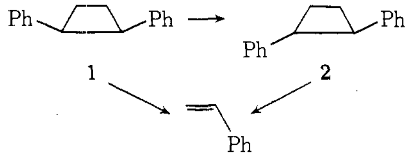
Geometric Isomerization and Cycloreversion in 1,2-Diphenylcyclobutane. Photochemical *vs.* Thermal Activation[1]

Summary: The ratio of cracking to geometric isomerization is 2.0 ± 0.3, 7.1 ± 0.7, and 2.6 ± 0.2 for *cis*-1,2-diphenylcyclobutane activated thermally, by direct irradiation, and by acetone sensitization, respectively, indicating that there may be a significant concerted component to cycloreversion in the singlet excited state.

Sir: A number of studies compared losses in stereochemistry attending cyclobutane cycloreversion, the Norrish type II photoelimination, and nitrogen extrusion from cyclic azo compounds.[2] In an extension of this discussion which attempted to establish structure–spin–reactivity relationships for thermal and photochemical reactions in principle involving diradicals, we would like to furnish data concerning the decomposition of 1,2-diphenylcyclobutane in which the reactivity "fingerprint" of cracking *vs.* geometrical isomerization for several modes of activation may be readily compared.

Solutions of *cis*-1,2-diphenylcyclobutane[3] in tetrachloroethylene were heated at 190–210°. Decomposition and the appearance of styrene and trans isomer **2** were followed by nmr. The reactions were quantitative, smoothly first order, and unaffected in rate by use of a more polar solvent (nitrobenzene) or by increasing the surface to volume ratio by the introduction of glass wool. Rate constants over one half-life for cracking and isomerization of **1** (200°) were 5.2 ± 0.4 × 10^{-5} and 2.4 ± 0.1 × 10^{-5} $\sec^{-1}$, respectively. From data at three temperatures, Arrhenius parameters were calculated: for cracking, E_a = 35.8 kcal/mol, log A = 12.8; for isomerization, E_a = 35.6 kcal/mol, log A = 12.9. The decomposition of **1** was uncomplicated kinetically since **2** was stable under the conditions. Clean, first-order disappearance of **2** did occur at 230° (k = 3.7 ± 0.3 × 10^{-4} $\sec^{-1}$), giving styrene only with even traces of **1** unobserved.



Irradiations of 0.02 *M* solutions of **1** or **2** at 254 nm gave styrene and cyclobutane isomer as major products by glc along with an unidentified peak which is presumed to be 1-phenyltetralin or 1-phenyltetrahydroazulene, reported previously[4] as low yield photochemical products at high conversion. Parallel irradiations (10–15% conversion) using a merry-go-round apparatus and a toluene/2-heptene actinometer[5] produced quantum yields which are summarized in Table I.

Quantum efficiencies for decomposition of **1** in the presence of triplet sensitizers such as benzophenone, acetophenone, and *m*-methoxyacetophenone were exceedingly low.[6] On the other hand, acetone (as solvent) provided sensitization with reaction efficiency comparable to direction irradiation (see Table I), suggesting that the quantum yield data in acetone reflect reaction of triplet excited cyclobutane since quenching of acetone singlets should be inefficient. In agreement is the effective sensitization of a phenylcyclopropane chromophore by acetone[10] and the rapid quenching of the type II photoelimination of 4-methyl-2-pentanone by 1,1,2,2-tetraphenylcyclopropane.[9]

The data concerning retention of configuration in **1** as measured by the product ratio of styrene/**2**[2d] for the different modes of activation are compiled in Table II. We assign the lowest singlet state of **1** as the excited species giving rise to products in direct irradiation since the reactions are not quenched by 2-heptene[11] or dimethyl maleate (E_T (estd) = 72 kcal/mol[12]) (see Table I), although a short-lived triplet (apparently not formed *via* acetone sensitization; compare product ratios) cannot be ruled out. Also assumed is that a single excited state partitions to products upon direct and sensitized irradiation, so that quantum yield ratios are rate constant ratios. For additional comparison the results of decomposition of azo compound **3** as reported by Kopecky[13] are included.

Table I
Quantum Yields in the Photolysis of *cis*- and *trans*-1,2-Diphenylcyclobutane

Cyclobutane	Solvent	ϕ_{styrene}	ϕ_{isomer}
1	MeCN	0.019	0.003
1	MeOH	0.018	0.002
1	MeCN (1.0 *M trans*-2-heptene)[a]	0.018	0.002
1	MeCN (0.1 *M* dimethyl maleate)[a]	0.021	0.006
1	Acetone[b]	0.018	0.007
2	MeCN	0.018	0.007

[a] Light absorbed by cyclobutane. [b] Light absorbed by acetone.

