisation of the diketoester (**5**) we submitted (**4**) to the same reaction conditions (95% H_2SO_4, room temp., 16 h) in an attempt to prepare (**1**). However, we found that the properties of the product obtained (60%; m.p. 100—102 °C) were not consistent with the structure (**1**); rather the spectral data were consistent with the lactonic structure (**10**) [M^+, m/z 212; i.r., ν 1745 and 1718 cm^{-1}; ^1H n.m.r., δ 3.8 (3H, s), 1.42 (3H, s), 2.6 (1H, m), and 1.75—2.2 (9H, m); ^{13}C n.m.r., δ 172.7, 171.9, 82.9, 52.6, 51.9, 38.0, 30.9, 30.0, 29.6, 24.7, and 20.6 p.p.m.]. In order to confirm this result an *X*-ray analysis was undertaken.



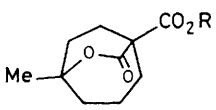
(**1**) R = Me, X = CH_2
(**2**) R = Et, X = CH_2
(**3**) R = Me, X = S



(**4**) R = Me, X = CH_2
(**5**) R = Et, X = CH_2
(**6**) R = Et, X = CH_2CH_2
(**7**) R = Me, X = S



(**8**) R = Me, X = CH_2
(**9**) R = Et, X = CH_2CH_2



(**10**) R = Me
(**11**) R = Et

Crystal data: triclinic, $a = 7.177(2)$, $b = 6.669(2)$, $c = 12.898(4)$ Å, $\alpha = 119.0(1)$, $\beta = 91.8(1)$, $\gamma = 88.5(1)°$, space group $P\bar{1}$, $Z = 2$, $R = 0.047$ for 1317 independent reflections having $I/\sigma(I) > 3.0$.†

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

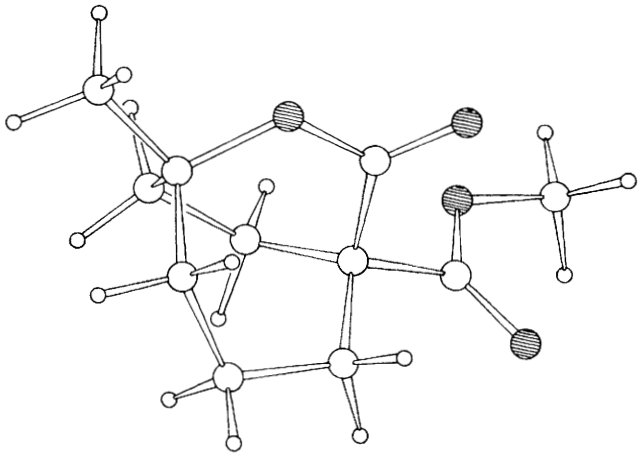


Figure 1. *X*-Ray structure of the lactone (**10**).

The *X*-ray structure is shown in Figure 1, and it confirms the product as the lactone (**10**). Rearrangements leading to similar cycloheptane systems have been observed previously[2] although lactones obtained in those systems were γ-lactones whereas (**10**) is a δ-lactone. Using short reaction times the alkene (**8**) was isolated along with (**10**) but further treatment of (**8**) with H_2SO_4 led to its conversion into (**10**). Reaction of the related diketoesters (**6**) and (**7**) with H_2SO_4 did not lead to lactone formation but instead gave (**9**) and (**3**) respectively. This behaviour is attributed to the lower strain present in (**9**) and (**3**) compared to (**8**).

In the light of these results we have repeated the literature reaction with (**5**) and find the ^1H and ^{13}C n.m.r. spectra of the product (75%; m.p. 58—59 °C, lit.[1] 61—62 °C) to be almost identical with those of (**10**) apart from differences associated with the change from a methyl to an ethyl ester. Thus the compound described in the literature is not in fact (**2**) but is (**11**).

This ring system has also been obtained by phenylselenyl or phenylsulphenyl lactonisation of a cycloheptene-carboxylic acid.[3]

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