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PHOTOCHEMICAL STUDIES[1]

IRRADIATION INDUCED TRANSFORMATIONS OF REVERSIBLY DISSOCIATING CYCLOPENTADIENONE-DIMERS AND THEIR MONOMERS

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Abstract—Irradiation of dissociating cyclopentadienone-dimers (**2 b, c, e**) results in formation of two types of cage-products (**5** and **8**) in very low quantum yields and good, but wavelength and phase dependent chemical yields. *Both* processes are intramolecular; for **2b** this was shown using isotopic labeling and mass-spectrometric techniques. Sensitization and quenching experiments indicate that triplet states are involved. The mechanistic pathways are discussed. The cyclopentadienones(**1 b, c, e**) were isolated for the first time and irradiation of **1b** in the solid gave exclusively the symmetric cage (**8b**).

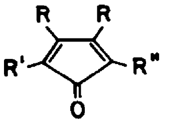
We wish to elaborate in this paper our findings on the photochemical behaviour of certain tetrasubstituted cyclopentadienones and, in particular of their reversibly dissociating dimers. This is a subgroup of the large and versatile class of cyclopentadienones (**1**) and derivatives,[3] which hold our attention in recent years.[1,2,4–6]

After having dealt with the unsubstituted, non-dissociating dimer (**2a**),[4] which undergoes all theoretically derived transformations,[1] be they thermal or photochemical ones, we were fascinated by this structural and mechanistic multiformity and turned our attention to substituted derivatives of **2**. In this framework we have investigated a number of non-dissociating dimers, e.g. **2**(R = Ph, R′ = R″ = H),[6] while this report is concerned with the reversibly dimerising cyclopentadienones (**1 b-e**), bearing aryl substituents in the 3 and 4 positions and alkyl substituents in the 2 and 5 positions, and the corresponding dimers. Special attention was paid to **2b** and **1b**.

RESULTS AND DISCUSSION

The dimers (**2b, c** and **d**) were prepared following known literature reports[7,8] and the unknown compound (**2e**) was synthesized along analogous procedures. While the gross dimeric structure of these compounds had been put forward,[3,7] and the IR and UV spectra are diagnostic in this respect, we were soon confronted with the problem of intimate structure, viz: configuration of the tricyclic skeleton as well as the relative positions of the substituents. The latter were assigned following a straightforward correlation of ^{1}H NMR chemical shifts of the Me substituents as described in Table 1, which includes for the sake of comparison also some non-dissociating dimers.[2,6] An examination of molecular models readily enabled us to rationalize the observed data, e.g. by deshielding of the vinylic-C_4–Me protons or the strong shielding of the *exo*-C_2–Me protons by the juxtaposed bridge-CO (*cf* **2**).

This brings us, inevitably to the problem of configuration. The latter is depicted as *endo* in **2** as had been inferred[9] but never proven until recently.[2b,5b,10] In our hands this worked the following way[2,5b] (Scheme 1): the dimers (**2b** and **2c**) were reduced by $NaBH_4$ to the hydroxy-ketones (**3b** and **3c**) in 94 and 70% yield, respectively.[11] These two were irradiated directly in 1,4-dioxan ($\lambda > 300$ nm) whereby intramolecular 2 + 2-cycloaddition (well established in such systems, as discussed in Refs. 1 and 4 and below) leads to the cage compounds (**4b** and **4c**) in 92 and 83% yields, respectively. Finally, the hydroxyketones (**4b** and **4c**) were oxidized by Jones' reagent to the cage-diketones (**5b** and **5c**) in 91 and 61% yields, respectively, the structures of which were assigned by conventional spectroscopic analysis *vide infra* as well as by a most recently developed mass-spectrometric analysis.[12] Alternatively, **2b** was also reduced by $LiAlH_4$ *or* LAH to the diol **6** (80%) which underwent photo-induced closure (94%) to **7** which, in its turn, was oxidized to give the identical cage diketone **5b** (85%).[11] The *endo* configuration of the dimers **2b** and **2c** was thus established and since a similar sequence



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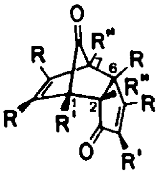

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	a	b	c	d	e
R	H	Ph	Ph	Ph	p-Tol
R'	H	Me	Et	Pr	Me
R"	H	Me	Me	Me	Me

Scheme 1

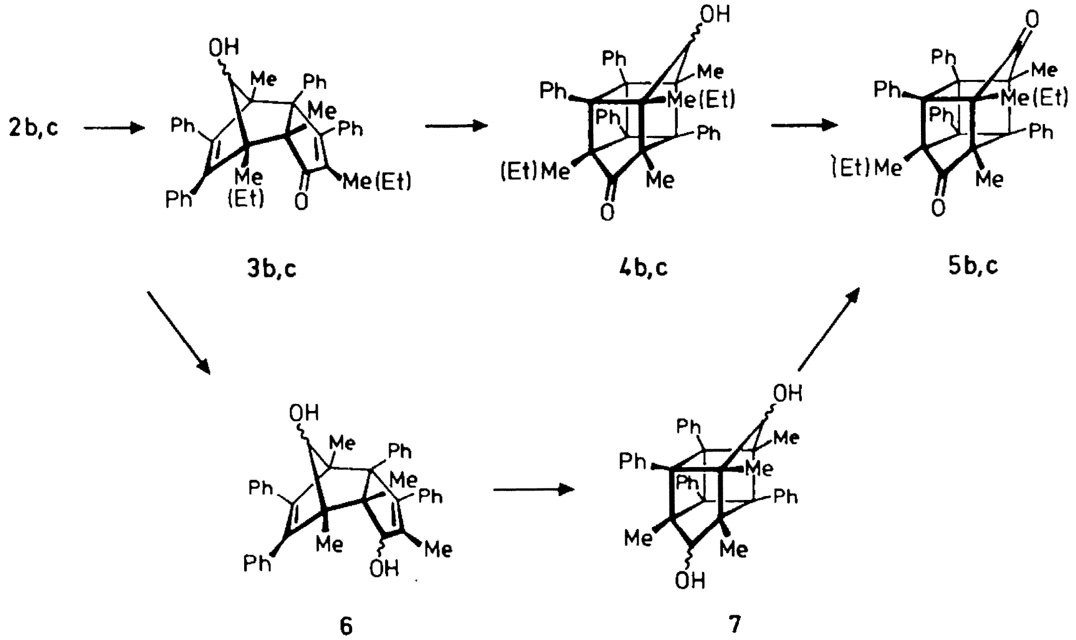
Table 1. ^{1}H NMR chemical shifts of methyl protons in **2**[a]

