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A New Synthetic Method of [2.2]Cyclophanes from [3.3]Cyclophane-2,11-diones via Photodecarbonylation

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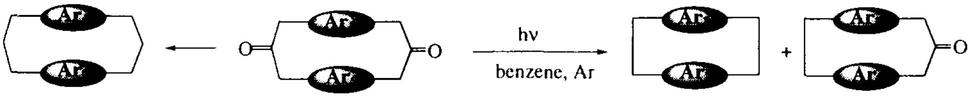
Abstract: Photoirradiation of [3.3]cyclophane-2,11-diones with a high-pressure Hg lamp in benzene provides the corresponding [2.2]cyclophanes in high yields along with [3.2]-cyclophane-2-ones. © 1998 Elsevier Science Ltd. All rights reserved.

Electronically excited carbonyl compounds undergo various reactions, in which α-cleavage in solution constitutes an important synthetic method.[1] Quinkert et al. first reported the light-induced decarbonylation of ketones in benzene in 1963,[2a] and found that 1,3-diphenyl-2-propanones afford 1,2-diphenylethanes in high yields.[2a-d] In the course of our study on multilayered [3.3]metacyclophanes, we noticed that the n-π* bands of the structural units, [3.3]metacyclophane-2,11-diones, appear in the 280-330 nm region.[3] We found that photoexcitation of the n-π* bands of [3.3]cyclophane-2,11-diones **1** in benzene extrudes carbon monoxide smoothly to give [2.2]cyclophanes **2** in high yields, and this method constitutes an alternative simple and general synthetic method of [2.2]cyclophanes (Scheme 1).



4 1 **Scheme 1** 2 3

Irradiation of [3.3]cyclophane-2,11-dione in benzene with a high-pressure Hg lamp gives the corresponding [2.2]cyclophane in satisfactory yield.[4] The isolated yields of products and irradiation times are summarized in Table 1. The reactions of [3.3]metapara- and paracyclophane-2,11-diones **8** and **11** proceed smoothly to give [2.2]metapara- and paracyclophanes **9** and **12** in high yields, while the reaction is rather slow but [2.2]metacyclophane **6** is obtained in 78% yield along with [3.2]metacyclophane-2-one **7** from [3.3]metacyclophane-2,11-dione **5**. This method is also applicable to the synthesis of [2.2]pyridinophane **15**, while tribridged ketone **17** is inert toward the reaction conditions. We can safely say that the reaction conditions can be adjusted to the preferential formation of [3.2]cyclophane-2-one **3**, from the time-control reaction of **9**. When irradiation was stopped at 1 hour, 14% of **10** and 85% of **11** was isolated, and at 30 min., **10**, **11**, and the starting material **9** were isolated in 43%, 47%, and 10% yield, respectively. The intramolecular fashion of this reaction is supported by the exclusive formation of unsymmetrical [2.2]- and [3.2]cyclophanes from unsymmetrical starting ketones, as exemplified by **8** and **14**.

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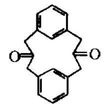
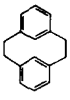
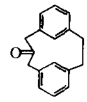
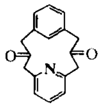
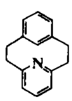
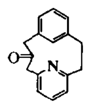
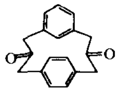
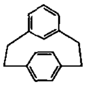
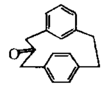
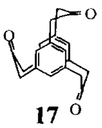
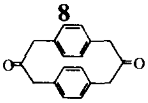
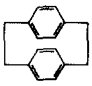
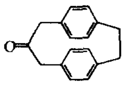
Recently, Vögtle et al. reported that flash vacuum pyrolysis (10^{-5} torr, 610-650 °C) of [3.3]cyclophane-2,11-diones affords [2.2]cyclophanes in moderate yields.[5] The advantage of our photochemical method over Vögtle's and other conventional methods[6,7] is the simple and easy experimental procedures, which do not require special apparatus or reagents, and the high yields obtained. Thus, [3.3]cyclophane-2,11-diones, which are readily accessible by the TosMIC coupling,[8] serve as common precursors to the synthesis of [3.3] cyclophane **4** and [2.2]cyclophane **2**. Further study on the scope and limitations of our method is in progress and the results will be reported elsewhere.

Table 1. Yields of [2.2]cyclophanes and [3.2]cyclophane-2-ones.[4,9,10]

Dione	Time (h) of irradiation	Product Yields (%)	Dione	Time (h) of irradiation	Product Yields (%)
 **5**	24.5	  **6**, 78% **7**, 22%	 **14**	45	  **15**, 56% **16**, 14%
 **8**	5	  **9**, 94% **10**, 0%	 **17**	20	no reaction
 **11**	4	  **12**, 97% **13**, 0%			

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References and Notes

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3. Shinmyozu, T. et al. unpublished results.
4. Typical Procedure: A benzene solution (1 L) of [3.3]cyclophane-2,11-dione **1** (8.0×10^{-4} moles), flushed for 30 min with argon, is irradiated with a high pressure Hg lamp (400 W) as internal light source at ambient temperatures while argon is bubbled. Progress of the reaction is monitored by TLC (silica gel, CH_2Cl_2 or CH_2Cl_2/AcOEt=5/1). After the starting ketone is consumed, the solvent is removed *in vacuo* and the residue is purified by silica gel (alumina in case of **14**) preparative TLC.
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9. Physical properties and ^{1}H NMR data of **6**, **9**, **12**, and **15** were in complete agreement with those reported.
10. All new compounds **7**, **10**, **16** show satisfactory spectroscopic and elemental analysis data.