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Chemical and Photochemical Behavior of Nondissociating Cyclopentadienone Dimers[1]

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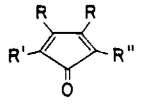
The nondissociating character and endo configuration of the substituted cyclopentadienone dimers **2c**,**d** along with the novel "mixed dimers" **2e**,**f** were unequivocally demonstrated. Irradiation of the dimers **2c**,**d** brings about *only* reversible 1,3-rearrangement to **11c**,**d** of all the possible modes available to the system (Scheme IV). In contrast to that, the "mixed dimers" **2e**,**f** undergo *only* internal cycloaddition to the dissymmetric cage products **6e**,**f**. Stereoelectronic arguments are put forward to rationalize this behavior in a general framework of this class of compounds.

In the framework of our research activities on cyclopentadienones and their dimers, we have elaborated on the photochemical transformations of dissociating cyclopentadienone dimers, e.g., **2b**.[1] We now present details of an investigation of a series of substituted, nondissociating cyclopentadienone dimers,[3] including a novel category of "mixed dimers".

To familiarize the reader with the subject,[4-8] nonsubstituted or moderately substituted cyclopentadienones (**1**, Chart I), namely, lacking substitution in 2- and/or 5-position, have no finite lifetime in ordinary laboratory conditions and dimerize irreversibly (with exception of certain *tert*-butyl-substituted cyclopentadienones[8]). This has been known for two decades for the parent system (**1a**)[5] and since the turn of the century for substituted derivatives like **1c**,**d**.[6,4] The process has been recognized as a Diels–Alder (${}_{\pi}4 + {}_{\pi}2$) type leading to the obvious structure **2**,[4-7] the reason for the elusiveness of cyclopentadienone and many of its derivatives being their antiaromatic character.[8]

The photochemical as well as thermal behavior of the parent dimer **2a** has been dealt with,[9] and the interesting findings have prompted us to examine further substituted derivatives.[3] To this end we prepared the dimers (**2c**,**d**) of 3,4-diphenyl- and 2-methyl-3,4-diphenylcyclopentadienone using known procedures.[6,7] These consist essentially of two steps: the base-catalyzed condensation of benzil and acetone or its homologue to give the corresponding hydroxy ketones **3c**,**d** and the latter's acid-catalyzed dehydration (*p*-TsOH in boiling CCl_4) to the cyclopentadienones **1c**,**d**, which dimerize instantaneously to **2c**,**d**.

Chart I[a]



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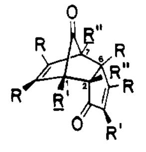

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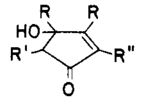
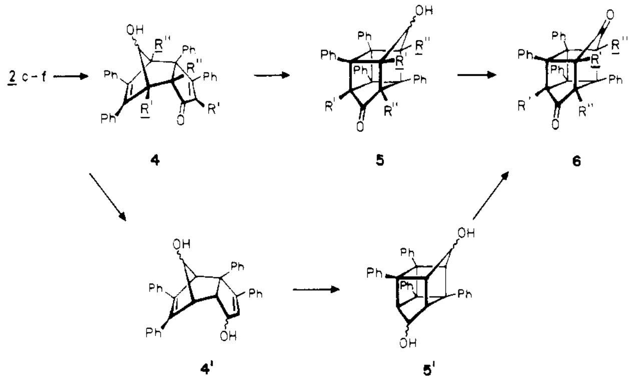


3

	a	b	c	d	e	f	g
R	H	Ph	Ph	Ph	Ph	Ph	Ph
R′	H	Me	H	Me	Me	Me	H
R″	H	Me	H	H	Me	Me	Me
$\underline{R}'$	H	Me	H	Me	H	Me	H
$\underline{R}''$	H	Me	H	H	H	H	H

[a] The notation for the R substituents is used throughout the paper. Underlined R′ and R″ are represented by italic $\underline{R}'$ and $\underline{R}''$ in the text.

Scheme I



For reasons which will become apparent below, we became interested in mixed "dimers", i.e., cycloaddition products of two different cyclopentadienones. Such compounds have not been recorded, in spite of the vast amount of literature covering this field of research.[4] We carried this out by performing the dehydration of **3c** or **3d** in the presence of the dissociating dimer **2b**, whereby **2e** and **2f** were isolated as the *sole products*. This was taken as an indication that no thermodynamic control occurs; i.e., as the cyclopentadienones **1c** and **1d** form, they are kinetically trapped by **1b** to give the products **2e** and **2f** which are, moreover, nondissociating "dimers" (vide infra).