b	2x[c]	δ_{Me}	2y[c]	δ_{Me}	2z[c]	δ_{Me}	2b	δ_{Me}	2c	δ_{Me}	2d	δ_{Me}	2e	δ_{Me}
R_4'	Me	2.00	Me	2.20	Me	2.18	Me	2.25	Et		Pr		Me	2.27
R_2''	Me	0.80	H		Me	0.70	Me	0.58	Me	0.60	Me	0.60	Me	0.60
R_1'	H		Me	1.34	Me	1.17	Me	1.25	Et		Pr		Me	1.25
R_7''	H		H		H		Me	1.65	Me	1.60	Me	1.65	Me	1.60
R	Ph		Ph		Ph		Ph		Ph		Ph		p-Tol	

a) Measured at 60 MHz in $CDCl_3$ solutions with TMS as internal standard, δ in ppm. Only the methyls bound directly to the cyclopentadienone ring are given.

b) The substituents are listed according to the numbering in formula 2.

c) The first three compounds, arbitrarily named 2x, y and z are taken from ref. 6.

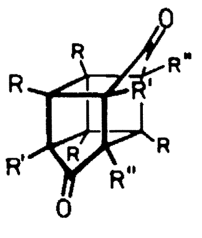


has also been carried out for a number of non-dissociating dimers[2b,6,10] (*cf* also Table 1) indicating full consistency in the investigated dimers, one may conclude that the *endo* configuration largely prevails in the whole series.[11]

We turn now to the photochemistry of the dimers **2b,c** and **e**. Direct irradiation ($\lambda > 290$ nm) of **2b**, provided two products in temperature-, phase- and wavelength dependent yields *vide infra*. Both, according to their physical properties (Table 2) were devoid of any double bonds conjugated to either the phenyl- or the CO groups and the latter appeared as strained, bridge-CO's. This indicated that we deal with cage compounds which can have only three possible structures: **5b**, **8b** and **9b**. The dissymetric structure **5b** (point symmetry C_2) was readily assigned to one of the products by virtue of its ^{1}H NMR spectrum in which two Me-proton signals occur, one for each equivalent pair of Me's. This assignment was, of course, directly and conclusively confirmed by the just described reaction sequence (Scheme 1), the end product of which **5b** was identical with the above photoproduct.

The second photoproduct turned out to be a symmetric cage diketone, judging from the fact that all 12 Me protons are isochronous, but proof for one of the two possible structures **8b** (point symmetry C_{2v}) and **9b** (D_{2h}) had to be put forward. Attempts to provide such proof by chemical means failed, due to the symmetric photoproduct's extremely low solubility in all solvents (which, incidently rendered impossible crystal growing for X-ray diffraction analysis) and exceeding inertness towards chemical attack, e.g. by nucleophilic reagents. The only reaction that we succeeded in performing was its slow reduction by $LiAlH_4$ *or* LAH in boiling tetrahydrofuran to a diol **10** which stubbornly resisted derivatization by a variety of acyl chlorides, including phosgene. Dehydration was achieved only slowly and under drastic, acid catalysed (P_2O_5/boiling benzene) conditions, to give a rearranged, unsymmetric ether.

Eventually this problem has been solved by a specially designed, unconventional approach combining mass-spectrometry with isotopic labeling and symmetry considerations,[12] and structure **8b** was the winner. Specifically, the perdeuterated dimer (**2b**-$^2H_{32}$) was heated in solution together with an equimolar quantity of **2b** to give a statistical mixture of non-deuterated-(**2b**), half-deuterated-(**2b**-$^2H_{16}$) and perdeuterated dimer (**2b**-$^2H_{32}$) in the ratio of 1:2:1, respectively (eqn 1). Irradiation of this mixture gave the symmetric cage (**8b**) in the same isotopic ratio and now a mass-spectrometric measurement showed $(M/2)^+$ ions of *only m/e* 260 and 276, corresponding to the monomeric halves **1b** and **1b**-$^2H_{16}$. This proved that we deal indeed with structure **8b** (where only one mode of fragmentation into two halves is possible) and not with **9b** (for which two statistically equally probable modes of halving are conceivable, in which case the *half-labeled* cage **9b**-$^2H_{16}$ would have to split into ions 260, 266, 270 and 276).[12]



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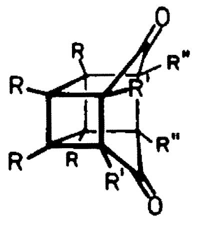

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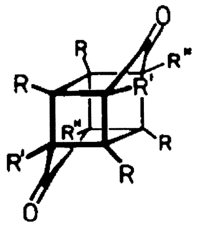

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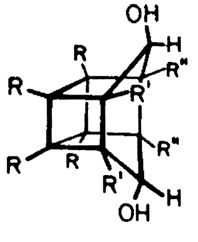

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Table 2. Spectral characteristics of the dimers (**2**)[a] and their photoproducts.

