

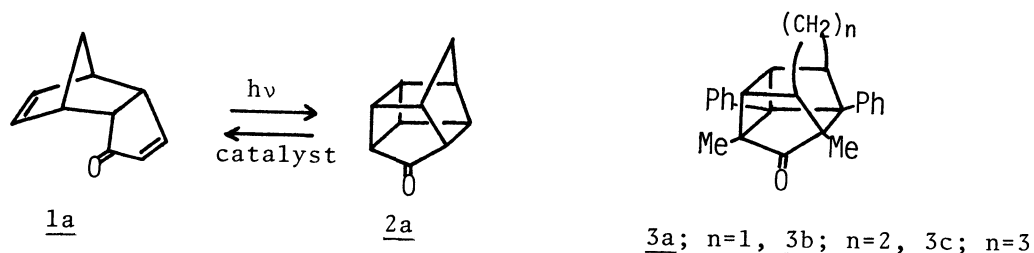
SYNTHESIS AND [2+2]-CYCLOREVERSION OF CAGE KETONES<sup>1)</sup>

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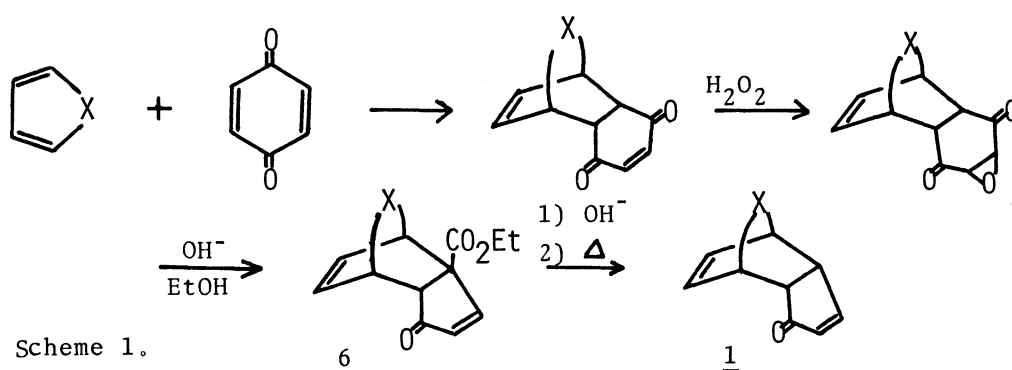
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A series of pentacyclic cage ketones 2b-d having no substituent was synthesized by the photochemical [2+2]-cycloaddition reaction of corresponding tricyclic dienones 1b-d. The cage ketones 2b-d underwent thermal [2+2]-cycloreversion to give dienones 1b-d. The reactivities were dependent on the length of the bridge "X".

[2+2]-Cycloreversions have attracted much attention from a theoretical and synthetic point of view.<sup>2)</sup> Some [2+2]-cycloreversions in cage molecules have been discussed in connection with storage of solar energy.<sup>3)</sup> The reversible reaction between dienone 1a and cage ketone 2a has been investigated for this purpose.<sup>4)</sup> On the other hand, we have found that diphenylated cage ketones 3b,c thermally underwent decarbonylation instead of the ring opening of a strained cyclobutane in which the influence of the bridge "X" and the phenyl substituents was pointed out.<sup>5)</sup> It is of interest, therefore, to synthesize unsubstituted cage ketones 2 possessing various kinds of bridge "X" and investigate their thermal behaviors. It is important, particularly, to compare the reactivities of a series of cage ketones 2a-e. We report here the synthesis and the [2+2]-cycloreversion of cage ketones 2.

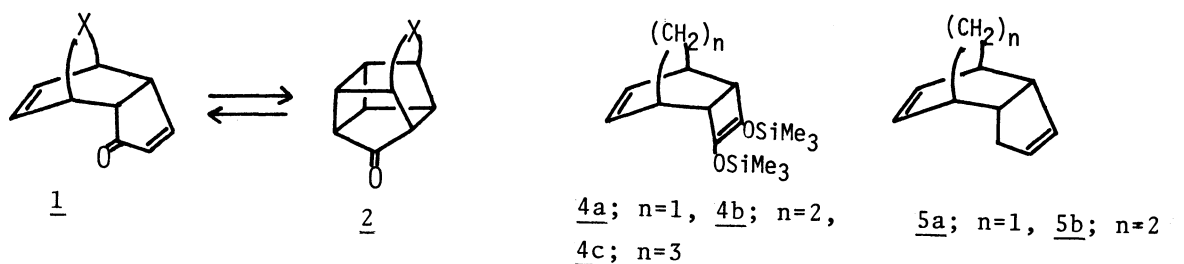


In order to obtain hitherto-unknown cage ketones 2b-e, dienones 1b-e were first synthesized. The dienone 1b was synthesized by the method of Herz shown in Scheme 1 starting from benzoquinone and cyclohexadiene.<sup>6)</sup> This method could be applied for the synthesis of other dienones 1c,d using cycloheptadiene and cyclooctatetraene, respectively, as dienes for the Diels-Alder reaction.<sup>7)</sup> Bicyclo-[4.3.0]nona-3,8-dien-7-one 1e was prepared from a cycloadduct between butadiene and 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene by dechlorination, hydrolysis, and the Cope rearrangement.<sup>7)</sup>

