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Thermal Cleavage of the 3,4 Bond in a Cyclobutane-1,2-dione

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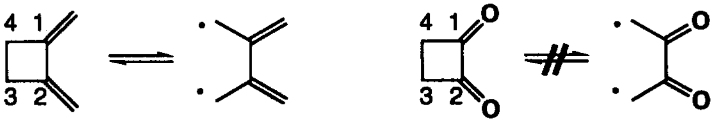
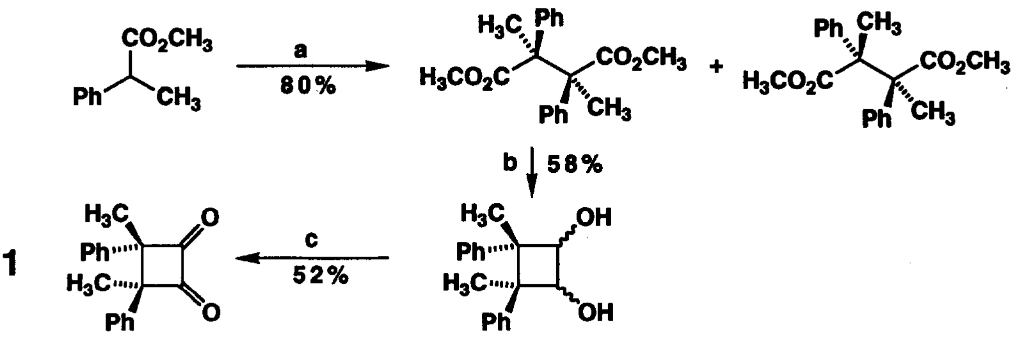
Abstract: Pyrolysis of *trans*-3,4-dimethyl-3,4-diphenylcyclobutane-1,2-dione results in an isomerization interpreted to involve formation of a dioxatetramethyleneethane biradical. This biradical would arise from a hitherto unprecedented 3,4 bond cleavage.

The biradical tetramethyleneethane, in which there has been much recent experimental[1] and theoretical[2] interest, can be generated reversibly by thermal cleavage of the weakest bond -- the C3-C4 bond -- of 1,2-bismethylenecyclobutane.[3] Generation of the dioxa- analog of tetramethyleneethane by the corresponding C3-C4 homolysis of cyclobutane-1,2-dione is not possible, however (at least under normal thermal reaction conditions), because this bond is the *strongest* in the ring, according to Benson group additivity calculations[4] (*vide infra*). The weakest is the C1-C2 bond.



One could imagine changing the relative bond strengths of cyclobutane-1,2-dione by substitution, and in fact, evidence has been found for both C1-C2 and C1-C4 homolysis in certain derivatives,[5] but, to our knowledge, there has hitherto been no report of C3-C4 cleavage. We now describe such a reaction, occurring in *trans*-3,4-dimethyl-3,4-diphenylcyclobutanedione (1). Its synthesis is summarized in Scheme 1.



Scheme 1. Synthesis of *trans*-3,4-dimethyl-3,4-diphenylcyclobutane-1,2-dione. Reagents are as follows: (a) (i) NBS/CCl_4; (ii) Zn/$CuCl_2$, cat. $HgBr_2$.[6] (b) (i) $LiAlH_4$; (ii) ClCOCOCl/DMSO, Et_3N; (iii) $TiCl_3(DME)_2$, Zn/Cu. (c) ClCOCOCl/DMSO, Et_3N.

The stereochemistry of the product was determined by x-ray diffraction (Figure 1).

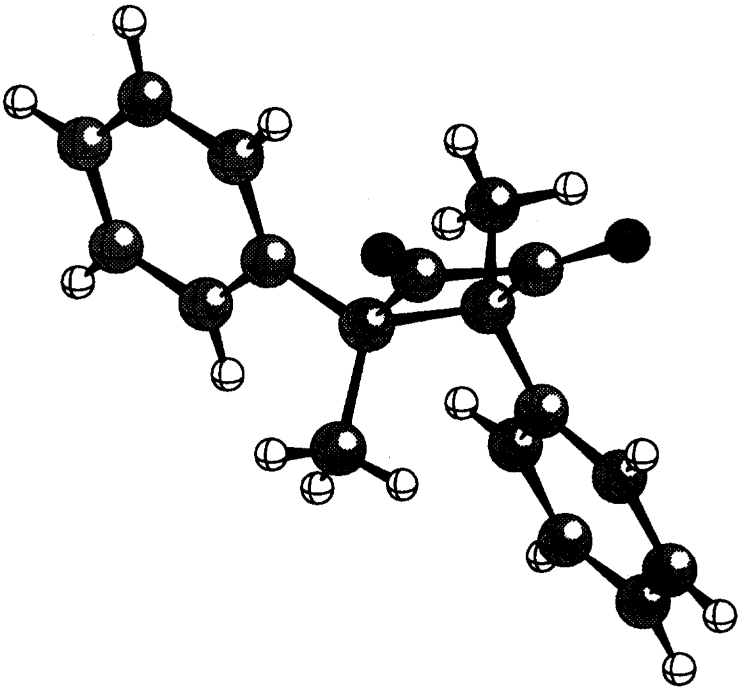
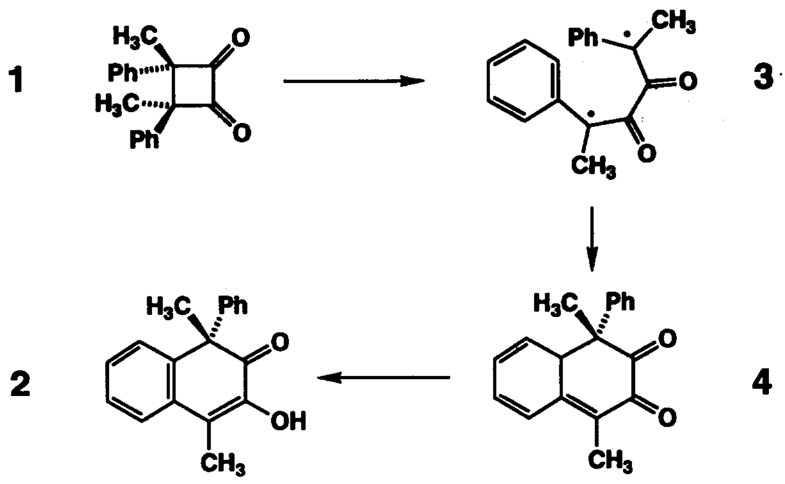


