

## Communications to the Editor

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THE ROLE OF THROUGH-BOND INTERACTION IN THERMAL BEHAVIOR  
OF CAGE MOLECULES

Yasushi Okamoto,<sup>a</sup> Kazunobu Harano,<sup>a</sup> Masami Yasuda,<sup>a</sup>  
Eiji Ōsawa,<sup>b</sup> and Ken Kanematsu\*,<sup>a</sup>  
Faculty of Pharmaceutical Sciences, Kyushu University 62,<sup>a</sup>  
Fukuoka 812 and Department of Chemistry, Faculty of Science,  
Hokkaido University,<sup>b</sup> Sapporo 060, Japan

The cage triketone 2 revealed different reactivities toward the thermal condition according to the substituents: the cyclobutane ring cleavage for alkyl substituents and the decarbonylation for methoxycarbonyl ones. The X-ray crystallographic study for the derivative of 2b showed a significantly long (1.635(7) Å) C(Ph)-C(Ph)  $\sigma$  bond. The reaction mechanisms are discussed in terms of frontier molecular orbital (FMO) theory combined with the results of molecular mechanics and semiempirical MNDO molecular calculations.

KEYWORDS— decarbonylation; cyclobutane ring cleavage; through-bond interaction; frontier molecular orbital; bond elongation

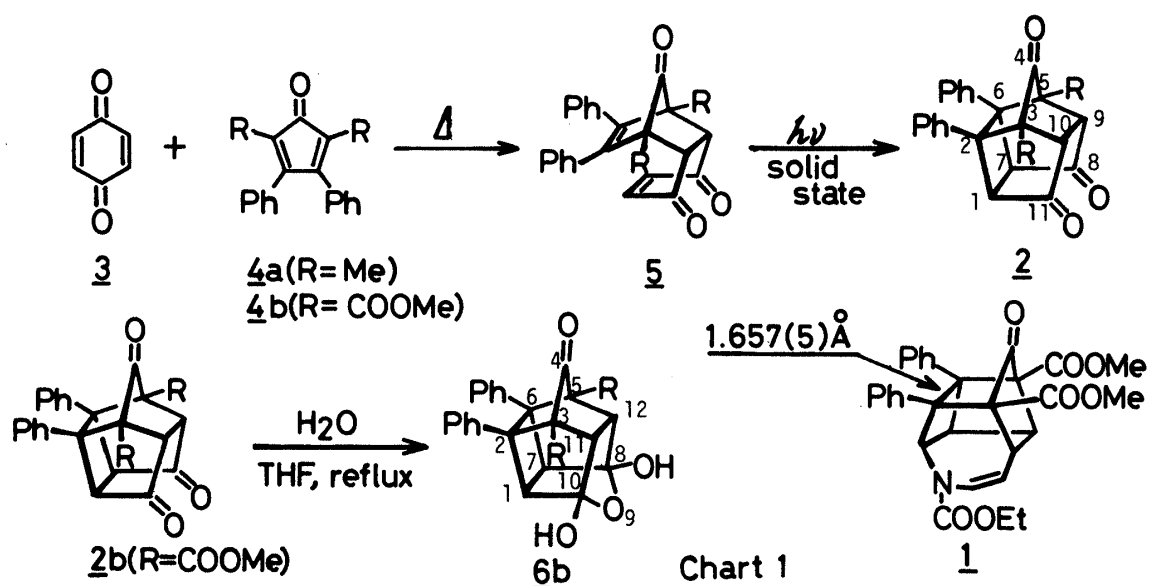
Considerable interest in the chemical behavior of cage molecules has increased during the past decade, since these compounds continue to play an important role in the understanding of many aspects of physical and synthetic organic chemistry. Especially, it should be noted that the thermal olefin metatheses to the cage molecules were applied to the new and general approach to linearly fused tricyclopentanoids of natural products as coriolin<sup>1a)</sup> and hirsutene.<sup>1b)</sup>

Recently, we found the bond elongation caused by enhanced through-bond interaction of vicinal diphenyl substituents, and have proposed that it plays a significant role for the decarbonylation reaction of the strained cage molecule 1.<sup>2)</sup>

Further studies on the chemical behavior and structural feature of cage triketone 2 are of particular interest in understanding the effects of through-bond interaction on the reactivity of strained cage molecules.