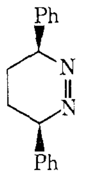
Table II
Stereoretention in the Decomposition of 1 and 3

Starting material	Mode of activation	Styrene/**2**[a]
1	Thermal (190–210°)	2.0 ± 0.3
1	Direct irradiation	7.1 ± 0.7
1	Sensitized irradiation	2.6 ± 0.2
3	Thermal (63–280°)	4.6 ± 0.4

[a] Errors are average deviations of product ratios or the square root of the sum of squares of rate constant uncertainties.

Clearly stereoretention values are not dramatically a function of mode of activation.[15] A common diradical **4**[16] could be involved in all cases if subtle dynamic effects produce the difference in partition to styrene and **2** (at most 67/33 *vs.* 88/12 for thermolysis and direct photolysis, respectively). In fact increased stereoretention in the series, thermal decomposition *vs.* azo compound fragmentation *vs.* direct photochemical activation, is in general agreement with the suggestion of Stephenson and Brauman[2a] that vibrationally excited diradicals may be involved in the latter two cases. However, in view of the recognition[2b,c] of mechanical forces which largely relieves the need for the "hot diradical" proposal for solution studies of several systems, the rapid internal relaxation from upper vibrational levels expected[19] for a species with as many atoms as **4**, and the observed dramatic independence of the decomposition of **3** on pressure,[14] we favor an alternative for an explanation of the small stereoretention differences. An economical suggestion is that concerted, perhaps orbital symmetry sanctioned, cycloreversion to styrene is an important contributor to the direct photolysis of **1** and the thermolysis of **3**. In agreement are reports[20] of high stereospecificity in the direct photochemical decomposition of a bicyclic cyclobutane related to **1** and **2**[20a] and in the thermal fragmentation of azo compounds related to **3**.[20b] Concerted fragmentation for **1** (photochemically) to give styrene and for **3** to the extent of 50 and 30%, respectively, combined with a common diradical component would rationalize the stereoretention results.

Using thermodynamic data[21] and the experimental activation energy for cracking of **1**, a ground-state potential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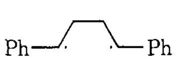
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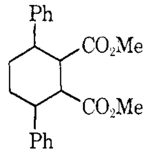
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surface with a secondary minimum ($\sim$10 kcal/mol deep) may be estimated. Despite the reasonably long lifetime (10^{-8} sec at 200°) indicated for a diradical on this surface, trapping by good "diylophiles" such as dimethyl maleate[22] and dodecanethiol[23] in pyrolysis (trapping agent used as solvent) and photolysis experiments is not observed. Expected products **5** and 1,4-diphenylbutane were obtained independently and shown to survive the decomposition conditions. The diradical dichotomy which persists involves a species which on the one hand may have a lifetime of a bond rotational period (for stereochemical loss *via* an intermediate) but which eludes direct detection ($\tau < 10^{-11}$ sec?). The latter elusiveness is predicted by theoretical calculation of the surfaces for small ring reorganizations.[24]

References and Notes

(1) (a) This work was presented in part at the Northeast Regional Meeting of the American Chemical Society, Rochester, N. Y., 1973, abstract no. 137. (b) Acknowledgment is made to the donors of the *Petroleum Research Fund, administered by the American Chemical* Society, for support of this research.

(2) (a) L. M. Stephenson and J. I. Brauman, *J. Amer. Chem. Soc.*, **93,** 1988 (1971); (b) C. P. Casey and R. A. Boggs, *ibid.*, **94,** 6457 (1972); (c) G. Jones, II, and M. E. Fantina, *J. Chem. Soc., Chem. Commun.*, 375 (1973); (d) G. Jones, II, *J. Chem. Educ.*, 175 (1974); (e) L. M. Stephenson and T. A. Gibson, *J. Amer. Chem. Soc.*, **94**, 4599 (1972).

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(4) M. Sauerbier, *Chem. Ztg.*, **95,** 530 (1972).

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(6) *Traces of styrene and* **2** *were produced in these sensitization runs*, and benzophenone was the most effective energy transfer agent (ϕ_{styrene} = 0.004). This parallels behavior reported earlier by Brown.[7] It would appear that use of these and other low energy sensitizers (E_T < 74 kcal/mol) is effective through chemical or nonvertical energy transfer[8] (perhaps to an available low energy "diradical" triplet as with the *1,2-diphenylcyclopropanes*[8b,9]) *rather* than through the conventional mechanism.

(7) (a) W. G. Brown and R. L. Markevich, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, O-139. (b) We are indebted to Dr. Brown for providing data prior to publication.