Figure 1. Computer-generated perspective drawing of **1** from single-crystal x-ray diffraction analysis.

Pyrolysis of **1** in dodecane solution at temperatures between 120.3 and 149.1 °C resulted in clean conversion to compound **2**.[7] The kinetics for the reaction were determined by monitoring the disappearance of the U.V. absorption of **1** at 506 nm. First-order behavior was observed, with temperature-dependent rate constants corresponding to activation parameters of $\Delta H^{\ddagger} = 30.9 \pm 1.5$ kcal/mol and $\Delta S^{\ddagger} = -1.1 \pm 3.7$ cal/(mol K) (quoted uncertainties represent the 95% confidence interval for four temperatures). The reaction showed little sensitivity to solvent polarity -- the rate constants at 140.6 °C being 7.37×10^{-4} s^{-1} in DMSO, 7.03×10^{-4} s^{-1} in pyridine, and (at 140.5 °C) 2.20×10^{-4} s^{-1} in dodecane. The less than fourfold rate difference between DMSO and dodecane disfavors a reaction mechanism involving dipolar intermediates, and the lack of inhibition when the rearrangement was conducted in pyridine disfavors a reaction catalyzed by adventitious acid. While conversion of **1** to **4** could formally occur by a concerted [1,3] sigmatropic rearrangement, the energetic accessibility of the biradical **3** suggested by the calculations below, and the probable steric hindrance to the [1,3] sigmatropic shift cause us to favor the mechanism indicated in Scheme 2.



Scheme 2. Proposed mechanism for thermal conversion of 1 to 2

Benson group additivities[4] can be used to calculate the enthalpies of conversion of parent cyclobutane-1,2-dione to the biradical generated by 1,2, 1,4, and 3,4 cleavage. Using a value of -37 kcal/mol for the heat of formation of cyclobutane-1,2-dione,[8] the reaction enthalpies are calculated to be respectively 36, 46, and 50 kcal/mol. The experimental activation enthalpy of 38±2 kcal/mol for conversion of cyclobutane-1,2-dione to ethylene and carbon monoxide[9] is thus permissive of the intermediacy of only the first of these biradicals.

The corresponding reaction enthalpies for **1** are estimated to be 36, 33, and 24 kcal/mol. In this case the experimental activation enthalpy of 30.9±1.5 kcal/mol might be permissive of all three biradicals (given the uncertainties in estimation of their heats of formation), but the product, **2**, can only sensibly be formed from the biradical **3**, derived by 3,4 cleavage. If the heat of formation estimates are reliable, the figures would indicate that **3** faces a barrier for reclosure to **1** of about 7 kcal/mol. No evidence for stereochemical scrambling of the reactant or for cleavage to methylphenylketene could be detected, suggesting that the reaction converting **3** to **4** has a lower barrier than those for reclosure to **1** or cleavage to the ketene.

Photolysis of **1** in C_6D_6 solution, using a high-pressure mercury lamp with a pyrex filter resulted in quantitative decarbonylation to give (*E*)- and (*Z*)-dimethylstilbenes. The difference in the thermal and photochemical products indicates that the photochemistry cannot occur simply by conversion of an excited electronic state into a high vibrational state of S_0. The mechanism proposed for decarbonylation of tetramethylcyclobutane-1,2-dione by Verheijdt and Cerfontain,[10] involving direct conversion of an excited electronic state of the diketone to the biradical derived from 1,2 cleavage, would be consistent with our results.

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7. Spectral data for **2** are as follows: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.88 (s, 3H), 2.39 (s, 3H), 6.54 (br s, 1H, exchanges with D_2O), 6.9-7.6 (m, 9H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.12, 26.97, 54.44, 124.47, 125.72, 127.06, 127.15, 127.37, 127.69, 128.51, 128.61, 131.21, 142.60, 143.14, 143.39, 196.63. IR (neat) 3400, 3000, 1660, 1630 cm^{-1}.
8. This figure comes from Benson group additivities (reference 4), assuming a ring strain equal to that of cyclobutene, plus 3 kcal/mol additional destabilization due to the carbonyl dipole-dipole interaction (reference 8).
9. Cao, J.-R.; Back, R.A. *Can. J. Chem.* **1985**, *63*, 2945-2948. These authors argue that the activation energy that they measure for cyclobutanedione decarbonylation is too low for a reaction involving a biradical. However, the figures quoted in the present text suggest this is not the case. Further evidence in favor of a biradical mechanism comes from studies showing partial loss of stereochemistry during the decarbonylation (Chickos, J.S.; Al-Nawwar, K. *Tetrahedron Lett.* **1985**, *26*, 1127-1130).
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