When, however, equimolar amounts of **3c** and **3d** were dehydrated together as above, no mixed "dimer" (**2g**) was obtained, and the respective, normal dimers **2c** and **2d** were exclusively isolated. The compelling explanation of this finding is that the dehydration rates of **3c** and **3d**

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(1) (a) Photochemical Studies. Part 20. Part 19: B. Fuchs, M. Pasternak, and B. Pazhenchevsky, *Tetrahedron*, **36**, 3443 (1980). (b) See also part 18 [B. Fuchs, *Isr. J. Chem.*, **20**, 207 (1980)] for a unified treatment of the structural and stereochemical features of the transformation modes of cyclopentadienones and their dimers.

(2) (a) Taken in part from the Ph.D. Thesis of M.P., Tel-Aviv University, 1977. (b) Taken in part from the M.Sc. Thesis of B.P., Tel-Aviv University, 1972.

(3) For preliminary communications of some parts of this work, see: (a) B. Fuchs, *J. Am. Chem. Soc.*, **93**, 2544 (1971); (b) B. Fuchs and B. Pazhenchevsky, *Tetrahedron Lett.*, 3047 (1972).

(4) (a) C. F. H. Allen, *Chem. Rev.*, **37**, 209 (1945); (b) C. F. H. Allen, *ibid.*, **62**, 653 (1962); (c) M. A. Ogliaruso, M. G. Romanelli, and E. I. Becker, *ibid.*, **65**, 261 (1965).

(5) (a) C. H. DePuy and B. W. Ponder, *J. Am. Chem. Soc.*, **81**, 4629 (1959); (b) E. Vogel and E.-G. Wyes, *Angew. Chem.*, **74**, 489 (1962).

(6) (a) F. R. Japp and G. D. Lander, *J. Chem. Soc.*, **71**, 123 (1897); (b) F. R. Japp and A. M. Meldrum, *ibid.*, **79**, 1024 (1901).

(7) (a) C. F. H. Allen and J. W. Gates, *J. Am. Chem. Soc.*, **64**, 2120 (1942); (b) *ibid.*, **64**, 2123 (1942); (c) C. F. H. Allen and J. A. Van Allan, *J. Org. Chem.*, **10**, 333 (1945); (d) *ibid.*, **17**, 845 (1952); (e) *ibid.*, **20**, 315 (1955); (f) *ibid.*, **14**, 1051 (1949); (g) C. F. H. Allen and J. A. Van Allan, *J. Am. Chem. Soc.*, **72**, 5165 (1950).

(8) (a) E. W. Garbisch, Jr., and R. F. Sprecher, *J. Am. Chem. Soc.*, **88**, 3434 (1966); (b) *ibid.*, **91**, 6585 (1971).

(9) (a) U. Klinsmann, J. Gauthier, K. Schaffner, M. Pasternak, and B. Fuchs, *Helv. Chim. Acta*, **55**, 2643 (1972); (b) E. Baggiolini, E. G. Herzog, S. Iwasaki, R. Schorta and K. Schaffner, *ibid.*, **50**, 297 (1967).

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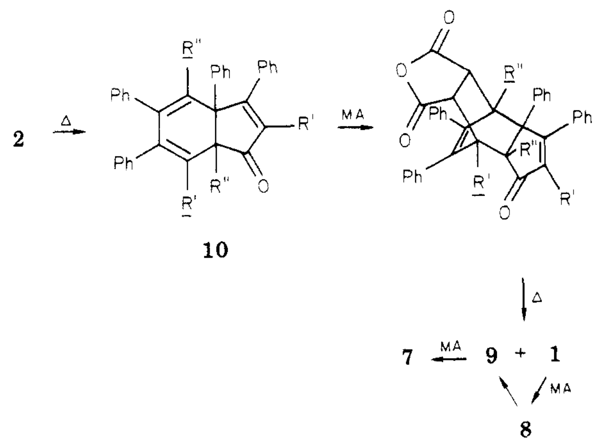
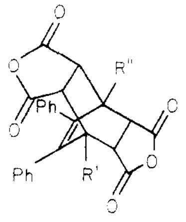
Scheme II



differ appreciably, thus preventing efficient encounters between **1c** and **1d** as they are formed. The rates of formation of the dimers **2c** and **2d** were indeed found by NMR techniques to differ by nearly 3 orders of magnitude (in favor of **2c**).