	(2)[a]		5			8		
	b	e	b	c	e	b	c	e
ν_{CO}^{KBr}, cm^{-1}	1765 1690	1760 1680	1750	1745	1750	1750	1750	1750
$\lambda_{max}^{dioxane}$, nm(ε)	223(34,600) 280(24,500)	218(28,800) 265(18,600) 290(18,300)	220(23,200)	236(13,000)	227(21,400)	220(24,500)	237(15,000)	225(19,000)
$\delta_{CH_3}^{CDCl_3/TMS}$			0.5(6H) 1.85(6H)	0.55(3H) 1.7(3H)	0.45(6H) 1.75(6H)	1.2 (12H)	0.95(6H)	1.35(12H)
m/e (%)	520(<1) 260(100)	576(<1) 258(100)	520(5) 260(51)	548(4) 274(42)	576(5) 288(48)	520(4) 260(100)	548(3) 274(100)	576(4) 288(100)

a) The data for 2c are largely similar to those of 2b.[7]

b) The NMR data of the dimers are given in Table 1.

c) Taken in hot pyridine-d_5.

With the structural problem solved, we turned to examine the scope of this photochemical behaviour. The closely related dimer **2e** yielded, on irradiation two similar photoproducts: a dissymmetric (C_2) cage **5e** and a symmetric (C_{2v}) one **8e** (Table 2). However, when more substantial changes were made, such as increasing the bulkiness of the α-substituents, the photorearrangements became more sluggish until they stopped altogether. Thus, both dimers **2c** and **2d** fail to photoreact at room temperature (*ca* 30°) or higher and only **2c** does photorearrange at lower temperature (*ca* 8°) to give, albeit in lesser yield and efficiency, *only* the symmetric cage **8c** (Table 2); the dissymetric one **5c** became though available by the roundabout sequence (Scheme 1). Furthermore, it was found that all the available dissymmetric cages (**5b,c,e**) open up on irradiation ($\lambda > 300$ nm) back to the dimers (**2**), whereas the symmetric cages (**8**) do not (although they are very slowly photo-decomposing to an ill-defined mixture of products). Interestingly, while the dissymetric cages (**5**) are thermally stable the symmetric ones (**8**) undergo at or above *ca* 110° a

$$(\underline{2b}) + (\underline{2b}\text{-}{}^2H_{32}) \xrightarrow{\Delta} 2(\underline{1b}) + 2(\underline{1b}\text{-}{}^2H_{16}) \rightleftarrows \tfrac{1}{2}(\underline{2b}) + (\underline{2b}\text{-}{}^2H_{16}) + \tfrac{1}{2}(\underline{2b}\text{-}{}^2H_{32}) \qquad (1)$$

$$\underline{8b},c,e \overset{h\nu}{\underset{\Delta}{\leftrightarrows}} \underline{2b},c,e \overset{h\nu}{\underset{h\nu}{\rightleftarrows}} \underline{5b},e \qquad (2)$$

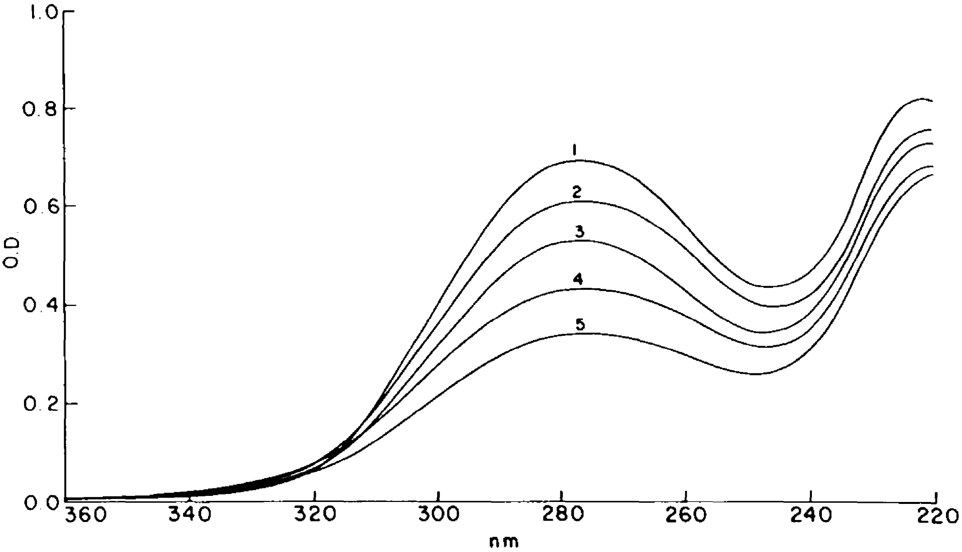


Fig. 1. Irradiation and disappearance of **2b** at 265 nm (*ca* 10 nm bandwith) in 1,4-dioxan, as monitored by UV spectrophotometry. The absorbed energy: 2, 5.64×10^{-5}; 3, 1.5×10^{-4}; 4, 3.76×10^{-3}; 5, 1.32×10^{-3} einsteins.