The cage triketones 2a,b were synthesized according to a procedure previously described.<sup>3),4)</sup> The cycloproduct (5) of p-benzoquinone 3 and 2,5-disubstituted-3,4-diphenylcyclopentadienone 4 was irradiated in solid state to give the desired photoproduct (2) (Chart 1). The structures of these compounds were determined by their spectral data (IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR) in comparison with those which were previously reported.<sup>3)</sup> The keto group of 2b is more congested than that of 2a; the carbonyl stretching frequency (1808 cm<sup>-1</sup>) is 53 cm<sup>-1</sup> higher than that of 2a.<sup>5)</sup>

To confirm the presence of bond elongation caused by an enhanced through-bond interaction, we have undertaken an X-ray crystallographic study for 2.



Since well-formed crystals of **2** were not available, a chemical conversion was carried out; **2b** readily gave the oxa-cage compound **6b** on treatment with water, thus a single crystal X-ray diffraction study was effected. As shown in Figure 1, the

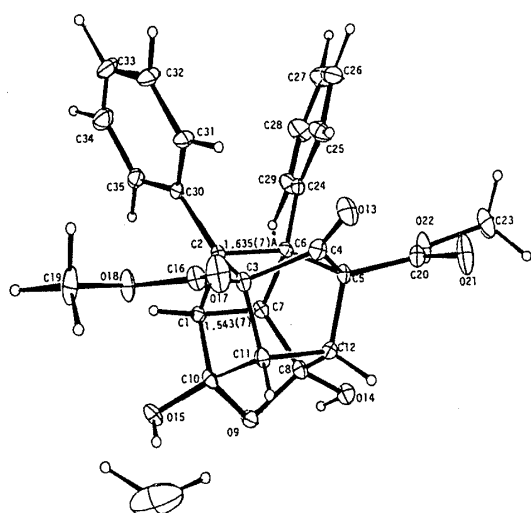


Figure 1. Molecular Structure of **6b**<sup>6)</sup>

most remarkable feature of **6b** is the face-to-face conformation<sup>7)</sup> of the two phenyl groups and the significantly long C<sub>2</sub>-C<sub>6</sub> σ bond (1.635(7) Å). Unfortunately, as described above, we could not know the precise bond length of C<sub>2</sub>-C<sub>6</sub> in **2b**. However, on the basis of our previous study,<sup>2)</sup> we can assume that **2b** has approximately the same bond length as **6b**. The fact that calculated C<sub>2</sub>-C<sub>6</sub> bond length of **2** using Allinger's MM2 force field is considerably shorter than that using semiempirical MO (MNDO) method also indicates that the through-bond interaction, which is an electrostatic interaction, is operative in this case (Table I).

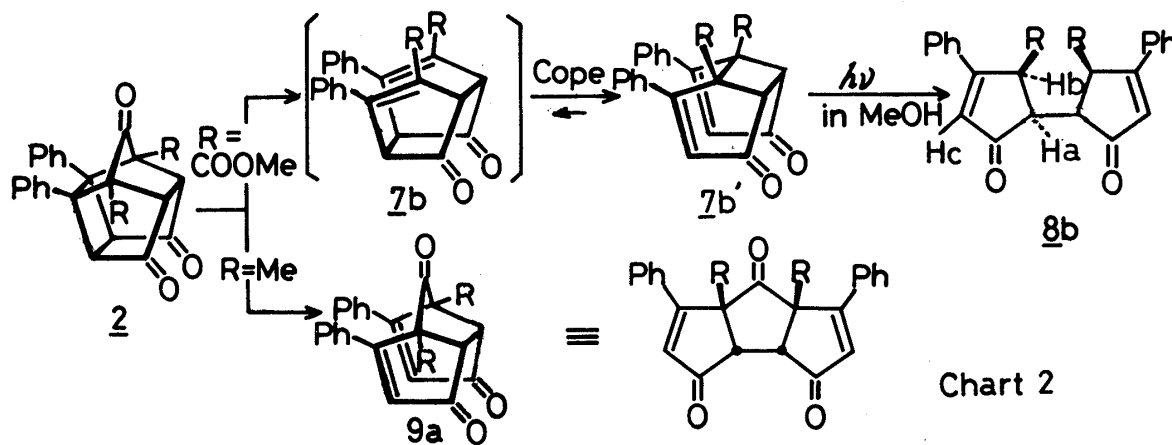
Long C-C bonds as mentioned above should be susceptible to rapid cleavage as can be seen by comparing the results of Mehta,<sup>4)</sup> with those of our previous papers.<sup>2)</sup>