The next step was to prove beyond doubt the endo configuration of the various dimers 2 and their nondissociating character. The former had been proven for **2a**[5b] but not for substituted derivatives. Recently[1a,2,10,11] this was done for dissociating dimers, and in the present work an analogous sequence of reactions was used,[2,3b,10] namely (Scheme I): NaBH$_4$ reduction of **2c–f** to the corresponding hydroxy ketones **4c–f** (**2c** gave the diol **4′** as major product); these closed under irradiation to the cage compounds **5c–f** (or **4′** → **5′**) which were oxidized (Jones reagent) to the dissymmetric cage diketones **6c–f**. Hence, the dimers **2c–f** must have an endo configuration. This conclusion, in fact, draws support from the NMR chemical shifts of the methyl protons in the various dimers 2 and their derivatives (cf. also ref 1a).

As to the thermal stability of the dimers 2, we encountered some ambiguity in the literature concerning **2d**. Although classified as nondissociating,[4,6] it had been claimed[7c] that dissociation takes place at 220 °C since it reacts with maleic anhydride (MA), to give a dianhydride (**7d**); this had been interpreted[7c] to arise from cycloaddition of the dissociated **2d** with MA to give **8d** followed by a pyrolytic decarbonylation to **9d**, which takes up an additional MA molecule to give **7d**.[12]



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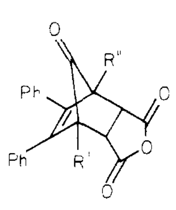

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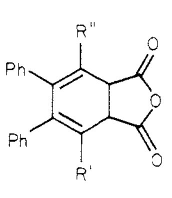

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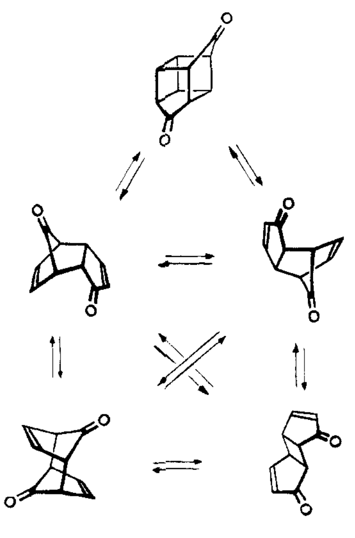
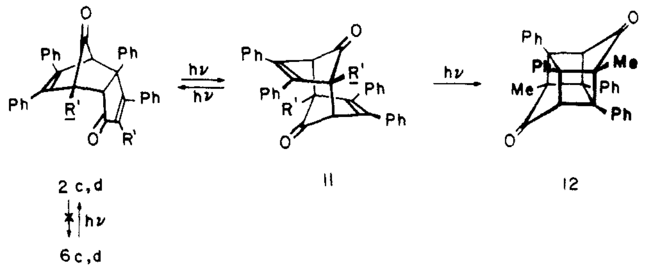
We found that the dimers **2c,d** as well as the mixed "dimers" **2e,f** never change color on being heated in solution, as dissociation to the monomers 1 would require. Furthermore, on being heated in presence of an excess of MA, the dianhydrides 7 are obtainable as follows: **2c** → **7c**; **2d** → **7d**; **2e** → **7c** + **7b**; **2f** → **7d** + **7b**.

Scheme III



Scheme IV



We suggest, however, that a different route from that initially inferred[7c] is followed, as outlined in Scheme II, where the decarbonylation of 2 to 10 is actually the first step. In absence of MA, the dihydroindenones 10 are indeed the sole pyrolysis products of the dimers 2 [with exception of **2c**, the decarbonylation product (**10c**) of which undergoes further rearrangement to 3,3,5,6-tetraphenylindanone[7e,12]]. To conclude this chapter on the thermal behavior of nondissociating dimers 2, we consider it worth mentioning that we were not able to detect any Cope [3.3] rearrangement, at least not on the NMR time scale; no further efforts were, however, made for detection of such *slow* processes, in analogy to **2a**.[9a]

We turn now to the photochemical transformations of the nondissociating, substituted dimers 2. The results obtained in the investigation of the parent dimer (**2a**)[9] have led to the formulation of a scheme of transformation modes of *endo*-cyclopentadienone dimers (Scheme III),[1b] each of which had been realized experimentally. Excluding the intramolecular [$_\pi 2 + {}_\pi 2$] cycloaddition, all rearrangements consist of cleavage of the weak, doubly allylic, C_6–C_7 bond and appropriate bond formation by thermal [3,3] or photochemical [1,3] shifts.