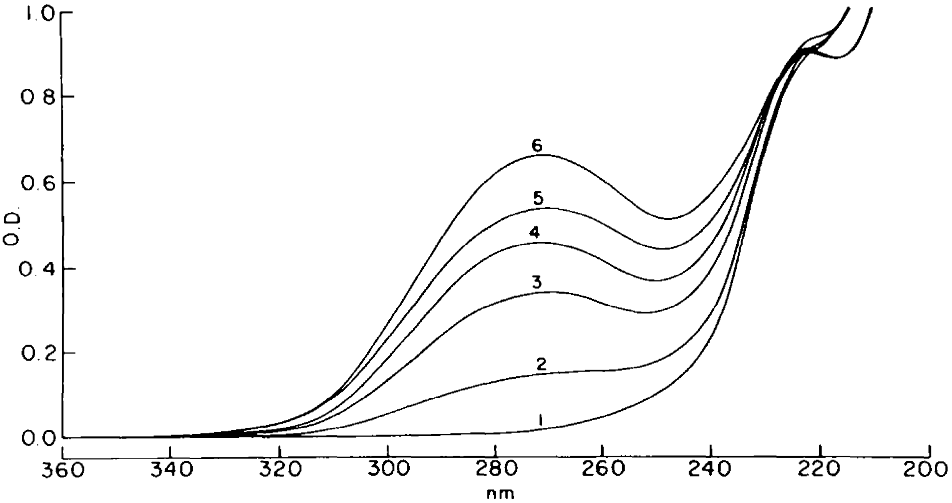


Fig. 2. Irradiation of **5b** at 338 nm (*ca* 10 nm bandwidth) in iso-octane, as monitored by UV spectrophotometry. The absorbed energy: 2, 1.41×10^{-5}; 3, 4.23×10^{-5}; 4, 7.05×10^{-5}; 5, 9.88×10^{-5}; 6, 2.82×10^{-4} einsteins.

thermal reversion to the dimers (**2**). All these transformations are summarized in eqn (2); *cf* also Figs. 1 and 2.

The next step was to probe into the excited states involved in these photo-transformations and this was done mainly on **2b** and its products. It should be said at this point, that our quantitative work was seriously hampered by the fact that we dealt with high-molecular-weight, high-melting products, of very low solubility and very similar UV spectra. This made quantum-yields of product formation at low conversion virtually impossible to determine, allowing only rough evaluation at high conversion, using low precision product isolation techniques. The results of irradiation of **2b** in various conditions, viz. different wavelengths (including sensitization and quenching experiments), solvents and temperatures are tabulated in Table 3. Quantum yields for disappearance of **2b** at various wavelengths, as evaluated by UV spectroscopy in 1,4-dioxane are: ϕ_{284} 17×10^{-3}, ϕ_{311} 2×10^{-3}, ϕ_{338} 3×10^{-4}, ϕ_{365} 1×10^{-4} (see Fig. 1).

It is evident that no quantitative photochemical study could be effectively conducted under the circumstances, with the peculiar systems in our hands. One could, however, draw a number of qualitative conclusions from the data in Table 3, backed up by some additional results. The latter can be summarized, as follows: Low-temperature ($\leq -20°$) irradiation of **2b** in acetonitrile gave *no photoproducts* of any kind. The dissymmetric cage (**5b**) undergoes also xanthone-sensitized photolysis (at λ 350 nm) to give **8b** via the dimer (**2b**). Moreover, the direct-irradiation-induced opening of **5b** back to **2b** (eqn (2) and Fig. 2) is wavelength dependent, diminishing with increasing conversion and at $\lambda \geq 350$ nm. That is probably why, the yield of **5b** is significantly higher in items 2 and 3 (Table 3). As to emission, **2b**, **5b** and **8b** do not fluoresce but **2b** exhibits a strong, long-lived phosphorescence at 77 K,[13] as befits a heavily substituted cyclopentenone with a π-π^* lowest emitting triplet.[14]

Irradiation of the dimer **2b** leads, hence, to a triplet excited state which yields two photoproducts, **5b** and **8b** by two different routes, apparently. This is supported by the differential quenching and sensitization results (items 5–8) as well as by the appreciable solvent effect (items 9–12).

At this point, it is well worth considering a mechanistic problem which kept puzzling us all along this work.[5] This concerns the very formation of the symmetric cage (**8b**) in the above described photochemical process (eqn 2) and is analysed below.

In principle, the formation of a symmetric cage structure (**8**) can be envisaged either by a bimolecular combination of monomeric units (**1**) or by unimolecular rearrangement of an *exo* dimer (Scheme 2). This qualifying statement is unconditional, i.e. an

Table 3. Irradiation induced transformation of **2b** in various conditions.[a]

Item	Phase	λ^a,sens.,quen.	Irr.time,hrs.	5b	8b	% Conversion[i]
1	1,4-dioxane		94	1	48	67
2	1,4-dioxane		48	11	42	65
3	1,4-dioxane	> 340[b]	"	22	52	82
4	1,4-dioxane	320[c,d]	"	3	8	55
5	acetone	> 280[c]	"	1	12	49
6	1,4-dioxane	xanthen-9-one[b,e]	"		10	
7	1,4-dioxane	1,3-cyclohexadiene[b,f]	"	18	32	80
8	1,4-dioxane	O_2[g]	"	4	18	54
9	benzene		"	6	30	66
10	chloroform		"	11	5	75
11	ethanol		"	5	32	80
12	acetic acid		"	8	52	85
13	solid[h]		15	50	10	

a) The irradiations were performed on deoxygenated 0.01M solutions in Pyrex tubes at ca. 30°C, using a Rayonet-type photo-reactor with 32 Sylvania BLB-FT8 lamps with an emission band of ca. 60nm half-width, peaking at 350 nm, unless otherwise specified. The yields were determined gravimetrically after crystallization of 5b and 8b.

b) A cut-off filter solution was used absorbing all irradiation below 340nm[4].

c) RPR 3000 lamps were used, emitting at 300 nm.

d) Acetone was used as a filter, in a ca. 1 cm thick outer jacket.

