Flash Thermolysis of Spiro[2,3]hexan-4-ones. A Case of Vinylketen Generation

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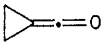
Summary Flash thermolysis of spiro[2,3]hexan-4-ones leads to vinylketen formation.

($\sigma^2 + \sigma^2$) CYCLOREVERSION is known to be an operative reaction for either photochemical[1] or thermal[2] generation of ketens. We report our attempts to generate the still unknown dimethylene keten (**1**) by pyrolysis of spiro[2,3]-hexan-4-ones under flash thermolytic conditions.[3] (700—1000 °C, contact time 5—20 ms).

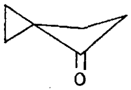
The results reported in the Table concern the cyclobutanones (**2**) and (**3**) both bearing a cyclopropyl ring adjacent to the carbonyl group.

As shown in the Table pyrolysis of (**2**) at 900 °C undergoes a non-selective cleavage of the C_4 ring to give products **a**—**d** besides a small amount of **e** without traces of dimethylene keten (**1**).

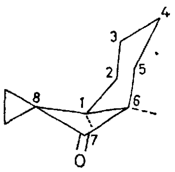
The formation of allene might be interpreted as a consequence of spontaneous decarbonylation of the presumed dimethyleneketen (**1**). This was ruled out by subjecting (**2**) to a copyrolysis experiment using a ten fold excess of methanol, which gave methyl vinylacetate (**g**) instead of methyl cyclopropylcarboxylate.



(1)



(2)



(3)

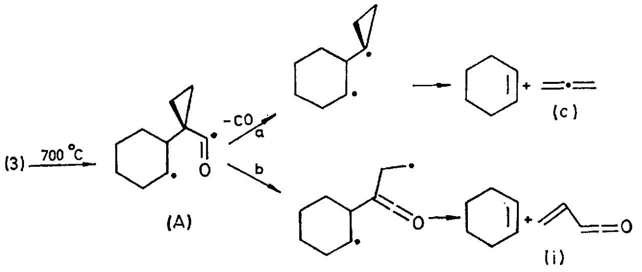
On the other hand, the spirocyclopropane (**3**) shows a specific cleavage of the cyclobutane ring at 700 °C with the formation of products **h**, **c**, **e**, and a red compound stable up to −160 °C, identified as vinylketen[6] by the following experiments. (a) The product **i** was generated from (**3**) and trapped in a methanol matrix at −196 °C; as the temperature is raised, the red intermediate disappeared and methyl vinylacetate was isolated. (b) When (**3**) was copyrolysed with methanol, the same distribution of products is obtained.

TABLE

Sample[a]	t/°C	% Conversion	Products[b]
(**2**)	800	<10	—
(**2**)	900	>90	**a, b, c, d, e**
(**2**) + MeOH	900	—	**a, c, d, f, g**
(**3**)	700	$\geqslant 60$	**h, c, e, i**
(**3**)	800	*ca.* 100	**h, c, e**
(**3**) + MeOH	700	*ca.* 60	**h, c, g**

[a] (**2**) is obtained from ref. 4; (**3**) is prepared from 8-hydroxybicyclo[4,2,0]octan-7-one[5]. [b] (**a**) methylenecyclopropane, (**b**) keten, (**c**) allene, (**d**) ethylene, (**e**) propyne, (**f**) methyl acetate, (**g**) methyl vinylacetate, (**h**) cyclohexene, (**i**) vinylketen. All products and samples, except (**i**), were identified by their i.r., n.m.r., and mass spectra.

The reaction might involve a stepwise biradical process rather than a concerted cleavage as has been proposed for the thermal fragmentation of alkylcyclobutanone derivatives.[7,8]



SCHEME

The product distribution is consistent with breaking of the weak $>\underset{6}{C}-\underset{7}{C}=O$ bond of (**3**) which leads us to propose two competitive pathways from the biradical (A) (Scheme). (a) a decarbonylation process which occurs to give **c** *via* dimethylenecarbene; (b) a type of cyclopropylcarbinyl homoallyl radical rearrangement[9] which leads to vinylketen (**i**).

A direct consequence of vinylketen generation is the formation of propyne (**e**) arising *via* the vinylcarbene[10] obtained by decarbonylation.

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[9] See for example 'Molecular Rearrangements,' ed. P. de Mayo, Wiley, part I, 1963, p. 440.

[10] R. D. Streeper and P. D. Gardner, *Tetrahedron Letters*, 1973, 767, and references therein.