Flash Thermolysis of Trimethylsilyl 2-Oxobicyclo[3.3.1]nonane-1-carboxylate: Formation of a Strained Bridgehead Enol Ether

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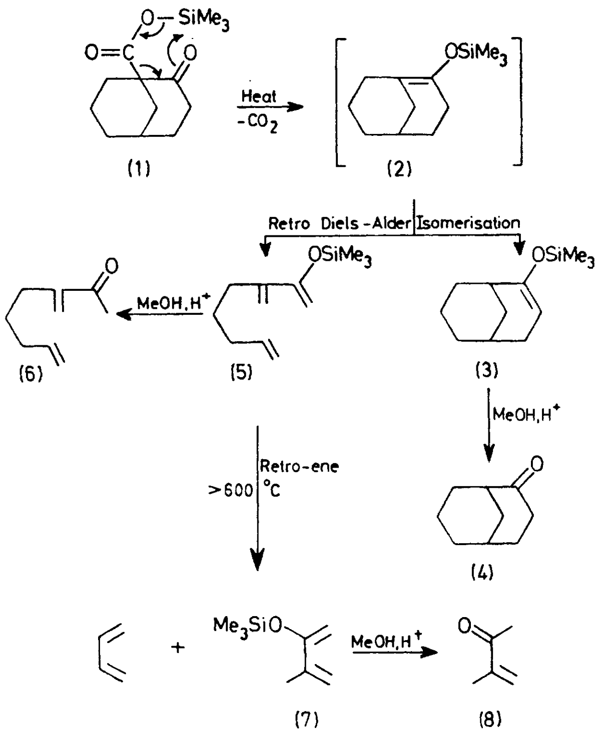
Summary Flash thermolysis of the trimethylsilyl ester (**1**) gives rise to enol ethers (**3**) and (**5**) whose formation is best explained *via* the strained bridgehead enol ether (**2**).

In the past few years intense research has been directed towards the preparation of strained bridgehead olefins.[1] In particular, it has been suggested that the smooth decarboxylation of some bicyclic β-ketoacids should proceed *via* strained bridgehead enols,[2] but the presence of such intermediates has never been shown. We report here evidence for the formation of a bridgehead trimethylsilyl enol ether during the thermal decarboxylation[3] of the ester (**1**).

The ester (**1**) was prepared in 80% yield by reaction of the corresponding acid[4] with trimethylsilyl chloride in the presence of pyridine. The flash thermolyses[5] were carried out at different temperatures and the products formed were isolated, according to their volatility, by two different procedures:† (a) for slightly volatile compounds the 'sandwich technique' was used; the cold Dewar flask was coated with dry pentane before and after the thermolysis in order to prevent contact of the products with moisture; the pentane solution was dried, concentrated *in vacuo*, and the residue was analysed by vapour phase chromatography; (b) volatile products were directly distilled from the cold Dewar flask.

As shown in the Table, the main slightly volatile compounds obtained were the two enol ethers (**3**) and (**5**), accompanied by their hydrolysis products, the ketones (**4**) and (**6**).‡ The volatile fraction was a mixture of $O(SiMe_3)_2$,



Scheme 1

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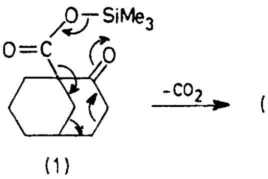
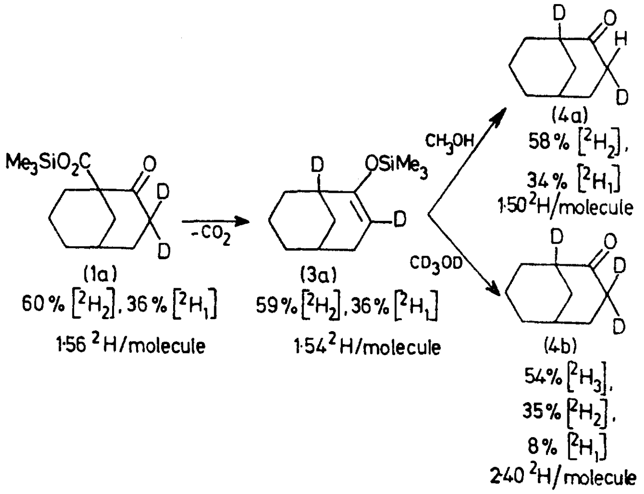
† At least two thermolyses were necessary to identify all the reaction products, but attempts to distil less volatile compounds directly from the cold wall led to total hydrolysis of the enol ethers formed.

