Regiospecific Thermal Cleavage of Some Oxetan Photoadducts: Carbonyl–Olefin Metathesis in Sequential Photochemical and Thermal Steps

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Summary Pyrolysis of oxetan photoadducts of acetone with the methyl esters of maleic and fumaric acids results in homogeneous cracking which is regiospecific and in a sense opposite to the mode of photoformation.

APART from the work of one group[1] which has examined the thermal cleavage of a number of simply substituted oxetans, the structure–reactivity factors governing decomposition of these small ring heterocycles has not been systematically examined. We now report the thermal transformations of some oxetans which are readily available *via* the photochemical Paterno–Buchi reaction with emphasis on the synthetic utility of a photolysis–pyrolysis sequence involving carbonyl–olefin metathesis [equation (1), no stereochemistry intended].

When 10—20% solutions of the stereoisomeric oxetandicarboxylates (**1**) and (**2**)[2] in diphenylmethane were heated (280—300°) in Pyrex ampoules, a smooth first-order (up to four half-lives) disappearance of the oxetan derivative was observed accompanied by the appearance of the butenoate (**3**) (90% yield by n.m.r. spectroscopy, based on recovered oxetan). The following control experiments were informative. (i) Methylglyoxylate,[3] the expected but unobserved cracking co-product, was found to be unstable under the conditions of oxetan pyrolysis. (Intractable material was produced in this experiment as well as with oxetan as starting material.) (ii) G.l.c. analysis of product mixtures revealed that cycloreversion to give acetone and dimethyl fumarate (maleate) was negligible ($<$ 0·5% at *ca.* 90% conversion). (iii) Aside from olefin isomerization,[4] mixtures of acetone and fumaric (maleic) ester were relatively stable at 290°, confirming that the cycloreversion is regiospecific. (iv) Geometric isomerization of the starting oxetans was not observed ($<$ 1% over a range of conversions to 85%).† (v) The observed (n.m.r.) first-order rate constant for the disappearance of (**2**) (virtually unaffected by addition of glass wool to the pyrolysis ampoules or by change in solvent to *o*-dichlorobenzene) was $3{\cdot}97 \pm 0{\cdot}19 \times 10^{-4}\ \mathrm{s}^{-1}$ (290·0°).

For comparison, the photoadduct (**4**)[5] of acetone with maleic anhydride was pyrolysed at 300°. The decomposition (slower than for the diester series) eventually gave a

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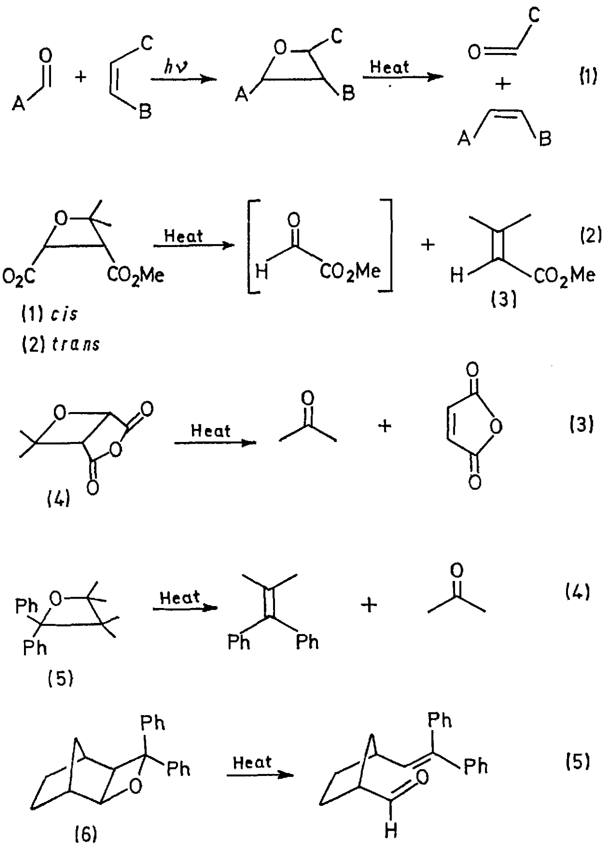
† If initial C–C bond breaking to produce an intermediate is important for the oxetans, the lack of geometrical isomerization is in contrast to the results of pyrolysis of the diastereomeric dimethyl cyclobutane-1,2-dicarboxylates. For the latter, cracking and isomerization occur at about equal rates; see the following communication.



complex mixture of products, but the appearance of acetone (28%) and maleic anhydride (trace) [equation (3)] could be followed during the early stages of reaction [35% disappearance of (4)].‡

While the transformations here involve simple carbonyl compounds and olefins (starting materials and products) carbonyl–olefin metathesis *via* photocycloaddition–pyrolysis may be general and synthetically useful, particularly when the intermediate is a bicyclic oxetan. On pyrolysis the benzophenone photoadducts (**5**) and (**6**) gave metathesis products as shown in equations (4) and (5). These conversions were clean, and the regioselectivity of the cracking was 71 and 100%, respectively.[6] While cracking of oxetans may be carried out in some cases by mild acid catalysis,[7] other pathways (rearrangement) may intervene under these conditions.[8] Homogeneous cycloreversions then may present a desirable synthetic alternative. In fact, the oxetan (**2**) reacts ($CDCl_3$; trace of HCl; room temp.) to give an unidentified mixture which does not include the products of cracking in either sense.

The pyrolysis results are consistent with a rate-determining transition state characterized by the breaking of the weakest C–O bond either as the leading process (concerted mechanism) or completely (two-step mechanism, diradical or dipolar intermediate). Additionally, in view of the observed cracking of the anhydride (**4**) in the sense opposite to (**1**) and (**2**), bond weakening may be a subtle function of substituents *and* geometry.

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‡ Maleic anhydride in a separate experiment was shown to decompose slowly at 300°. Since the reactions both in the diester series and for the anhydride were not stoicheiometrically clean, we cannot rule out decomposition by some route other than σ^2 + [illegible] cycloreversion, but a more complex initial fragmentation leading to the observed products seems unlikely.

[1] (a) M. Bartok, *Acta Chim. Acad. Sci. Hung.*, 1967, **51**, 403; (b) M. Bartok and B. Kozma, *ibid.*, 1967, **52**, 83.

[2] E. Albone, *J. Amer. Chem. Soc.*, 1968, **90**, 4663.

[3] Prepared by ozonolysis of dimethyl maleate; J. J. Pappas, W. P. Keaveney, E. Gancher, and M. Berger, *Tetrahedron Letters*, 1966 4273.

[4] W. W. Kwie and W. C. Gardiner, jun., *Tetrahedron Letters*, 1963, 405.

[5] N. J. Turro and P. A. Wriede, *J. Org. Chem.*, 1969, **34**, 3562.

[6] Details will be reported elsewhere.

[7] Cracking of (**6**) as shown has been reported (D. Scharf and F. Korte, *Tetrahedron Letters*, 1963, 821; G. Adams, C. Bibby, and R. Grigg, *J.C.S. Chem. Comm.*, 1972, 491) to be Lewis acid-catalysed, and this route provided a convenient proof of pyrolysis product structure. Significantly, all the oxetan pyrolyses reported here were carried out in base-washed solvents and glassware.

[8] S. Searles, in 'The Chemistry of Heterocyclic Compounds,' part 2, ed A. Weissberger, Wiley, New York, 1964.