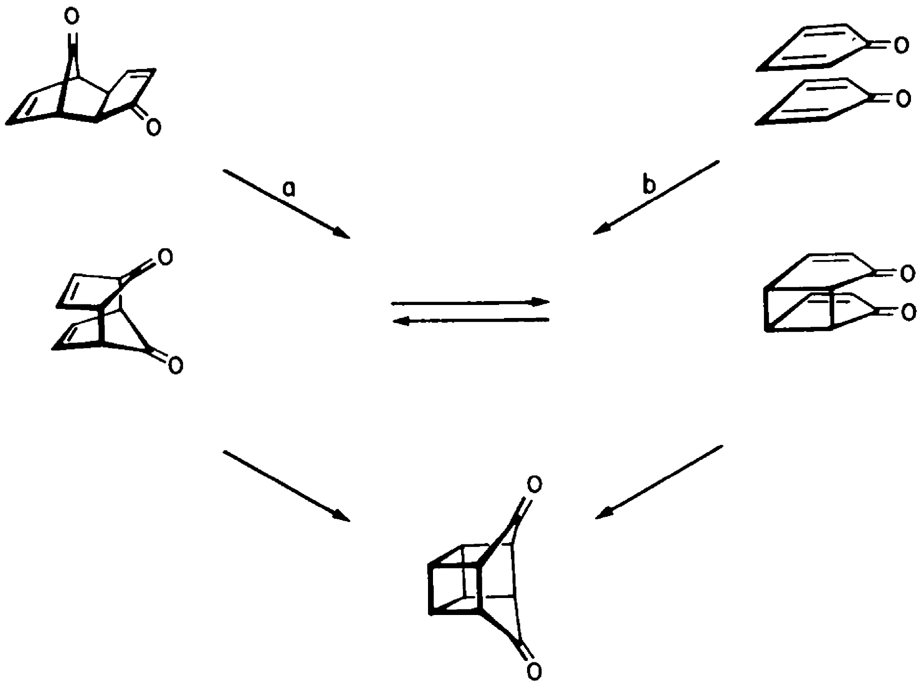
e) E_T 74 kcal/mol. Senzitizer concentration - 0.15M. The experimental conditions did not allow minor product isolation, beyond that of the virtually insoluble 8b.

f) E_T 53 kcal/mol. Quencher concentration - 1.0M. Compare with item 3.

g) Oxygen saturated solution.

h) Pure, dry and ground crystals of 2b were irradiated using a Hanovia 450 w, medium pressure Hg lamp.

i) An ill-defined mixture of by-products is also formed, as seen by TLC, but defying attempts of resolution and identification. No special efforts were, however, invested in this direction (see however discussion).



Scheme 2

endo dimer (**2**) could under no circumstances give a symmetric cage (**8**) by an *intramolecular* rearrangement process, that is without breaking *both* C_1–C_2 and C_6–C_7 bonds.[1] This point had, therefore to be settled, before making any further mechanistic inferences.

We decided to perform this task by making use of the labelled compounds which served to establish the structure of **8b**[12] as well as of the ideas underlying that approach *vide supra*. The key experiment was the irradiation of an equimolar mixture of **2b** and **2b**-$^2H_{32}$ in solution at 0°. The idea was that, if a full dissociation to the monomers is followed by a random photodimerization to the cage photoproduct (**8**), the latter should occur as a statistical mixture of **8b**, **8b**-$^2H_{16}$ and **8b**-$^2H_{32}$ in ratio 1:2:1, respectively. This would be, of course, readily detectable by mass-spectrometric techniques,[12] provided one could check and ensure the reliability of the method. To start with, two factors have to be taken into account for causing spurious scrambling: the monomer **1** ⇆ dimer **2** equilibrium in dark solution, at various temperatures and in the mass-spectrometer's inlet probe. After establishing those, the unreacted dimer and the cage products from the above irradiation were isolated (all operations performed at 0° or below) and measured (Table 4). The results are conclusive: while the dark equilibrium at 0° causes *ca* 5% scrambling in the dimer, irradiation doubles this amount indicating that a small but

Table 4. Relative abundances of the molecular ions of isotopic mixtures stemming from equimolar (**2b** + **2b** – $^2H_{32}$) = D

		m/e^a		
		520	536	552
1.	D (initial cryst. mixt.)^a	21	1	21
2.	D from 0°C dark run^b	11.5	1	12.9
3.	D from 25°C " "^{b}	3.1	1	3.1
4.	D from 100°C " "^{b}	0.5	1	0.5
5.	Recovered dimer from photo-run^c	6.0	1	7.1
6.	Symmetric cage " " "^{c}	26.0	1	32.0
7.	Dissym. cage " " "^{c}	21.0	1	24.0

a) Only the relevant fragment ions are given, normalized to the 2b - $^2H_{16}$ ion m/e 536.

b) Crystals isolated from solutions held in the dark at the given temperatures for 15 hrs.

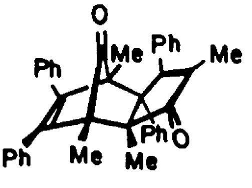
c) Crystals isolated from solutions irradiated (350 nm lamps) at 0°C for 15 hrs and worked up at the same temperature.

definite photodissociation to the monomer takes place; however, the cage products (**5b** and **8b**) show no significant scrambling within the error of the measurement. Moreover, the symmetric cage displays even a higher ratio than theoretically expected, an enhancement (probably a mass-spectrometric artifact) we can not explain, as yet. In any case, we take the above results as a clear indication that *both* cage compounds (**5b** and **8b**) are the products of photo induced *intramolecular* processes.

While for **5b**, this is a reasonable, rather inevitable conclusion, in case of **8b** this brings us back to the question: *how* does an intramolecular process lead to **8b**? The answer must be, either by rearrangement (see Schema 2a) of the *exo*-dimer (**11**)[11] in which case the latter is an elusive species, present only in small, non-isolable amounts in solution and in the solid, or from the ubiquitous *endo*-dimer (**2b**), in which case the "intramolecularity" could be accounted for by invoking an excimer in a sequence D → D* → [M*.M] → Product + 2M (D = dimer, M = monomer, [M*.M] = excimer).[2,10] We can not at this stage, provide an answer to this interesting, albeit difficult problem: even the irradiation in solid phase (item 12, Table 3)[10] is equivocal in this sense. We hope, though, that further chemical and photophysical investigation may eventually break this impasse.

