Evidence against a Keten Intermediate in the "Homo-Favorskii" Reaction

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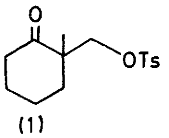
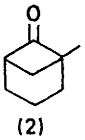
Summary Conversion of the deuteriated ketone (**5**) into (**10**) proceeds in base without scrambling of the label, indicating that the symmetrical keten (**13**) is not a free intermediate in this transformation.



(1)



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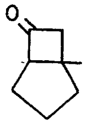

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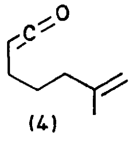

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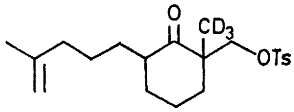

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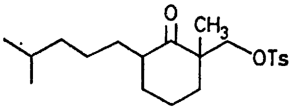

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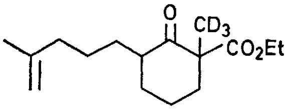

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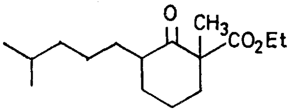

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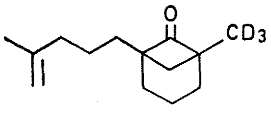

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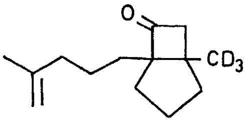

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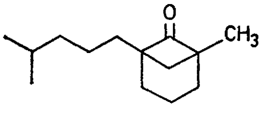

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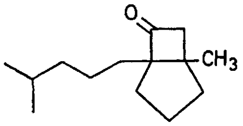

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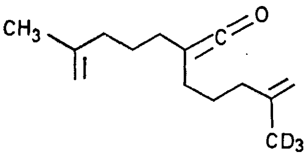

(13)

The base-catalysed converison[1] of (**1**) into (**2**) and (**3**) typifies a reaction for which there are many examples.[2,3] In a recent study Bisceglia and Cheer[4] investigated the possibility that the keten (**4**), which is known[5] to yield (**3**), might be an intermediate in the transformation of (**1**) to (**3**). Having found that independently generated (**4**) could be trapped as an adduct with dihydropyran, they then showed that under similar conditions no (**4**) was trapped on treatment of (**1**) with base. They concluded that these experiments suggest that (**4**) is not an intermediate in formation of (**3**) from (**1**). Our own experiments concerning this general question were based on an attempt to trap the putative keten intermediate intramolecularly, and they lead to a similar conclusion.

The keto-tosylates (**5**) and (**6**) were prepared from 2-ethoxycarbonylcyclohexanone. Alkylation of the keto-ester following known procedures[6] yielded (**7**) and (**8**), which were converted into (**5**) and (**6**) through a sequence[3] of reduction to diol, selective tosylation, and reoxidation. Treatment of (**5**) with sodium hydroxide in aqueous methanol under reflux led to a 2:3 mixture of (**9**) and (**10**) in 56% yield, while similar reaction of (**6**) gave essentially the same proportion and yield of (**11**) and (**12**). The structures of these products rest on spectroscopic data, as well as comparison with earlier related reactions.[1-3] The position of the label as shown in structures (**9**) and (**10**) follows from ^{1}H n.m.r. (220 MHz) measurements showing no signal for a methyl group attached to saturated carbon in these compounds. This was substantiated by side chain hydrogenation of (**9**) and (**10**) to furnish products identical with (**11**) and (**12**), respectively, by g.l.c. retention time and i.r., n.m.r., and m.s. measurements, except for the differences expected from replacement of bridgehead CH_3 by CD_3.

The possible keten intermediate from (**5**) is the structurally symmetric (**13**). Failure to observe any scrambling of the deuterium label of (**5**) on conversion into (**10**) indicates that (**13**) cannot be an intermediate in this transformation, insofar as (**13**) represents a free, rotationally relaxed species. This requirement places an upper limit of *ca.* 10^{-9} s on the lifetime of free (**13**) as a precursor of (**10**). The previous conclusion[4] concerning the possible intermediacy of a keten in this transformation is thus supported by independent evidence which is not derived from comparison of two separate trapping experiments.

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[2] For example, F. Nerdel, D. Frank, and H. Marschall, *Chem. Ber.*, 1967, **100**, 720; Y. Tsuda, T. Tanno, A. Ukai, and K. Isobe, *Tetrahedron Letters*, 1971, 2009; E. Wenkert, P. Bakuzis, R. J. Baumgarten, C. L. Leicht, and H. P. Schenk, *J. Amer. Chem. Soc.*, 1971, **93**, 3208.

[3] H. Marschall, *Chem. Ber.*, 1972, **105**, 541.

[4] R. H. Bisceglia and C. J. Cheer, *J.C.S. Chem. Comm.*, 1973, 165.

[5] S. W. Baldwin and E. H. Page, jun., *J.C.S. Chem. Comm.*, 1972, 1337.

[6] K. Sisido, K. Utimoto, and T. Isida, *J. Org. Chem.*, 1964, **29**, 3361; K. Mori and M. Matsui, *Tetrahedron*, 1966, **22**, 879.