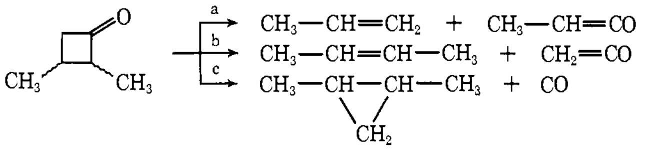
Stereochemistry of the Thermal and Photolytic Decomposition of *cis*- and *trans*-2,3-Dimethylcyclobutanone in the Gas Phase[1]

Sir:

A comparison of the photochemical decomposition modes with the unimolecular, thermal decomposition of cyclobutanone in the gas phase has led to a mechanistic proposal that the internal conversion process ($S_1 \rightsquigarrow S_0$) is surprisingly efficient.[2] Furthermore, the importance of the intersystem crossing process ($S_1 \rightsquigarrow T_1$) in the direct photolysis of cyclobutanone was stressed,[3] on the basis of the result that the triplet benzene photosensitization of cyclobutanone gave c-C_3H_6 and CO exclusively,[3] in contrast to the thermal decomposition, which gave C_2H_4 and CH_2CO, with $E_a = 52.0$ kcal/mol.[4] In order to obtain additional details of this model kinetic system, we have carried out the pyrolysis and photolysis of *cis*- and *trans*-2,3-dimethylcyclobutanone (DMCB),[5] molecules which are capable of providing the crucial stereochemical information about the unimolecular decomposition processes of interest.

The noteworthy results are: (1) pyrolysis at 325° of *cis*- or *trans*-DMCB gives *cis*- or *trans*-2-butene, respectively, with retention of the stereochemical configuration (>98%) during the ring fission path b (see Scheme I); (2) likewise, direct photolysis[6] at 313 nm (23°) gives predominantly retention of configuration in the 2-butene products, *cis*-DMCB giving a *trans*- to *cis*-2-butene ratio of ~0.15, and *trans*-DMCB giving a ratio of ~12; (3) the decarbonylation process c is absent in pyrolysis [c ≤ 0.01(a + b)]; (4) the ring fission processes a and b are absent in the $^3B_{1u}$ benzene-sensitized decomposition of *cis*- and *trans*-DMCB [c ≥ 50(a + b)], and the ratio of *trans*- to *cis*-1,2-dimethylcyclopropane (DMCP) produced is ~2.6; (5) the ring fission processes predominate over the decarbonylation in the direct photolysis (313 nm) [c ≈ 0.12(a + b)]; and (6) the ratio of products a/b is ~1.1 for the pyrolysis of *trans*-DMCB and ~6 for *cis*-DMCB, while this ratio in the direct photolysis is 0.9 and 1.3, respectively.

Scheme I



The most significant conclusion drawn from the above results is that the stereochemistry of the ring fission process b from the ground state is entirely consistent with that predicted for the concerted, cycloreversion process by the conservation of orbital symmetry.[7] We believe that our pyrolysis result, together with the results obtained in the thermal addition of olefins to ketenes,[8] illustrates nicely the reversibility of the cycloaddition–cycloreversion process.

The reason for the negligible participation of the cycloreversion processes (a and b) in the triplet-benzene-sensitized decomposition (E_T = 85 kcal/mol) may lie in the fact that the production of an electronically excited ketene (or 2-butene counterpart) from the electronically excited (triplet) DMCB is slightly endothermic and could have an appreciable activation barrier; therefore, an alternative decarbonylation process (c), presumably involving a diradical intermediate, could predominate instead, since the *trans*/*cis* ratio of ~2.6 for DMCP product obtained in observation 4 is nearly equal to the ratio of 2.9 obtained in the triplet CH_2 addition to *cis*- and *trans*-2-butenes involving a diradical intermediate.[9] It is also reassuring to find that observations 2 and 5 are consistent with the earlier proposed photodecomposition mechanism involving the $S_1 \rightsquigarrow S_0$ internal converson process.[2] The observation (6) that the rate of the ring fission mode a in pyrolysis is enhanced for *cis*-DMCB over that for *trans*-DMCB is familiar to the similar observation made for *cis*- and *trans*-1,2-dimethylcyclobutane.[10] However, any simple analogy could be an inadequate explanation, since the cyclobutane pyrolysis involves a nonconcerted, diradical intermediate,[11] unlike the cyclobutanone pyrolysis. We hope that our continued efforts made in the detailed study of this system will bring about a satisfactory understanding of the factors which control the rates in various unimolecular reaction channels of the ground and excited states.

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(5) Our assignments of the isomeric *cis* and *trans* structures (based on nmr, ir, and order of vpc elution) are consistent with the assignments made by N. J. Turro and R. B. Gagosian, *J. Amer. Chem. Soc.*, **92**, 2036 (1970), and J.-L. Ripoll and J. M. Conia, *Bull. Chim. Soc. Fr.*, 2755 (1965).

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Howard A. J. Carless, Edward K. C. Lee
Department of Chemistry, University of California
Irvine, California 92664

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Carbon-13 Fourier-Transform Nuclear Magnetic Resonance. I. Comparison of a Simple Spin–Echo Procedure with Other Methods

Sir:

Interest in Fourier-transform nuclear magnetic resonance (FT nmr) as an alternative to continuous-wave high-resolution nmr (CW nmr) for nuclei with poor sensitivity and low natural abundance is due to the expectation of large improvements in signal-to-noise