It was soon realized[3] that the substituted, nondissociating dimers **2c,d** are not as diverse in their photochemical behavior. Thus, direct irradiation of **2c** or **2d** (at $\lambda > 300$ nm) gave only the 1,3-rearranged diketones **11c** or **11d**, respectively (Scheme IV). The extremely low solubility of these products precluded reliable quantitative monitoring at low conversion. Only the quantum yields of disapperances of **2c** were therefore measured and were found to be ϕ 0.01 (284 nm) and 0.001 (311 nm). The process could be quenched by oxygen or 1,3-cyclohexadiene and sensitized by thioxanthen-9-one. Unexpectedly, the excitation of **2c** or **2d** does not lead to the cage compounds 6 but rather to the reverse transformation; i.e., photolytic opening of **6c,d** to the corresponding dimers 2 occurs

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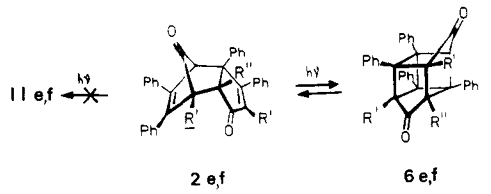
[10] K. N. Houk and D. J. Northington, *Tetrahedron Lett.*, 303 (1972).

[11] B. Fuchs, B. Pazhenchevsky, and M. Pasternak, *Tetrahedron Lett.*, 3051 (1972).

[12] B. Fuchs, *J. Chem. Soc.*, 68 (1968). The sequence 3c $\xrightarrow{MA}$ 8c → 9c $\xrightarrow{MA}$ 7c was actually described there.

Scheme V



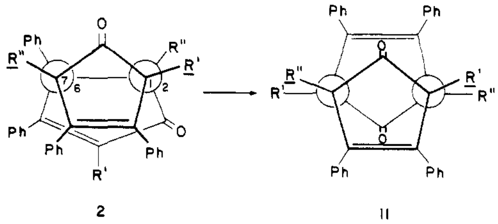
(Scheme IV, left). Similarly, the centrosymmetric β,γ-unsaturated ketones **11c,d**, when irradiated in suspension, return to the dimers **2c,d**. However, in case of **11d** an interesting accompanying photoproduct was isolated (in 7% yield) and unequivocally proven to have the centrosymmetric cage structure **12**.[13] This is taken to be a rare example of a photochemically allowed ($_\pi2_s + {}_\pi2_s + {}_\sigma2_s + {}_\sigma2_s$), eight-centered, pericyclic reaction[14] of **11d** in which the two five-membered rings undergo a glide motion, one with respect to the other, while good orbital overlap between the bonding centers is maintained.

The mixed "dimers" **2e,f** were similarly subjected to irradiation ($\lambda > 300$ nm), but here we were actually surprised when only the dissymmetric cage compounds **6e,f** were isolated (Scheme V). It is really difficult to provide a straightforward rationale for this peculiar behavior of nondissociaing dimers, i.e., the exclusive formation of **6e,f** by irradiation of **2e,f** in contrast to the complete absence of **6** in the photolysis of **2b,c**, and the other way around with **11**. Although we do not have, at this stage, the photophysical details of the above mentioned processes, we feel that it is not the difference in the reactivity of the electronically excited state that causes the different photochemical outcome for **2e,f** vs. **2c,d** but rather the steric effects brought about by the different substitution pattern. We have elaborated recently[1b] on the profound influence of substitution and hence steric effects on the thermal and photochemical behavior of cyclopentadienones and their dimers. We may now attempt to rationalize the apparently divergent behavior of the just-described nondissociating dimers by putting it in proper perspective.[1]

It has been shown[1a,11] that the dissociating dimers, i.e., those substituted in positions 1, 2, 6, and 7 (e.g., **2b**), do *not* undergo the photochemical 1,3-rearrangement to type **11** products, in contrast to the nondissociating dimers (**2c,d**) but in analogy with the "mixed" ones (**2e,f**) (vide supra). Furthermore, no thermal [3,3] Cope rearrangement could be detected by NMR in any of the above-mentioned systems, while it was seen to occur (on the NMR time scale) in the dimer of a cyclopentadienone (**1**) where the 3,4-positions are condensed into a phenanthrene system, i.e., R,R = *o,o'*-biphenylene.[15]

