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THE STEREOCHEMICAL COURSE OF THERMALLY INDUCED OXETANE FRAGMENTATION

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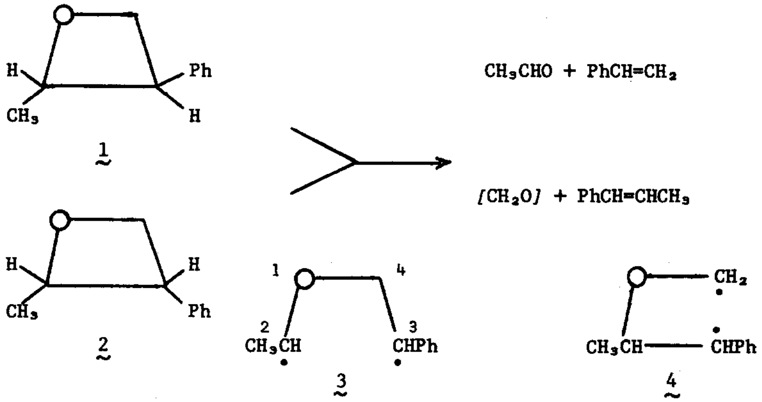
In order to explore the carbonyl-olefin metathesis synthon,[1] we have conducted an array of tests of oxetane decompositions involving substituent and medium effects and stereochemistry and now report for the first time the stereochemical course of pyrolysis of a pair of oxetane diastereomers.

The 2-methyl-3-phenyloxetanes (1 and 2) were obtained by photolysis of acetaldehyde and styrene.[2] The 5:1 mixture of diastereomers (favoring 1) was separated by glc, and the stereochemistry of the photoadducts determined by reference to nmr spectral data. The minor oxetane was assigned the cis configuration based on its doublet absorption at 0.92δ ppm (CCl_4), indicating a relatively shielded methyl[3] (compared to 1.44δ for the major photoadduct).

Acetaldehyde, styrene, and the isomeric 1-phenyl-1-propenes were identified by glc as the volatile products of pyrolysis of 1 and 2 in a packed flow system at 410-470° (contact time, 5-10 sec). Analysis of the olefins with reference to an internal standard indicated a material balance ($>$ 95%) between the oxetanes and cycloreversion products. Oxetane fraction 1 (98% trans) at moderate conversion (32-78%) produced styrene and the phenyl propenes in a 2.6:1 ratio; propene stereochemistry was 93% trans and recovered oxetane had 98% trans configuration.[4]

Oxetane fraction 2 (93% cis) at 38-58% conversion also gave cracking products regioselectively (86% styrene), and the propenes had 63% cis stereochemistry. The percentage of trans isomer in the recovered oxetane from pyrolysis of fraction 2 had increased to 20%. The olefins were stable under the pyrolysis conditions; in particular, *cis*-1-phenyl-1-propene (originally 96% cis) was recovered virtually unchanged (94% cis) on pyrolysis at 440°.



The data indicate high stereoselectivity but not stereospecificity for the thermal oxetane cycloreversions.[5,6] We estimate that retention of configuration in product olefin is 95 ± 2% and 72 ± 4% for **1** and **2**, respectively, corrected for isomeric contamination in starting oxetane and (for cis) for a small amount of isomeric oxetane produced during pyrolysis, the observation of which is clearly outside of experimental error.

Considering the observed stereochemical losses in starting material and products, one might implicate diradicals, **3** and **4**, as important intermediates or transition states[7] leading to product. Cyclobutane decompositions provide close analogy, but for several systems,[8] in which substituent ponderal effects should not retard stereochemical loss,[9] near equilibrium distributions of stereoisomeric product olefins (long thought to support diradical intermediacy) are obtained on thermal cracking. The stereochemical crossover for **2** is not nearly that which is to be expected for destruction of a rotationally equilibrated diradical.[10] On the other hand, modest stereorandomization is consistent with the apparent retarded rotation about benzylic centers suggested recently for species related to 4.[11]

We have noted[1] the absence of geometrical isomerization for one oxetane pair with comparison to a cyclobutane model. The isomerization 2 → 1 is a rare example of such a reaction for this ring system.[12] Stereoretention (the ratio of cracking to isomerization[9a]) may be approximated by the ratio of average yields of styrene and 1 (32/13 = 2.5) at 48% average conversion of 2. Corresponding stereoretention values for *cis*-1, 2-dimethyl- and *cis*-1,2-diphenyl-cyclobutane are 4.0[13] and 2.1,[11e] respectively. Based on this measure of stereochemical loss, which assumes that styrene and geometrical isomer (*via* rotation about C_2-O) arise largely from a common diradical (3), mechanisms for the cyclobutane and oxetane ring systems appear strikingly similar.

Although we favor presently a decomposition pathway involving diradicals (or less likely dipolar species[6]) a combination of concerted paths cannot be ruled out by the stereochemical results. If the mechanism for oxetane cracking be an allowed concerted $\sigma_{2S} + \sigma_{2A}$ cycloreversion, the burden of antarafaciality may rest on either the incipient carbonyl or olefin moieties. Proper combination of these would produce the observed stereochemical results. Turro has suggested[14] that such participation by a nascent carbonyl group is important in the diabatic cycloreversion of 1,2-dioxetanes. Additionally, a concerted $\sigma_{2S} + \sigma_{2S}$ pathway for oxetane decomposition must be considered in light of recent suggestions concerning the importance of subjacent orbital energies[15] and configuration (charge transfer) interaction[16] in transition states.

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(4) The percentage values represent duplicate analysis of pyrolyses in triplicate, and average deviations suggest an error in percentages of ± 2%.

(5) Product ratios were not significantly a function of temperature, flow rate or extent of conversion.

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