Table 1. Photoreaction of dienones 1a-e

Compd	Bridge "X"	Isolated yield/% <sup>a)</sup> (Irradiation time/h)	Quantum yield
<u>1a</u>	CH <sub>2</sub>	70 (2.5)	0.37 <sup>b)</sup>
<u>1b</u>	(CH <sub>2</sub> ) <sub>2</sub>	62 (3.5)	0.17 <sup>c)</sup>
<u>1c</u>	(CH <sub>2</sub> ) <sub>3</sub>	70 (8)	0.08 <sup>c)</sup>
<u>1d</u>		69 (3.5)	0.37 <sup>c)</sup>
<u>1e</u>	none	0 (10)	0

a) A nitrogen purged solution of 1 (2.0 g) in 400 ml of acetonitrile was irradiated with a 450 W Riko high pressure mercury lamp (Pyrex filter). b) Ref. 4. c) Measured in acetonitrile using a merry-go-round apparatus with RUL 3500 lamps (330-380 nm).



Irradiation of dienones 1b-d in acetonitrile with a high pressure mercury lamp gave the corresponding cage ketones 2b-d in good yield<sup>8)</sup> although 2e could not be obtained at all. The result is summarized in Table 1. An interesting feature in these photoreactions is that the quantum yield depends on the length of the bridge "X", thus decreasing as the bridge becomes longer. The similar structural effect was observed in the [2+2]-photocycloaddition of dienes 4<sup>9)</sup> and 5<sup>10,11)</sup> in which the bridge effect was found in their yields.<sup>12)</sup> MO calculation has shown that the poor yields found in the photoreaction of 4b and 5b can be attributed to the lower reactivity of the bicyclo[2.2.2]octene type double bond compared to the norbornene type double bond.<sup>11)</sup> In our case, however, the isolated yields of 2a-c were comparable and fairly high. The effect of the bridge is found in their quantum yields.

This may be explained by the increasing distance between the double bonds in higher homologs in addition to the greater reactivity of the norbornene type double bond. The high quantum yield observed in 2d and no formation of 2e can be also explained by the distance between the reaction sites because the cyclobutene ring in 1d makes the distance shorter due to the steric effect, while no link in 1e makes the distance longer.

Cage ketones 2b-d obtained as above, upon pyrolysis at 480 °C using a conventional flow method, underwent a cleavage reaction of a strained four-membered ring to give dienones 1b-d in nearly quantitative yields. This reaction is different from that of diphenylated cage ketones 3b-c and reconfirms that the phenyl groups participate in the decarbonylation found in cage ketones 3.<sup>14)</sup> It should be noted that even 2c containing a three carbon bridge which is expected to undergo decarbonylation most readily<sup>5)</sup> underwent the [2+2]-cycloreversion. This reaction is also different from that of 2a in which decomposition to dihydroindene and cyclopentadiene occurs at 425 °C.<sup>15)</sup> This reason seems to be attributed to the thermal lability of dienone 1a because it decomposes with production of dihydroindene and cyclopentadiene at 425 °C, too. The clear reversible reaction found here is considered to be more promising for the light energy storage than that between 1a and 2a. It is undesirable, however, that the thermal reaction requires high temperatures. Therefore, we have investigated metal catalyzed reactions of cage ketones 2. It has already been reported that 1a isomerized to 2a at high temperatures in the presence of rhodium catalysts.<sup>4)</sup> Similarly, cage ketones 2b,c underwent the [2+2]-cycloreversion in the presence of a rhodium catalyst although high temperatures are still required. Relative rates of the reaction are shown in Table 2. Interestingly, it was found that the rate decreases as the length of the bridge becomes longer.

Table 2. Isomerization rates<sup>a)</sup> of cage ketones 2a-c catalyzed by Rh(PPh<sub>3</sub>)<sub>3</sub>Cl

Compd	Bridge "X"	10 <sup>4</sup> k/s <sup>-1</sup> <sup>b)</sup>	Rel. rate
<u>2a</u>	CH <sub>2</sub>	2.15	1
<u>2b</u>	(CH <sub>2</sub> ) <sub>2</sub>	1.04	0.5
<u>2c</u>	(CH <sub>2</sub> ) <sub>3</sub>	0.21	0.1

a) Kinetic study was carried out in diglyme at 180 °C.

b) Obtained from pseudo first-order rates at low conversion for disappearance of 2 (catalyst concentration is 0.05 mol dm<sup>-3</sup>).

This result may be explained by the difference of the local bond angle deformation, as suggested by Jones and Ramachandran.<sup>4)</sup>

These findings indicate that the thermal reactions of cage ketones accompanied by a rupture of a strained cyclobutane ring are very sensitive to the structural change as well as the substituent effects.

## References

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- 12) The yields of the corresponding cage compounds are as follows. 4a (80%), 4b (5%), 4c (0%), 5a (61%), 5b (5%).
- 13) Carboethoxy substituted dienes 6b-d underwent photochemical [2+2]-cycloaddition to give corresponding cage ketones more smoothly than 1b-d. This can be also explained by considering that the steric effect due to the substituent makes the distance shorter.
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