Tetrahedron Letters No. 35, pp 3703 - 3706, 1972. Pergamon Press. Printed in Great Britain.

FLASH THERMOLYSIS.
GENERATION AND REACTIVITY OF KETOKETENES IN INTRAMOLECULAR REACTIONS TOWARDS UNPOLARISED DOUBLE BONDS.

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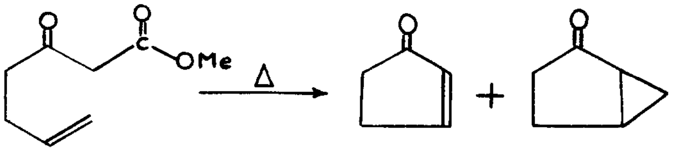
(Received in UK 25 July 1972; accepted for publication 30 July 1972)

Ketenes and their reactivity in cycloaddition reactions have been studied extensively and have found numerous applications in synthesis (1). But ketenes as part of conjugated systems have received much less attention, probably due to the high reactivity of such species and their ability to dimerise and/or trimerise in the absence of suitable substrates. In the recent literature, a few cases only can be encountered where ∝-ethylenic ketenes $(C=C-C=C=O)$ (2a,b), ∝-carbamoyl ketenes $(O=\underset{NHR}{C}-C=C=O)$ (2c) and ∝-carboalkoxyketenes $(O=\underset{OR}{C}-C=C=O)$ (2d) are involved in 1,2 <u>intermolecular</u> cycloaddition processes.

In the present work we report a significant example of the thermal generation of a ketoketene $(O=\underset{R}{C}-C=C=O)$ and its behaviour towards unpolarised double bonds in an <u>intramolecular</u> reaction.

We found that the thermolysis products of methyl oxo-3 hepten-6 oate 1 near 550°C under a pressure of 10^{-2} torr are cyclopentenone 3, bicyclo [3,1,0] hexan-2 one 4, methanol and methyl acetate, as demonstrated by comparison with authentic samples. Highly volatile products such as carbon monooxide could not be isolated under the experimental conditions used (10). The ratio ketone 3/ketone 4 is always roughly equal to four as shown by VPC analysis, whereas the ratio methyl acetate/methanol has been estimated to be 3.5 from the NMR spectrum of the recovered volatile products.



+ CH_3OH + $CH_3CO_2CH_3$

0,22 mole 0,78 mole

1 1 mole

3 0,80 mole

4 0,20 mole

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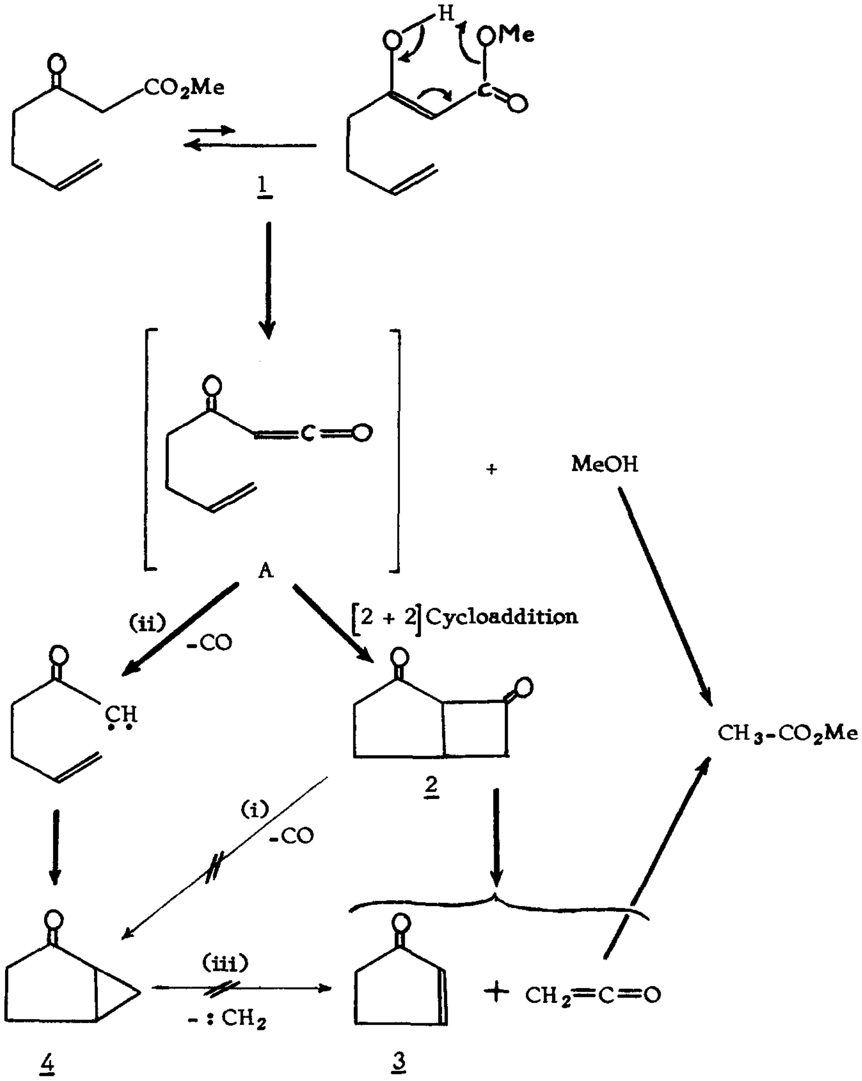
The formation of α-ketoketenes from β-ketoesters has until now been reported once in the literature (3) ; it has been explained by a keto-enol shift with subsequent loss of methanol through a six-centered transition state. In the same way, ketoketene A appears to be the first product formed during the thermolysis of the ketoester 1. This very reactive intermediate then collapses, as shown below, and gives rise, along two different pathways, to the observed ketones 3 and 4.