‡ Several thermolyses under the same conditions gave a constant (**3**) + (**4**)/(**5**) + (**6**) ratio but different proportions of enol ethers compared with ketones. This suggests that the ketones (**4**) and (**6**) effectively arise from hydrolysis of the enol ethers (a small amount of water is always trapped on the cold Dewar flask).

butadiene, and the enol ether (**7**).§ The yield of the latter two products was <5% when the thermolysis was conducted at ⩽600 °C; it increased sharply for thermolyses at 750 °C, with a decrease in the amount of (**5**). This suggests that butadiene and (**7**) are secondary products derived from compound (**5**). The structures of all the products were determined from their spectroscopic data (n.m.r., i.r., m.s.) and for (**3**) and (**4**) by comparison with authentic samples prepared by other methods.[6] Chemical confirmation was also obtained by acid hydrolysis of the enol ethers, (**3**), (**5**), and (**7**) to the corresponding ketones (**4**), (**6**), and (**8**).



SCHEME 2



SCHEME 3

The transient existence of the strained bridgehead enol ether (**2**) as the primary thermolysis product is strongly supported by the presence of its isomer (**3**) and of (**5**) (Scheme 1). The formation of (**3**) and (**5**) can be explained by assuming two competitive rearrangements of (**2**): (a) a [1,3] hydrogen shift giving rise to the more stable bicyclic enol ether (**3**) (such shifts have already been observed during the thermal preparation of other bridgehead olefins[7]); (b) a retro-Diels–Alder reaction[8] which, by opening of the cyclohexene ring, gives the triene (**5**). At high temperatures, this triene undergoes a retro-ene rupture leading to butadiene and the enol ether (**7**). However, one cannot exclude the direct formation of compound (**5**) from the keto-ester (**1**) through a ten-electron rearrangement¶ by-passing the species (**2**) (Scheme 2).

Additional support for the intermediate formation of (**2**) during the rearrangement (**1**) → (**3**) was given by the thermolysis of the deuterium labelled keto-ester (**1a**).[9] The deuterium content of all the products, found by mass spectrometry, is given in Scheme 3. The position of the deuterium atoms was determined from the n.m.r. spectra of the ketones (**4**), (**4a**), and (**4b**). In (**4**) the three hydrogen atoms adjacent to the carbonyl group gave signals at δ 2·4[9] and furthermore could be easily separated from the other signals by adding the shift reagent [Eu(fod)$_3$]. This absorption disappeared in the n.m.r. spectra of (**4a**) and (**4b**) [1·45H in (**4a**), 0·61H in (**4b**)], the remainder of the spectra being unchanged. This last experiment is a confirmation for the [1,3] hydrogen shift leading from the unstable species (**2**) to the enol ether (**3**). Such a suprafacial hydrogen shift, if concerted, is forbidden according to Woodward–Hoffmann rules, but the strain energy associated with the bridgehead double bond in bicyclo[3.3.1]non-1-ene, estimated as 12 kcal mol^{-1},[10] is sufficient to allow a violation of the rules, since an excess of energy of *ca.* 10 kcal mol^{-1} seems necessary.[11]

TABLE

		Distribution (%) of slightly volatile products[b]			
T/°C	% conversion[a]	(**3**)	(**4**)	(**5**)	(**6**)
550	25	55	37	3	5
600	57	51	20	20	9
650	72	36	6	49	9
700	86	15	4	75	6
750[c]	*ca.* 100	27	8	59	6

[a] Determined by n.m.r. spectroscopy by comparing the relative areas of the Me$_3$Si signals. [b] The proportions were evaluated by v.p.c. These values are the average of two or three thermolyses. [c] In this case a large amount (30% in weight) of volatile products is obtained.

We thank Professor J. M. Conia for his interest throughout this work.

(*Received*, 15*th January* 1976; *Com.* 031.)

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§ In some cases, a small quantity of the ketone (**8**) was observed.

¶ We thank one of the referees who suggested this possibility as well as the labelling experiment.

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