Indeed, refluxing in diphenyl-ether (DPE) resulted in the rapid decarbonylation to give unstable tricyclic compound **7b'** which might

Table I. Calculated Bond Lengths

| Compd.              | length (Å)                     |        |                                |        |
|---------------------|--------------------------------|--------|--------------------------------|--------|
|                     | C <sub>2</sub> -C <sub>6</sub> |        | C <sub>1</sub> -C <sub>7</sub> |        |
|                     | MM2                            | MNDO   | MM2                            | MNDO   |
| <b>2a</b> (R=Me)    | 1.5659                         | 1.6229 | 1.5521                         | 1.5592 |
| <b>2b</b> (R=COOMe) | 1.5724                         | 1.6265 | 1.5496                         | 1.5585 |

be derived from Cope rearrangement of 7b.<sup>8)</sup> The diene, upon irradiation in MeOH, provided the photo-induced reduction product 8b,<sup>9)</sup> supporting that the extrusion of carbon monoxide from 2b had occurred. On the other hand, 9a underwent ring closure to 2a upon irradiation of the same reaction conditions (Chart 2).



Interestingly, two independent reaction pathways were observed according to the substituents at C<sub>3</sub> and C<sub>5</sub> in spite of the presence of the diphenyl group in 2a and 2b. The result of 2b is in sharp contrast to Mehta's observation of 2a<sup>4)</sup>; the thermal decomposition of 2a gave the bis-enone 9a by preferential cleavage of the cyclobutane ring.

In either case, the C<sub>2</sub>-C<sub>6</sub> bond was cleaved in selective manner, indicating that the through-bond interaction is one of the important factors in thermally induced bond cleavage reaction.

In the case of these reactions, a distinction between a fully concerted reaction pathway and an involving diradical intermediate is not possible at the present stage. However, in the thermal decarbonylation of 2b, the reaction mechanism might be explained in terms of cyclic three-system interaction,<sup>10)</sup> in which interaction between the low-lying LUMO's of the bridged bond (C<sub>3</sub>-C<sub>4</sub> and C<sub>4</sub>-C<sub>5</sub>), lowered by the effect of the electron-withdrawing substituents, and the heightened HOMO of the elongated C<sub>2</sub>-C<sub>6</sub> bond are operative (Figure 2(b)).<sup>11)</sup>