We take these phenomena as being the result of a subtle interplay of electronic and steric effects with a strong preponderance of the latter. Basically, however, these effects are kinetically and/or thermodynamically *competitive*, and only on accepting this can one rationalize the above-described behavior. Thus, the fact that the tetramethyl dimer **2b** is dissociating[1,4] whereas the 1,2,6-trimethyl derivative **2f** is not compels us to conclude that substitution in position 7 is a *necessary* condition for a dimer in this series to be thermally dissociating,[1] as well as for it to under a rapid Cope rearrangement.[15] Photochemically, furthermore, assuming that the first step in any rearrangement of **2** involving σ bond dissociation would be the cleavage of the weakest doubly allylic C_6–C_7 bond, the following step leading to **11** should involve rotation of the biradicaloid (thermalized?) intermediate around the C_1–C_2 bond (Scheme VI), necessarily passing through a high-energy, eclipsed transition state. It appears that a necessary condition for the occurrence of the 1,3-rearrangement **2** → **11** (cf. Scheme IV) is the *absence* of substitution in position 2, otherwise preventing the rearrangement and allowing an alternative process, viz., the internal cycloaddition (**2** → **6**), to occur.

Scheme VI



Finally, it should be noted that irradiation of the dimers **2c–f** at higher energy (λ 250–300 nm) brings about some rearrangement but mainly decarbonylation to the corresponding inden-2-ones (**10c–f**), which can be isolated (in contrast to the pyrolytic decarbonylations discussed above).

We may now conclude by saying that we hope to have succeeded in throwing light on the many and subtle electronic and steric factors which affect the chemical and photochemical behavior of cyclopentadienone dimers with all its fascinating multiformity.[1] The understanding of this behavior will hopefully be completed soon by the results of photophysical probing into their excited states.

Experimental Section

Melting points are uncorrected. IR spectra were taken in KBr pellets unless otherwise specified. UV spectra were taken on a Cary-17 spectrophotometer in 1,4-dioxane, unless otherwise specified. NMR spectra were measured on JEOL JNM-C-60 HL and Varian HA-100 spectrometers in $CDCl_3$ solutions with Me_4Si as an internal standard, unless otherwise specified. Mass spectra were measured on a Du Pont 21-491B mass spectrometer.

Irradiations on a preparative scale were performed in Rayonet photoreactors using lamps with emitting bands at 254, 300, or 350 nm. Quartz or Pyrex vessels were used according to the wavelength range needed. Solutions were swept prior to irradiations with oxygen-free nitrogen or argon. Irradiations on an analytical scale for quantum yield determinations were performed on a JASCO CRM-FA Spectro-Irradiator equipped with an electronic integrator. The latter was periodically calibrated by potassium ferrioxalate actinometry.

Cyclopentadienone Dimers 2. The dimers **2c** and **2d** were prepared according to published procedures.[6,7] For the sake of comparison we present here their physical data, including those that have not been reported previously.

2c:[7a,b] mp 206 °C; ν_{max} 1690, 1780 (C=O); λ_{max} 233 nm (ϵ 14000), 287 (20000); δ 3.1 (d, 1), 3.8 (dd, 1), 4.4 (d, 1), ~7 (m, 21); m/e 464 (M^+), 232 ($M/2^+$).

2d:[7c] mp 226 °C; ν_{max} 1690, 1775; δ 1.32 (s, 3), 2.20 (s, 3), 2.75 (s, 1), 4.38 (s, 1), ~7 (m, 20); m/e 492 (M^+), 246 ($M/2^+$).

A solution of the hydroxy ketone **3c**[6] (5 g), the dissociating dimer **2b**[1a] (5.2 g), and a catalytic amount of *p*-toluenesulfonic acid in toluene (150 mL) was refluxed for 2 h with the use of a Dean–Stark water separator. The solution was evaporated to dryness and the residue crystallized from petroleum ether/ethyl acetate to give a single product (7.5 g, 76%), which was assigned the structure **2e** on the basis of the following and chemical data: mp 215–216 °C ν_{max} 1690, 1775 (C=O); λ_{max} 222 nm (ϵ 32300), 281 (28100); δ 0.8 (s, 3), 2.0 (s, 3), 3.25 (d, 1), 4.25 (d, 1), ~7 (m, 20); m/e 492 (M^+), 260 ($M - 232^+$), 232 ($M - 260^+$). Anal. Calcd for $C_{36}H_{28}O_2$: C, 87.80; H, 5.69. Found: C, 87.21; H, 5.75.

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[13] B. Fuchs and M. Pasternak, *J. Am. Chem. Soc.*, **100**, 6225 (1978).