To provide a complete picture on the photochemical behaviour of dissociating cyclopentadienone-dimers we should mention an additional irradiation-induced process, which takes place at lower wavelength.[2,5b,10] Thus, at 254 nm, the dimers **2b** and **2e** undergo efficient photo-decarbonylation to the corresponding dehydroindenone products (**12b** and **12e**) similar to other norbornen-7-one derivatives. This goes, apparently, via a higher, singlet excited state, involving probably the π,π^* transition of the β,γ-unsaturated CO chromophore.

Finally, a word about the processes which are *not* found to occur in **2b**, **c**, **d**, **e** in contrast to other, non-dissociating *endo*-dimers.[4,6] These are the photochemical 1,3-rearrangements to structures of type **13** and **14** and the thermal, degenerate Cope rearrangement of **2**, involving bond cleavage at C_6–C_7 and bond formation at C_4–C_9. The latter was sought by variable (high) temperature NMR techniques and could not be detected up to temperatures where complete dissociation takes place (see footnote i to Table 3).



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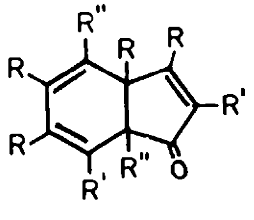

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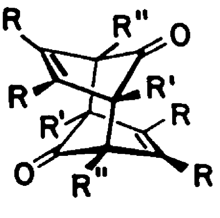

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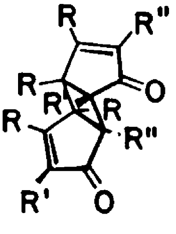

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We attribute this behaviour to a pronounced steric effect.[1] To begin with, such an effect is responsible for the dimers being dissociating or non-dissociating,[3] the heavy substitution turning the C_1–C_2 and C_6–C_7 bonds into "neopentylic" ones, i.e. relatively weak, elongated bonds, prone to cleavage to give stabilized biradical (oid) centers. Thus, once the process has started and the first, C_6–C_7 bond has cleaved as a result of thermal activation, the C_1–C_2 bond is bound to follow suit readily at the established high temperatures. As to the photochemical 1,3-rearrangements, one can easily envisage that in any such process, the C_6–C_7 cleavage *must* be followed by a rotation around the remaining C_1–C_2 bond, inevitably bringing about eclipsing between the C_1-R′ and C_2-R″ bonds (*cf* 2) in the transition state. Less expensive, alternate routes on the potential hypersurface are then bound to operate.

At this point, a certain diversion is in order. The possibility that the monomers (**1**) may be responsible for the photo-formation of the symmetric cage-compounds (**8**), had kept our sustained attention. The probing into this possibility met, however with the inherent difficulty of such cyclopentadienones (**1**) being notoriously elusive, *viz* they had never been isolated in pure solid state, and in solution they were usually accompanied by their dimers (**2**).[3]

To put this in the right perspective, cyclopentadienones are known to be unstable, pseudo-antiaromatic species.[16] Thus, cyclopentadienone itself (**1a**) has been prepared and looked at in extreme laboratory conditions (77K), and above −80° it exists only as its dimer (**2a**).[17] This is in contrast to certain other, tetrasubstituted cyclopentadienones such as the tetraphenyl derivative (tetracyclone)[3] or the tetra-t-butyl one[18] which are stable in their monomeric form due, respectively, to electronic alleviation of the "anti-aromaticity" and/or steric hindrance to dimerization.

Between these two extremes, there exists an entire domain of variably stable cyclopentadienones, the behaviour of which depends largely on whether the 2 and 5 position are non-, mono- or dialkyl substituted and on the bulkiness of the substituents.[3,19]

Specifically, regardless of the substitution in positions 3 and 4, if there is one or no substituent in 2 and/or 5 position (with exception of t-Bu groups[19]), irreversible dimerization to the *endo*-dimers **2** occurs.[3] If, however, *both* positions to the carbonyl of **1** are substituted by methyl or methyl/ethyl groups, the corresponding dimers (**2**) dissociate *in solution*,[3] being in temperature dependent equilibria with their monomers (**1**). This behaviour can be readily understood, using conventional stereochemical arguments.[1,3]

While seeking, and prior to obtaining evidence *vide supra* to indicate that **8b** is a product of what we regard, in essence, an intramolecular photo-transformation of the dimer (**2b**) we decided, in spite of the above described difficulties, to examine the possible involvement of the monomers (**1**) in these transformations. To this end we attempted and succeeded to isolate, for the first time in pure solid state, the unstable cyclopentadienones (**1b, c, e**), by thermally decomposing their solid dimers (**2b, c, e**) *in vacuo*, at temperatures below their melting—and decarbonylation points. The red products displayed the expected physical properties, as compared to an authentic sample of the *stable* 2,5-dipropyl-3,4-diphenyl-cyclopentadienone (**1**, R′ = R″ = n-Pr).[7a] They are dimerising only slowly at room temperature in the solid, but this can be greatly enhanced by grinding, banging or ultra-sound treatment. Pure solutions can be obtained by dissolving the red crystals in solvents at low temperatures, e.g. −70° or by heating *dilute* solutions to around 100°. Thus, variable temperature NMR spectroscopic measurements, indicated the extent of monomer (**1b**)/dimer (**2b**) equilibrium at different temperatures and concentrations, e.g. for 0.01 M (**2b**) and 0.001 M (**2b**) at 40°, [**1b**]/[**2b**] is 0.05 and 0.5 and at 100°, 0.5 and 1.5, respectively; UV spectroscopic measurements indicate that 10^{-5}M solutions at 100° are practically fully dissociated.

Excitingly, irradiation of **1b** *in the solid*, at all its absorption wavelengths, yields the symmetric cage (**8b**). This behaviour is not duplicated by **1c, d, e** so we deal, apparently with a specific topochemical process[20] exemplified in Scheme 2-b.

