# Intramolecular [2+2] Photocycloaddition. 14.[1] Cycloreversion of Cyclophanes Possessing a Cyclobutane Ring at Their Tether

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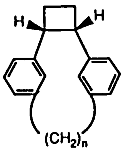
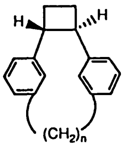
**Synopsis.** Thermal cycloreversion of ten cyclophanes possessing a cyclobutane ring at their tether was examined. The rates were affected not only by their strain but also by their structural characteristics, such as meta- or para-configuration. The relative rate difference covered a range on the order of $10^6$.

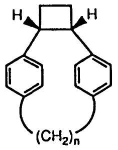
Cyclobutane itself has a strain energy of 27.3 kcal mol$^{-1}$,[2] so that it can be said to be a strained molecule. It is, however, rarely cleaved thermally; in gas phase, the activation energy of thermal cycloreversion was reported to be 62.5 kcal mol$^{-1}$.[3] This was attributed to the fact that the thermal [2σ+2σ] reaction is essentially forbidden on the basis of the symmetry conservation theory.[4]



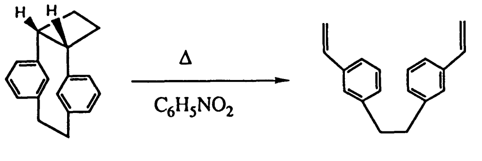
**1a** n=2
**b** n=3
**c** n=4
**d** n=5
**e** n=6



**2a** n=3
**b** n=4



**3a** n=3
**b** n=4
**c** n=5



(1)

Recently we have prepared several cyclophanes **1**—**3** having a cyclobutane ring at their tether.[5] These cyclobutane rings can be considered to be more strained than the parent compound because of the effect of the cyclophane fused structures. Therefore, these rings appear to be cleaved more readily than cyclobutane itself. We were prompted to examine the thermal cycloreversion of the cyclophanes at their cyclobutane rings and clarify the effects of the strain and the structural characteristics. In this report we would like to describe the details of our studies.

Thermolysis of **1**—**3** was carried out in nitrobenzene at 123 to 200 °C. The consumption of the cyclophanes was monitored by HPLC (reversed phase C-18, MeOH). Strain energies of cyclophanes **1**, **2**, and **3** were calculated by the MM2 method. Data are summarized in Table 1 and depicted in Fig. 1, where the three axes are the reaction rate at 200 °C (obtained directly or indirectly by extrapolation as shown in Table 1), the strain energy, and the structural characteristics, respectively. According to Fig. 1, it can be said that within a group of cyclophanes having the same structural characteristics, the larger strain the cyclophane has, the more readily its cyclobutane ring is cleaved. At the same time, however, the cyclobutane rings built in the less-strained metacyclophane skeleton undergo cycloreversion more readily than those in the more-strained paracyclophane skeleton.

Consequently, the strain of the cyclophane is not the only factor affecting the cycloreversion; the structural characteristics also affect the reaction considerably. Therefore, the mechanism seems not to be explained by simple [2σ+2σ] electrocyclic reversion, but to be interpreted in terms of the participation of the phenyl π-orbitals. According to the framework examination, the anti-bonding orbitals of the cyclobutane inner C–C bond in the paracyclophane skeleton are well oriented to interact with the phenyl π-orbital in a parallel manner, but in the flexible metacyclophane skeleton these orbitals cannot always be adjusted to interact with each other.[6] Accordingly, paracyclophanes stabilize the cyclobutane ring more than metacyclophanes. Hence, we propose a stepwise reversion for this thermal reaction;[7] i.e., the initial bond breaking of the cyclobutane

Table 1. Kinetic Parameters of Thermolysis of 1,2-Ethano[2.*n*]cyclophanes

| Compounds | Rate/×$10^{-5}$ s$^{-1}$ | | | | | | ΔH$^{\ne}$ | ΔS$^{\ne}$ | ΔG$^{\ne}$ 160 °C |
|---|---|---|---|---|---|---|---|---|---|
| | 123 °C | 132 °C | 142 °C | 185 °C | 190 °C | 200 °C | kcal mol$^{-1}$ | e.u. | kcal mol$^{-1}$ |
| **1a** | 4.66 | 13.7 | 37.0 | | | 10200$^{a)}$ | 36.6 | 13.4 | 30.8 |
| **1b** | | | | 11.3 | 17.7 | 54.1 | 40.4 | 10.8 | 35.8 |
| **1c** | | | | 5.58 | 6.57 | 14.1 | 26.3 | −21.7 | 35.7 |
| **1d** | | | | 0.12 | 2.87 | 0.67 | 45.4 | 13.1 | 39.7 |
| **1e** | | | | 0.32$^{b)}$ | 1.03$^{c)}$ | 1.27 | 30.0 | −18.3 | 38.0 |
| **2a** | | | | | | 47.9 | | | |
| **2b** | | | | | | 0.22 | | | |
| **3a** | | | | | | 18.3 | | | |
| **3b** | | | | 0.32 | 0.50 | 1.21 | 35.6 | −6.90 | 38.6 |
| **3c** | | | | | | 0.62 | | | |

a) Extrapolated. b) Temp 180 °C. c) Temp 195 °C.

