Intermediacy of a Keten in the "Homo-Favorskii" Reaction

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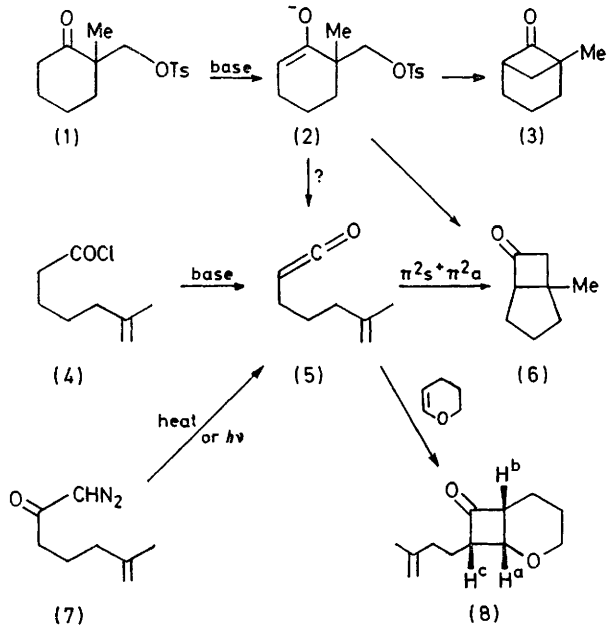
Summary Trapping experiments suggest that the keten (**5**) is not an intermediate in the base-catalysed formation of the cyclobutanone (**6**) from the ketone (**1**).

THE recent report of Baldwin and Page[2] suggesting the intermediacy of the keten (**5**) in the formation of the cyclobutanone (**6**) from the ketone (**1**) prompts us to report the

results of a recent investigation which suggests an alternative conclusion.



Our experiments confirm the findings of Baldwin and Page[2] that the keten (**5**), generated either by treatment of the acid chloride (**4**) with triethylamine or thermolysis of the diazoketone (**7**), produces the cyclobutanone (**6**). Addition of the acid chloride (**4**) to one equivalent of triethylamine in benzene under reflux produced the ketone (**6**) as the sole volatile product, in 35% yield, while thermolysis of the diazoketone (**7**) in dioxan under reflux also produces (**6**) in small amounts.

The intermediacy of the keten, first suggested by Yates and Fallis[3] represents a possible alternative to the other mechanistic paths previously suggested for this transformation,[4] all of which include the step of alkylation of an enolate ion at the carbonyl carbon atom.

To test the suggested intermediacy of (**5**) in the base-catalysed formation of (**6**) from (**1**), the keten was generated in the presence of a large excess of 2,3-dihydropyran. When a cold (−78 °C) solution of the acid chloride in dihydropyran was mixed with a cold (−78 °C) solution of triethylamine and the resulting solution heated to 100 °C for 3 h, a 50% yield of the intermolecular adduct (**8**) was obtained. Gas chromatography showed the absence of any intramolecular cycloadduct (**6**).

The adduct (**8**) was purified by column and thick layer chromatography on silica gel (5% ethyl acetate in cyclohexane and benzene, respectively). The structure of (**8**) follows from analytical and spectral evidence. The stereochemistry indicated is suggested by the n.m.r. spectrum which exhibits a one proton triplet at δ3·40, which on the basis of its chemical shift can be assigned to H^a in (**8**). The multiplicity indicates $J_{ab} = J_{ac}$, implying the all-*cis* stereochemistry indicated.

In contrast, when the keto-toluene-*p*-sulphonate (**1**) was treated with base (BuLi,NaOMe,NEt_3) in an excess of dihydropyran under reflux, both cyclobutanones (**3**) and (**6**) were formed but the trapped cycloadduct (**8**) could not be detected.

These experiments suggest that while the keten (**5**) is demonstrated to be an effective precursor to the cyclobutanone (**6**) it is not an intermediate in the transformation of (**1**) to (**6**).

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[1] Abstracted from the M.S. Thesis of R. H. Bisceglia, University of Rhode Island, 1972.
[2] S. W. Baldwin and E. H. Page, jun., *J.C.S. Chem. Comm.*, 1972, 1337.
[3] E. Wenkert, P. Bakuzis, R. J. Baumgarten, C. L. Leicht, and H. P. Schenk, *J. Amer. Chem. Soc.*, 1971, **93**, 3208.
[4] 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.