Next, we proceeded to examine the irradiation of **1b** in solution. This could be accomplished at −20° and below (to avoid any appreciable dimerization), and *no reaction* took place. But neither did the dimer (**2b**) photoreact at −20° and below, indicating lack of enough activation energy. We therefore tried to irradiate (350 nm) a **1b** enriched solution of **2b** in 1,4-dioxane at 100°. The yield (44 %) of **8b** turned out to be *lower* than at room temperature (see Table 3, item 1) and similar results were obtained for the monomer **1e**. This confirms, in fact, our conclusion that the symmetric cage compounds (**8**) are indeed formed by intramolecular photorearrangement from the corresponding dimers and not from the monomers. The dual mechanism of formation of **8b**, viz from the dimer (**2b**) exclusively in solution but from the monomer (**1b**) in the crystal, apparently stems from the latter's fortuitous structure for topochemical reaction to occur.

EXPERIMENTAL

Mps 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 a Jeol JNM-C-60 HL and Varian HA-100 spectrometers in $CDCl_3$ solns with TMS as internal standards, unless otherwise specified. Mass spectra were measured on a Du Pont 21-491B mass spectrometer.

Irradiations on 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 O_2-free N_2 or argon. Irradiations on analytical scales 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**, **2b**, **2c** and **2b**-$^2H_{32}$ were prepared according to literature procedures.[7,12] Similarly so was **2d**.[8]

Synthesis of 2,5-dimethyl-3,4-di-p-toluylcyclopentadienone-dimer (**2e**)

(1) *p*-Tolil (23.8 g) and diethylketone (13 g) were added to an 1 % ethanolic KOH soln (200 ml) and the mixture was stirred for 30 hr. The solvent was removed *in vacuo*, the residue was taken up in CH_2CH_2 and the soln washed with water, dried and evaporated to dryness to give an oily residue (70 % yield) of two isomers (tlc) of 4-hydroxy-2,5-dimethyl-3,4-ditoluyl-cyclopent-2-enone ν_{max} 3570, 3470–3400 (OH), 1710 (C=O); *m/e* 306 (M^+); δ Me 0.65–1.28 (2xd, 3H) 1.99 (d, 3H).

(2) The product from above (19.5 g) was added to Ac_2O (12 ml) and 0.1 ml conc H_2SO_4 were added with stirring, which was continued for 90 min. Product started precipitating from the red soln after 10 min and throughout. After filtration and recrystallization from EtOH, 13.5 g (72 %) **2e** were obtained, m.p. 177. (Found: C, 87.10, H, 7.04. Calc. for $C_{42}H_{40}O_2$: C, 87.46, H, 6.99 %).

Reduction of the dimers **2b, c**

1. A mixture of the dimer (0.01 mol) and $NaBH_4$ (0.013 mol) in 200 ml EtOH + 100 ml 1,4-dioxane was stirred for 36 hr. The mixture was acidified using 10 % HCl aq, the organic solvents removed on a rotatory evaporator, water was added and the mixture was thoroughly extracted with $CHCl_3$. The organic soln was washed with sat. $NaHCO_3$ aq, sat. NaCl aq, dried filtered and evaporated to dryness. The products were crystallized from EtOH and shown to be the 10-hydroxyketones: **3b** (94 %), m.p. 186°, *m/e* 522 (M^+); ν_{max} 3480 (O—H), 1670 (C=O). λ_{max} (ε) 280 (17,400); 225 (26,000). δ 0.9 (s, 3H), 1.15 (s, 3H), 1.75 (s, 3H). 2.1 (s, 3H), 3.85 (d, 1H), 6.6–7.9 (m, 20H) and **3c** (69 %), m.p. 191, *m/e* 550 (M^+), ν_{max} 3460 (OH), 1670 (C=O). δ 0.42 (t, 3H), 0.98 (s, 3H), 1.30 (t, 3H), 1.78–2.20 (m, 5H), 2.40–2.82 (m, 3H), 4.15 (d, 1H), 6.7–7.4 (m, 20H).

2. An ethereal soln of the dimer **2b** (1.04 g) was added with stirring at 0° to a suspension of LAH_4 (1.9 g) in dry ether (150 ml). Stirring was continued for 96 hr and the reaction worked up by gradual addition of an ethereal soln of EtOAc, followed by satd Na_2SO_4 aq. After drying on $MgSO_4$ and filtering, the soln was evaporated to dryness and the residue crystallized from EtOH to give 0.82 g (80 %) of a product of isomers having one major component, i.e. a 3,10-dihydroxy derivative (**6b**), m.p. 226; *m/e* 524 (M^+); ν_{max} 3520 (OH); λ_{max} (ε) 262 (17,300), 223 (34,000); δ (+D_2O) 0.92 (s, 3H), 1.44 (s, 3H), 1.56 (s, 3H), 2.0 (s, 3H), 3.5 (s, 1H), 4.0 (s, 1H), 5.75–7.9 m (20H).

Irradiation of the reduction products **3b, c** *and* **6** *to the corresponding cage compounds* **4b, c** *and* **7**

The above reduction products **3b, c** and **6** in 1,4-dioxane soln (0.005M) were irradiated in pyrex vessels with 350 nm lamps until no starting material was left (tlc). The solvent was evaporated and the residue crystallized from EtOH to give the hydroxylated cage products: **4b**-(92 %); m.p. 300; *m/e* 522 (M^+); ν_{max} 3420 (OH), 1740 (C=O); λ_{max} (ε) 225 (27,000) δ (+D_2O) 0.50 (s, 3H), 0.67 (s, 3H), 1.6 (s, 3H), 1.82 (s, 3H), 4.42 (s, 1H) 6.5–7.4 (m, 20H), **4c**-(86 %); m.p. 278; *m/e* 550 (M^+); ν_{max} 3500 (OH), 1780 (C=O); **6**-(94 %); m.p. 280 (phase transition at 150°); *m/e* 524 (M^+); ν_{max} 3,300 (OH); λ_{max} (ε) 222 (27,600); δ (+D_2O) 0.78 (s, 6H), 1.68 (s, 6H), 4.2 (s, 2H), 6.4–7.6 (m, 20H).