[14] R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 8, 781 (1969).

[15] (a) B. Fuchs and M. Pasternak, and G. Scharf, *J. Chem. Soc., Chem. Commun.*, 53 (1976); (b) B. Fuchs and M. Pasternak, *Tetrahedron*, in press.

Similar treatment of the homologous hydroxy ketone **3d** gave also only one product (68%) identified as a "mixed dimer" (**2f**): mp 194–195 °C; ν_{max} 1690, 1780 (C=O); λ_{max} 218 nm (ϵ 31 200), 276 (26 700); δ 0.7 (s, 3), 1.17 (s, 3), 2.18 (s, 3), 4.38 (s, 1), ~7 (m, 20); *m/e* 506 (M^+), 260 ($M - 246^+$), 246 ($M - 260^+$). Anal. Calcd for $C_{37}H_{30}O_2$: C, 87.75; H, 5.93. Found: C, 87.13; H, 5.95.

Similar dehydration of an equimolar mixture of the hydroxy ketones **3c** and **3d** gave, however, only a mixture of the dimers **2c** and **2d**, and no "mixed dimer" **2g** could be isolated.

Reaction between the dimers 2e,f and maleic anhydride (MA) was carried out by heating 0.001 mol of dimer with 0.005 mol of MA in refluxing xylene (50 mL) for 48 h. A mixture of the dianhydrides **7b,c** (76%) was obtained from **2e** and **7b,d** (90%) from **2f**.

Experimental Procedures for Scheme I. Reduction of dimers **2** was carried out by using 0.026 mol of $NaBH_4$ on 0.002 mol of dimer dissolved in a 2:1 mixture of ethanol–1,4-dioxane. After 6 h at room temperature, the reaction mixture was acidified with 10% HCl, and the solution was concentrated by flash evaporation and extracted with chloroform. The organic solution was washed with saturated sodium bicarbonate solution and water, dried, and evaporated. The products were as follows: **2c** → **4′** (diol 60%); mp 193–194 °C; ν_{max} 3500 (3380) (OH); δ 3.7–5.7 (m, 7), 6.5 (s, 1), ~7 (m, 20); *m/e* 468 (M^+), 234 ($M/2^+$). Anal. Calcd for $C_{34}H_{28}O_2$: C, 87.18; H, 5.98. Found: C, 86.85; H, 6.02.

2d → **4d** (hydroxy ketone 42%): mp 224–225 °C; ν_{max} 3400 (OH), 1670 (C=O); δ 1.30 (s, 3), 1.78 (s, 3), 1.93 (d, 1), 3.21 (s, 1), 4.07 (br d, 1), 4.24 (d, 1), ~7 (m, 20); *m/e* 494 (M^+). Anal. Calcd for $C_{36}H_{30}O_2$: C, 87.45; H, 6.07. Found: C, 87.26; H, 6.11.

2e → **4e** (hydroxy ketone 85%): mp 207 °C; ν_{max} 3430 (OH), 1670 (C=O); λ_{max} 225 nm (ϵ 35 900), 280 (27 400); δ ($CDCl_3/D_2O$) 1.40 (s, 3), 1.88 (s, 3), 3.15 (s, 1), 4.3–4.6 (m, 2); *m/e* 494 (M^+).

2f → **4f** (hydroxy ketone 90%): mp 222 °C; ν_{max} 3460 (OH), 1670 (C=O); λ_{max} 223 nm (ϵ 31 200), 276 (24 100); δ ($CDCl_3/D_2O$) 1.20 (br s, 6), 1.95 (s, 3), 4.15 (m, 1), 4.38 (d, 1); *m/e* 508 (M^+).

Irradiation Induced Closure of the Above Reduction Products. A 1,4-dioxane solution (0.01 M) of hydroxy ketone (or diol) was irradiated at 250 nm until most of the starting material has reacted. The mixture was evaporated to dryness, and the residue was crystallized, usually from ethanol.

4′ → **5′** (cage diol 80%): mp 292 °C; ν_{max} 3520 (3300) (OH); δ 3.7 (m, 2 H), 4.1 (m, 2 H), 4.4 (m, 2 H), 4.9 (m, 2 H), ~7 (m, 20); *m/e* 468. Anal. Calcd for $C_{34}H_{28}O_2$: C, 87.15; H, 6.02. Found: C, 86.47; H, 6.04.