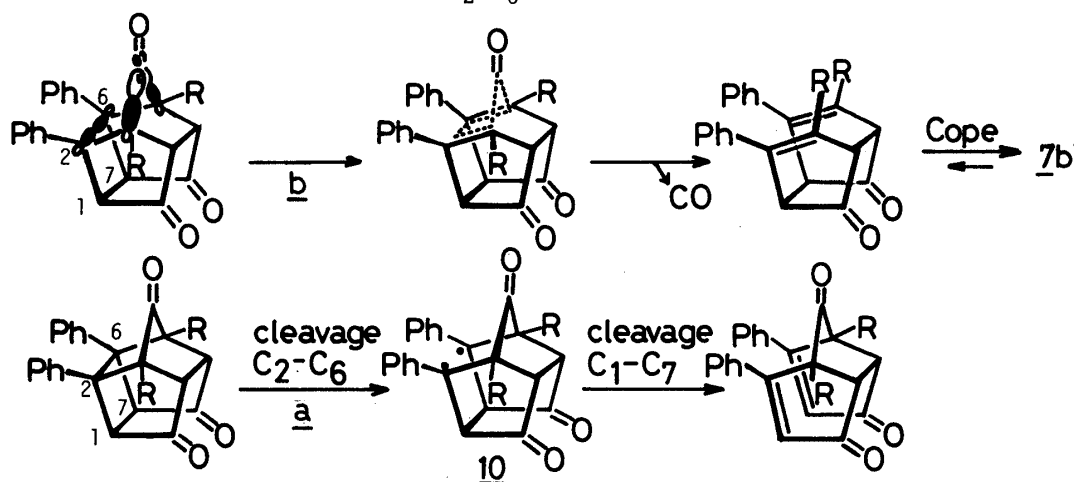


Figure 2. Possible Transition State for Thermal Reaction of 2

In contrast, from the fact that the cage triketone 2a undergoes thermally forbidden cycloreversion reaction at moderate temperature, another possible mechanism is considered as follows: the preferential cleavage of the elongated  $C_2-C_6$  bond caused by enhanced through-bond interaction leads to the formation of the diradical intermediate 10. The resulting diradical 10 still interacts through the  $\sigma$  bond ( $C_1-C_7$ ), and this weakened  $\sigma$  bond undergoes cleavage to form the thermodynamically stable bis-enone system (9a) (Figure 2(a)).

Thus, phenyl participation at  $C_2$  and  $C_6$  shows a leading role in thermally induced bond cleavage reactions as well as the nature of the substituents at  $C_3$  and  $C_5$  in the cage triketone 2.

Further detailed mechanistic studies of the ring cleavage reaction of the cage triketone 2 are in progress, and will be published elsewhere.

#### REFERENCES AND NOTES

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- 4) G. Mehta, A. Srikrishna, A. V. Reddy, and M. S. Nair, Tetrahedron, 37, 4543 (1981), and references cited therein.
- 5) The difference may be attributed to F-strain effects. The crystal structure of 6b (Figure 1) showed three carbonyl dipoles in a syn-parallel fashion, indicating the presence of large congestion around the bridged carbonyl group.
- 6) The crystal data of 6b are as follows; mp 268°C (dec.); Space group  $P2_1/a$  (monoclinic);  $a = 19.688(7)$ ,  $b = 7.277(1)$ ,  $c = 17.201(6)$  Å,  $\beta = 108.95(3)^\circ$ ,  $V = 2331(1)$  Å<sup>3</sup>,  $D_m(KI/H_2O) = 1.388$ ,  $D_c = 1.402$  g/cm<sup>3</sup>;  $R_{final} = 0.048$ .
- 7) Twist angles for ring planes with regard to the  $C_2-C_6$  bond are  $73.3^\circ$ ,  $-107.3^\circ$  for  $C_2$  phenyl, and  $-92.5^\circ$  and  $81.6^\circ$  for  $C_6$  phenyl ring.
- 8) Due to the existence of a small amount of Cope rearrangement isomer (7b) as shown by the NMR inspection, further purification of 7b' failed.
- 9) Physical and spectral data for 8b are as follows; mp 244-246°C; yield 40% from 2b; <sup>1</sup>H-NMR ( $\delta$ , CDCl<sub>3</sub>) 3.26 (dd, Ha(or Hb),  $J_{Ha,Hb} = 2.0$  Hz,  $J_{Ha,Hb'} = 1.0$  Hz, 2H), 3.66 (s, 2 x OCH<sub>3</sub>, 6H), 4.31 (ddd, Hb(or Ha),  $J_{Hb,Hc} = 1.5$  Hz, 2H), 6.68 (d, Hc, 2H), 7.36-7.67 (m, Ph-H, 10H); IR (cm<sup>-1</sup>, nujol) 1740, 1683, 1600; UV  $\lambda_{max}^{MeOH}$  nm(log $\epsilon$ ) 286 (4.44).
- 10) S. Inagaki, H. Fujimoto, and K. Fukui, J. Am. Chem. Soc., 98, 4693(1976).
- 11) Another reaction pathway involving a diradical intermediate like 10 could be also considered. However, from the fact that the cycloreversion product could not be detected in the reaction of 2b, it seems to be more reasonable to consider the concerted pathway as described above.

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