Unlike the stable 6-methyl bicyclo [3,2,0] heptan-2,7 dione (5), diketone 2 is known to be unstable (4) and, considering the conditions under which it is formed, there is no surprise that most of it suffers directly ketene cleavage to yield cyclopentenone 3. However, the crude pyrolysis mixture shows, inter alia, in IR, a weak $\gamma_{C=O}$ band at 1786 cm^{-1}. Such wave-numbers are given for cyclobutanones even fused with a cyclopentanone ring, the two carbonyls being in β position one from the other (4). This suggests strongly the presence of a small amount of the diketone 2 in this crude mixture.

How compound 4 arises is less evident. Formally, there are two possible ways : (i) carbon monooxide extrusion from diketone 2, (ii) decarbonylation of ketoketene A and via the so formed ketocarbene, addition reaction on the terminal double bond. Or, it is known that cyclobutanone itself gives less than 1% cyclopropane at 373°C, the main reaction being ketene formation (99%) (6a) ; on the other hand, ketene (6b) and methylketene (6c) are known to undergo decarbonylation, the former in an extent of about 50% at 560°C. Consequently, pathway (i) is rather unlikely and most of 4 is the result of the well-established ketocarbene addition reaction.

One could have imagined that cyclopentenone 3 arises from ketone 4 through a carbene extrusion reaction. Generally, two factors seem to govern the feasibility of such reactions, by lowering the transition state energy (7) : - the precursor (i.e. ketone 4) must have a high ground-state energy resulting from geometrically or sterically strain ; - the non-carbene fragment must be thermodynamically stable. Dimethoxycarbene (8a) and dichlorocarbene (8b) formation in those conditions have been reported, as well as carbene itself (8c).

In order to check this possibility in our case, an authentic sample of bicyclo [3,1,0] hexan-2 one 4 has been synthetised by Gutsche's method (9). Submitted to the same conditions as ketoester 1, compound 4 has been recovered quantitatively and fully unchanged. Therefore pathway (iii) can be totally ruled out.

Finally, a last argument about the consistency of this mechanism lies in the fact that ketone 3 and methyl acetate are formed in approximatively the same extent, establishing that the former arises only from the [2 + 2] cycloaddition product 2, whereas ketone 4 is the result of the decarbonylation of ketoketene A, followed by internal attack of the double bond.

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(10) Apparatus and pyrolysis technique will be published elsewhere later on. Under the given thermal conditions, an average contact time of the products in the furnace is about 2 seconds. Each experiment has been performed with 200 mg of ketoester 1.