4d → **5d** (cage hydroxy ketone 90%): mp 162 °C; ν_{max} 3490 (3300) (OH), 1750 (C=O); δ 0.72 (s, 3), 1.42 (s, 3), 2.05 (s, 1), 3.10 (s, 1), 4.18 (s, 1), 4.54 (s, 1), ~7 (m, 20); *m/e* 494 (M^+).

4e → **5e** (cage hydroxy ketone 92%): mp 171 °C; ν_{max} 3440 (OH), 1750 (C=O); λ_{max} 225 nm (e 21 300); δ ($CDCl_3/D_2O$) 1.1 (s, 3), 1.47 (s, 3), 2.57 (d, 1), 4.15 (s, 1), 5.05 (s, 1) ~7 (m, 20); *m/e* 494 (M^+).

4f → **5f** (cage hydroxy ketone 88%): mp 239 °C; ν_{max} 3480 (OH), 1750 (CO); λ_{max} 223 nm (ϵ 34 200); δ ($CDCl_3/D_2O$) 0.65 (s, 3), 1.05 (s, 3), 1.67 (s, 3), 4.25 (s, 1), 4.6 (s, 1), ~7 (m, 20); *m/e* 508 (M^+).

Jones Oxidation of the Cage Alcohols to the Diketones 6. To a solution of hydroxy derivative (10^{-3} mol) in acetone (15 mL) was gradually added 2.5 mL of Jones reagent (0.7 g of CrO_3 + 0.6 mL of H_2SO_4(concn) + 5 mL of H_2O) at room temperature. After an additional hour, the reaction mixture was poured into water (25 mL) and extracted with chloroform. The organic fraction was dried and evaporated, and the residue was recrystallized, generally from ether/petroleum ether.

5′ → **6c** (cage diketone 52%): mp 117 °C; ν_{max} 1755 (C=O); δ 3.07 (s, 2), 3.92 (s, 2), ~7 (m, 20); *m/e* 464 (M^+). Anal. Calcd for $C_{34}H_{24}O_2$: C, 87.93; H, 5.17. Found: C, 87.80; H, 5.22.

5d → **6d** (cage diketone 43%): mp 225 °C; ν_{max} 1760 (C=O); λ_{max} 225 nm (ϵ 19 000); δ 0.64 (s, 3), 1.52 (s, 3), 2.96 (s, 1), 3.96 (s, 1), ~7 (m, 20); *m/e* 492 (M^+). Anal. Calcd for $C_{36}H_{28}O_2$: C, 87.80; H, 5.69. Found: C, 87.49; H, 5.68.

5e → **6e** (cage diketone 80%): mp 265 °C; ν_{max} 1750 (C=O); λ_{max} 225 nm (ϵ 29 000); δ 0.90 (s, 3), 1.60 (s, 3), 2.64 (d, 1), 3.85 (d, 1), ~7 (m, 20); *m/e* 492 (M^+). Anal. Calcd for $C_{36}H_{28}O_2$: C, 87.80; H, 5.69. Found: C, 87.21; H, 5.75.

5f → **6f** (cage diketone 80%): mp 228 °C; ν_{max} 1750 (C=O); λ_{max} 225 nm (ϵ 35 400); δ 0.40 (s, 3), 0.70 (s, 3), 1.72 (s, 3), 4.05 (s, 1), ~7 (m, 20); *m/e* 506 (M^+). Anal. Calcd for $C_{37}H_{30}O_2$: C, 87.75; H, 5.93. Found: C, 87.45; H, 5.99.

Irradiations of the Dimers 2 at $\lambda > 300$ nm. A 1,4-dioxane solution (0.05 M) of the dimer in a Pyrex tube was swept with nitrogen or argon for ca. 15 min and irradiated with 350-nm lamps for 24 h. The precipitated product was collected and the mother liquor worked up as usual.

Irradiation of **2c** gave the centrosymmetric, unsaturated diketone **11c** in 36% yield along with 1% of unidentified byproducts. **11c**: mp 245 °C; ν_{max} 1770 (C=O); λ_{max} 238 nm (ϵ 4400), 280 (24 000); *m/e* 464 (M^+), 232 ($M/2^+$). Anal. Calcd for $C_{34}H_{24}O_2$: C, 87.93; H, 5.17. Found: C, 88.15; H, 5.10.

Prolonged irradiation brings about an increase in the yield of **11c** (up to 45%) but also of the mixture of the byproducts (ca. 40%).

Quenching experiments using *cis*- and *trans*-piperylene (1.5 M) under the same conditions (350 nm) caused a decrease in the yield of **11c** to 5%, similarly, oxygen-saturated solutions inhibited the formation of **11c** (11%).