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(10) E. W. Yankee, F. D. Badea, N. E. Howe, and D. J. Cram, *J. Amer. Chem. Soc.*, **95,** 4210 (1973).

(11) Isomerization of olefins was not detected. Toluene by comparison is an effective sensitizer of 2-heptene isomerization.[5]

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(13) (a) K. R. Kopecky and S. Evani, *Can. J. Chem.*, **47,** 4041 (1969). (b) We are grateful to Professor Kopecky for providing additional data prior to publication. (c) This information along with the results[14] of studies concerning the effect of pressure on the decomposition of **3** indicate that the azo compound decomposition product ratio (stereoretention) is not significantly temperature or pressure dependent. Our data for **1** likewise do not reveal a temperature dependence.

(14) R. C. Neuman and E. W. Ertley, *Tetrahedron Lett.*, 1225 (1972).

(15) For comparison see the values for stereoretention[2d] which range over three orders of magnitude depending on substitution for several types of reaction involving in principle 1,4 diradicals. The comparison of photochemical stereoretention in **1** and **2** will be discussed in the full paper.

(16) The effect of phenyl substitution on the activation energy for thermal cracking of **1** (lower than that for cyclobutane[17] by 15 kcal/mol/phenyl) is more consistent with the diradical mechanism than with a concerted process in which the effect of phenyl is expected to be much smaller (3–5 kcal/mol).[18]

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(18) M. J. S. Dewar and L. E. Wade, *J. Amer. Chem. Soc.*, **95,** 290 (1973); (b) A. Viola, J. H. MacMillan, R. J. Proverb, and B. L. Yates, *ibid.*, **93,** 6967 (1972); (c) J. I. Brauman and W. C. Archie, Jr., *Tetrahedron*, **27,** 1275 (1971).

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(23) P. J. Wagner, P. A. Kelso, and R. G. Zepp, *J. Amer. Chem. Soc.*, **94,** 7480 (1972).

(24) For discussions of the problem, see L. M. Stephenson, T. A. Gibson, and J. I. Brauman, *J. Amer. Chem. Soc.*, **95,** 2849 (1973); L. Salem and C. Rowland, *Angew. Chem., Int. Ed., Engl.* **11,** 92 (1972); and ref 19.

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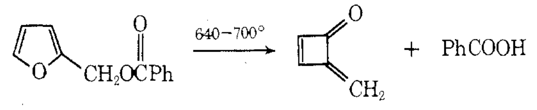
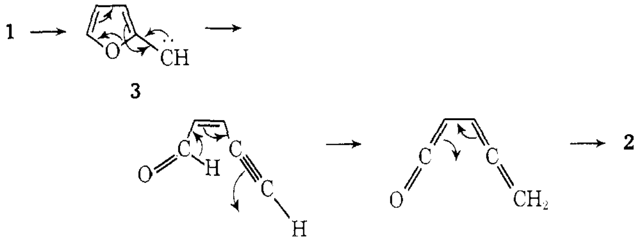
On the Mechanism of the Formation of Methylenecyclobutenone from the Pyrolysis of Furfuryl Benzoate

Summary: Aspects of the mechanism of the formation of methylenecyclobutenone by the pyrolysis of furfuryl benzoate are defined by the findings that pyrolysis of furfuryl-α,α-d_2 benzoate gives methylenecyclobutenone-*5,5*-d_2 and pyrolysis of 5-methylfurfuryl benzoate gives a good yield of 2,5-dimethylene-2,5-dihydrofuran.

Sir: Recently we reported that the low pressure ($\sim 10^{-4}$ Torr) gas phase pyrolysis of furfuryl benzoate (**1**) gives methylenecyclobutenone (**2**) in fair yield.[1]

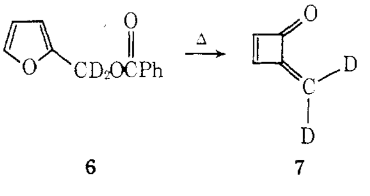

1 2 (40%)

A likely mechanism for this interesting reaction involves the initial formation of furfurylidene (**3**) by α elimination followed by rearrangement of this carbene to *cis*-pent-2-en-4-ynal (*cis*-**4**), rearrangement of *cis*-**4** to allenylketene (**5**), and rearrangement of **5** to **2**. This mechanism


3 *cis*-4 5

is supported by the fact that **3** is known to rearrange to **4**[2] and by the detection by ir and nmr spectroscopy of small amounts of *trans*-**4** in the pyrolysis product mixture from **1**.

This mechanism predicts that pyrolysis of the α,α-dideuterio ester (**6**) would give **2** that contains only one deuterium atom. We wish to report that the pyrolysis of **6**[3] gives a 40% yield of **2** which has both methylene protons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