Jones oxidation of hydroxylated cages **4b, c** *and* **6**

To the above hydroxy-compounds in acetone were added with stirring a 20 % excess of Jones' reagent (0.7 g CrO_3 + 0.6 ml H_2SO_4 conc in 5 ml H_2O). The mixture was stirred overnight and then poured into ice-water. The ppt was collected and crystallized from 1,4-dioxane, to give the diketo-dissymetric cages **5**. Thus **4b** and **6** gave **5b** (91 and 85 %) whereas **4c** gave **5c** (61 %) identical in all respects with the same compounds obtained by direct irradiation of the dimers **2b** and **c** *vide infra*.

Irradiation of the dimers **2b, c, d, e** (see also Tables 1 and 2)

Compound **2b** was irradiated in various conditions (see Table 3). The work up consisted in filtering off the crystals of the symmetric cage (**8b**), concentration of the soln and crystallization of the dissymmetric cage (**5b**) and crystallization from EtOH (or chromatography on silica gel) of the residue to give starting material and an ill defined mixture of byproducts in variable quantities (*cf* Table 3). Compound **5b**, m.p. 318 (d); (Found: C, 87.77, H, 6.10, Calc. for $C_{38}H_{32}O_2$: C, 87.69, H, 6.15 %).

Compound **8b**, m.p. 273 (d); (Found: C, 87.89, H, 6.05; Calc. for $C_{38}H_{32}O_2$: C, 87.69, H, 6.15 %).

The quantum yield determinations for disappearance of **2b**, was performed using UV-spectroscopic monitoring (see Fig. 1).

Compound **2c** was irradiated in 1,4-dioxane or acetonitrile at room temp to no avail. However, irradiation of 2 g in 400 ml acetonitrile in a pyrex vessel with 350 nm lamps *at* 5-8°, for 22 hr, gave a colourless ppt (0.32 g, 16 %) of **8c**, m.p. 205 (d); (Found: C, 87.38, H, 6.67, Calc. for $C_{40}H_{36}O_2$: C, 87.59, H, 6.57 %). The mother liquor contained only starting material.

Irradiation of **2d** gave no products in any conditions (solvents and temps).

Compound **2e** (0.58 g) in 1,4-dioxane (100 ml) was irradiated for 48 hr with 350 nm lamps in a pyrex vessel. A colorless ppt (0.12 g, 21 %) was collected and assigned structure **8e**, m.p. 240; (Found: C, 87.16; H, 6.95, Calc. for $C_{42}H_{40}O_2$: C, 87.46, H, 6.99 %). The filtrate was evaporated and the residue subjected to preparative tlc on silca gel plates, by elution with petrol ether-dichloromethane 3:1, to give **5e** (0.125 g, 22 %), m.p. 262 (d); (Found: C, 86.97, H, 7.05; Calc. for $C_{42}H_{40}O_2$: C, 87.46, H, 6.99 %). Starting material **2e** was also isolated (0.15 g) and the rest was an ill-defined mixture of byproducts.

Photochemical and thermal decarbonylation of dimers **2b** *and* **2e**

A 1,4-dioxane soln (10^{-3}M) of dimer was irradiated with 300 nm lamps in a quartz tube for 48 hr. The soln was evaporated and the residue crystallized from ether–MeOH, yields: 50 and 53 % of **12b** and **12e**, respectively. The same products were obtained by refluxing bromobenzene solns of **2b** and **2e** overnight, in yields of 60 and 25 % respectively.

Compound **12b**: m.p. 166°: *m/e* 492 (M^+): ν_{max} 1710 (C=O); λ_{max} (ε) 213 (14,800), 237 (9400). δ 0.68 (s, 3H), 0.9 (s, 3H), 1.45 (s, 3H), 1.85 (s, 3H), 6.8–7.3 (m, 20H).

Compound **12e**: m.p. 220°; *m/e* 548 (M^+): ν_{max} 1704 (C=O); δ 0.67 (s, 3H), 0.9 (s, 3H), 1.45 (s, 3H), 1.90 (s, 3H), 2.15 2.3 m (12H), 6.7–7.2 (m, 16H).

Isolation of 2,5-*dimethyl*-3,4-*diphenylcyclopentadienone* **1b** *and of its analogs* **1c** *and* **1e**

The crystalline dimer **2b** (0.1 g) was put in a sublimation apparatus and covered with a round filter paper sheet of appropriate diameter. Ice cooled water was circulated through the cold finger while heating the dimer at 145° in a vacuum of 10^{-3} torr. Care must be taken to allow no heat transport to the surface of the cold finger, by immersing a minimum of the sublimator in the heating bath. The orange solid which is deposited on the cold finger is collected (90 %): **1b**, m.p. 80° (phase transition to the colorless dimer **2b** which melts at 185°): ν_{max} 1710; λ_{max} (ε) 254 (19,900), 292 (9000), 404 (400), 423 (420), 446 (300); δ 1.8 (s, 6H).

The monomers **1c** and **1e** were obtained following exactly the same procedure.

Irradiation of **1b**

The monomer **1b** was irradiated in the solid, either as a thinly deposited layer on the cold-finger or as collected crystals, at each of its absorbing wavelengths. In all cases the symmetric cage (**8b**) was isolated in variably good yields, up to 80 %. No disymmetric cage (**5b**) was obtained and only the dimer **2b** was formed, probably as a thermal byproduct.

None of the other monomers (**1c, d, e**) under went a similar photo-transformation.

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