Sensitization with thioxanthone (2×10^{-4} M) by using the 350-nm lamps and a cutoff filter below 380 nm (2 g/L of $NaNO_2$ combined with a cutoff filter below 340 nm;[9] **2c** absorbs about 20% of the light) gave after 24 h **11c** in 29% yield. Under the same conditions **2c** itself absorbed all the light, and 28% **11c** was obtained.

Analytical direct irradiation (using the JASCO irradiator and UV monitoring) at *low conversions* gave two isosbestic points at 268 and 318 nm and quantum yields of dimer (**2c**) disappearance of 0.001 at 311 nm and 0.01 at 284 nm.

Irradiation of **2d** (350-nm lamps) gave only the unsaturated diketones **11d**: 85% yield; mp 270 °C; ν_{max} 1760 (C=O); λ_{max} 238 nm (ϵ 27 000), 272 (23 000); *m/e* 492 (M^+), 246 ($M/2^+$). Anal. Calcd for $C_{36}H_{28}O_2$: C, 87.80; H, 5.69. Found: C, 87.98; H, 5.81.

The process is suppressed entirely by oxygen saturation of the solution.

Irradiation of **2e** (350 nm) gave a photostationary mixture containing the cage product **6e** in 62% of yield. Similarly, **2f** gave **6f** in 70% yield (vide supra).

Irradiation of the Centrosymmetrical Unsaturated Diketones. Compounds **11c,d** suspended in dioxane (350-nm lamps) slowly gave back the dimers **2c** and **2d**, respectively. In the case of **11d**, however, an additional cage product, **12**, was obtained in 8% yield: mp 305 °C; ν_{max} 1750 (C=O); δ 0.92 (s, 6), 3.97 (s, 2), ~7 (m, 20); *m/e* 492 (M^+). Anal. Calcd for $C_{36}H_{28}O_2$: C, 87.80; H, 5.69. Found: C, 87.31; H, 5.79. The structure proof for **12** was described elsewhere.[13]

Irradiation ($\lambda > 300$ nm) of all cage compounds 6c–f leads back to the respective dimers **2c–f**. In case of **6c,d**, the insoluble, rearranged diketones **11c,d** are also formed in varying yields. In the case of **6e,f**, photostationary mixtures with **2e,f** are obtained, respectively.

Photochemical decarbonylation of 2c–f was accomplished by irradiating (254-nm lamps) deareated dioxane solutions in quartz tubes, whereby the 8,9-dihydroindenones (**10**) were obtained accompanied by small, variable amounts of byproducts.

In case of **2c,d**, the known 8,9-dihydroindenones **10c,d** were isolated.[7e,f]

In case of **2e,f**, the decarbonylation was over after 14 h (>90%), and the products were as follows, after crystallization from ether/pentane, respectively. **10e**: mp 230 °C; ν_{max} 1710 (C=O); λ_{max} 238 nm (ϵ 17 200); δ 0.75 (s, 3), 2.02 (s, 3), 5.55 (s, 1), 6.00 (s, 1), ~7 (m, 20); *m/e* 464 (M^+). **10f**: mp 190 °C; ν_{max} 1710 (C=O); λ_{max} (MeOH) 220 nm (ϵ 31 500); δ 0.72 (s, 3), 1.62 (s, 3), 2.05 (s, 3), 5.8 (s, 1), ~7 (m, 20). The latter two products, **10e,f**, are also obtained from the thermal decarbonylation of **2e,f** in refluxing bromobenzene.

Registry No. 2b, 35228-93-4; **2c**, 33494-01-8; **2d**, 38932-11-5; **2e**, 76807-41-5; **2f**, 76807-42-6; **3c**, 5587-78-0; **3d**, 14224-74-9; **4′**, 38932-14-8; **4d**, 38932-15-9; **4e**, 76807-43-7; **4f**, 76807-44-8; **5′**, 39025-05-3; **5d**, 39025-06-4; **5e**, 76807-45-9; **5f**, 76807-46-0; **6c**, 38932-12-6; **6d**, 38932-13-7; **6e**, 76807-47-1; **6f**, 76807-48-2; **7b**, 76807-49-3; **7c**, 72257-54-6; **7d**, 76831-56-6; **10e**, 76807-50-6; **10f**, 76807-51-7; **11c**, 33422-10-5; **11d**, 39025-10-0; **12**, 39025-07-5; maleic anhydride, 108-31-6.