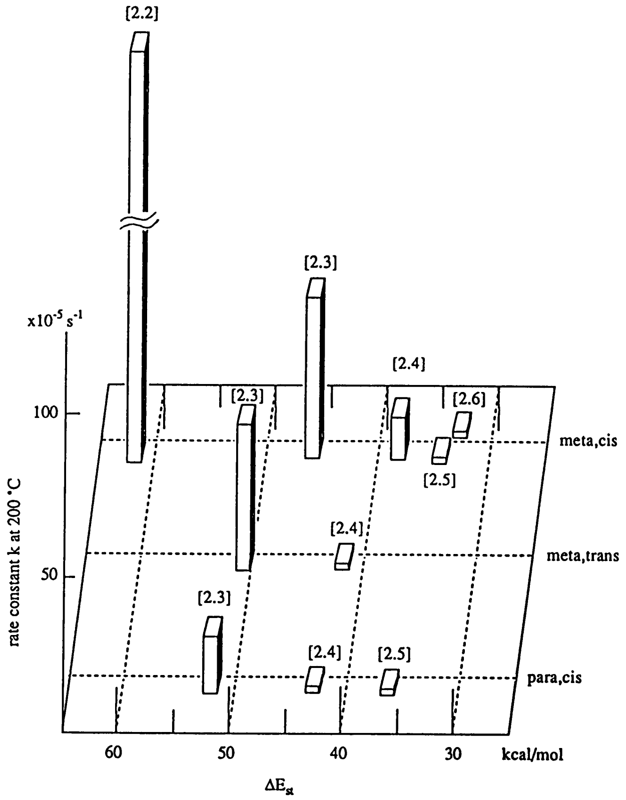


Fig. 1. Correlation between strain energies, rate constants of the thermal cycloreversion at 200 °C, and the structural characteristics of the cyclophanes.

inner C–C bond to make a biradical⁸⁾ at the benzyl positions followed by the cleavage of the outer C–C bond to make double bonds.

## Experimental

HPLC analysis was performed with a Shimadzu LC-6A pump, LC-6A UV detector, and RC4A data processor. MM2 calculations were done on an NEC PC9801 VM2 computer, using a program provided by Professor Eiji Osawa, Toyohashi College of Science and Technology. All cyclophanes were prepared by our method reported previously.⁵⁾ Nitrobenzene was purified by vaccum distillation. Other commercially available reagents of the highest grade were used without further purification, unless otherwise noted.

**Thermal Cycloreversion Cyclophanes Possessing a Cyclobutane Ring.** Into a 50 ml two-necked flask equipped with a balloon filled with $N_2$, a septum rubber, and a magnetic stirring bar, a cyclophane (ca. 30 mg) was set and dissolved in 10 ml of nitrobenzene. The flask was put in a thermosetting silicone oil bath. At the prescribed periods aliquots were withdrawn and analyzed by HPLC. The first order plot was taken up to 95% conversion. In all cases the plot was satisfactorily linear with an r value of 0.98 to 0.99.

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4) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim (1970).

5) J. Nishimura, Y. Horikoshi, Y. Wada, H. Takahashi, and M. Sato, *J. Am. Chem. Soc.*, **113**, 3485 (1991), and references cited therein.

6) The structure of metacyclophane, determined by X-ray crystallography and depicted in Ref. 5, clearly shows the situation.

7) G. W. Klumpp, "Reactivity in Organic Chemistry," John Wiley & Sons, New York (1982), p. 430.

8) Diethyl maleate or fumarate was combined in the thermolysis reaction mixture as was done for the trapping of a xylylene-type biradical from [2.2]paracyclophane by D. J. Cram and his co-worker (see H. J. Reich and D. J. Cram, *J. Am. Chem. Soc.*, **91**, 3517 (1969)). But any 1:1 addition products of the cyclophane and either ester were not obtained. As far as we have searched in the literature, the tetramethylene biradical is known as a short-lived species, is not trapped intermolecularly, and is not even observed by ESR spectroscopic methods. Therefore, the biradical in this reaction was supposed not to be trapped either.