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PHOTOCHEMICAL STUDIES—XXI[1]

DIMERS OF 3,4-(o,o'-BIPHENYLENE)CYCLOPENTADIENONES: THERMAL AND PHOTOCHEMICAL BEHAVIOUR

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Abstract—The 1,4-dimethyl-, 1,2,4-trimethyl and 1,2,4,7-tetramethyl substituted 3,4-(o,o'-biphenylene) cyclopentadienone-dimers (**6a–c**) were prepared and found to undergo photochemically *or thermally* a 1,3-rearrangement to the centrosymmetrical diketones (**11**). Only the tetramethyl derivative (**6a**) undergoes at room temperature a fast, degenerate [3.3] Cope rearrangement with $\Delta G^{\ddagger}_{249} = 11.4$ kcal mol^{-1} All these dimers and rearrangement products appear *not* to dissociate to their monomers, but react with dienophiles to give the adducts (**12**, **13**). A stepwise mechanism involving diradical intermediates (**19**) is invoked. The "mixed dimer" (**14**) was also prepared and studied. The steric and electronic effects determining the behaviour of these compounds are discussed.

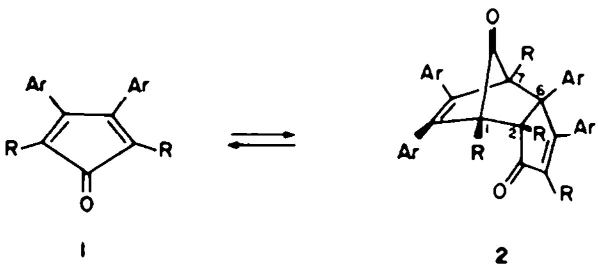
We have recently published detailed accounts on the thermal and photochemical behaviour of reversibly dissociating[3] and non-dissociating[1] cyclopentadienone-dimers (**2**). A series of interesting transformations was found in each case to provide not less interesting molecular structures by mechanisms involving a complex interplay of electronic and steric effects.[1-4] For better understanding of this paper, we should try to summarize this behaviour, without going into its details or mentioning its intricacies but including the main factors known to operate, as follows: (a) All dimerising cyclopentadienones (**1**)[6] have been found[1,3] to give *endo*-dimers (**2**), be they dissociating or not. (b) Non-dissociating dimers (NDD) undergo photochemical [1, 3] rearrangement to (**3**) *or* internal (${}_{\pi}2 + {}_{\pi}2$) cycloaddition to (**4**) (Eqn 2), depending on their substitution pattern.[1] Only the parent NDD (**2**, Ar=R=H) is known[5] to undergo *all theoretically possible* transformations[4], including a (slow) thermal Cope [3, 3] degenerate rearrangement, which could not be detected in any other case. (c) Dissociating dimers (DD) yield on irradiation the cage systems (**4**) and (**5**) (Eqn. 3) in wavelength, phase and temperature dependent ratios.[3] (d) All dimers end up decarbonylating on heating or *low wavelength* (< 300 nm) irradiation.[1,3] (e) The various processes appear to be competitive, the fine balance being determined on one hand by electronic factors such as the ability for radical stabilization in positions C_6, C_7 in (**2**), etc, and on the other hand by steric factors such as the number of substituents on the carbons α to the carbonyls (C_1, C_2, C_4, C_7), their bulk and position, etc.[1,3,4]

RESULTS

We present now the outcome of an investigation of a group of cyclopentadienone-dimers (**6**) bearing o,o'-biphenylene groupings in positions 5,6 and 8,9 (*cf* Ar substituents in formula 2). The quite unexpected results (*vide infra*) were at first in apparent conflict with existing knowledge in this field[1-5] but they could be shown to be consistent, unveiling new and exciting aspects and insight.

Chronologically, the first dimer we dealt with was the 1,2,4,7-tetramethyl substituted one (**6a**).[2,7,8] Its preparation was less straightforward than the tetraphenyl analog (**2** Ar=Ph, R=Me) or any of the other similar dimers,[3,6] in that the precursor 2,5-dimethyl-4-hydroxy-3,4-(o,o'-biphenylene)-2-cyclopentenone-1 (**7a**)[9] does not lend itself to acid-catalysed dehydration, but undergoes a 1,3-anionotropic shift instead. Thus, while treatment of **7a** with acetic anhydride/H_2SO_4 conc. gave a diastereomeric mixture of the rearranged 2-acetoxy compounds (**8**), thionyl chloride or acetyl chloride provided the corresponding 2-chloro derivatives (**9**). The latter readily underwent dehydrochlorination by ethanolic KOH, leading to the isolation of the expected dimer (**9a** → **6a**). If the monomeric cyclopentadienone (**10a**) is an intermediate in this process, it can be neither isolated nor detected by any spectroscopic means. This holds also for the solutions of **6a**, up to 110°C, in spite of the heavy substitution pattern, which had led to the expectation that we dealt with a dissociating cyclopentadienone-dimer.[3,6] Moreover, all attempts to isolate the crystalline monomer (**10a**) by high vacuum sublimation of the dimer (**6a**), similar to other closely analogous tetra-substituted cyclopentadienones,[3,10] invariably failed.

In addition to its failure to dissociate, the dimer (**6a**) exhibits other, unusual properties. Thus, its ^{13}C- and ^1H-NMR spectra exhibit two methyl–carbon (at 11.11 and 15.08 ppm) and two methyl–proton resonances (at 1.20 and 1.86 ppm, 6H each) instead of four in each case as the rigid formula **6a** would require. Obviously, the methyl groups are pair-wise equivalent and the only reasonable explanation we can provide is a rapid exchange between two pairs of methyl sites, relative to the NMR time scale, due to a thermal degenerate [3.3] Cope rearrangement (eqn 4) of the *endo*-dimer (**6a**). In this process, bonds are ruptured and formed alternately between the carbons 6,7 and 4,9. This process should be temperature dependent and indeed, in a series of variable temperature ^1H-NMR spectroscopic measurements down to − 75° (solubility limited) we were able to bring about a gradual broadening of the low field methyl signal, until it splits ending up in two well resolved singlets at 1.60 and 2.23 ppm, with a coalescence temperature of − 24° (Fig. 1). Based on a recently published NMR study of methyl-proton resonances in a variety of methyl-substituted cyclopentadienone-dimers[3] (*vide infra* and Table 1), we assign the low-temperature splitting to a slowdown of the



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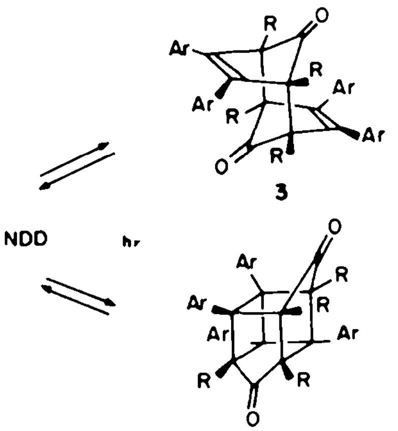
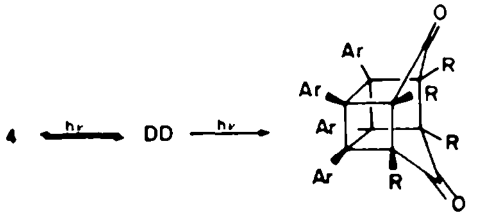


3 4 (2)



5 (3)

exchange between the methyls in positions 4 and 7 in **6a**. Since we deal here with a case of two non-interacting, equally populated sites, we use the approximation $\tau_c = \sqrt{2}/\pi\delta = 7.2 \times 10^{-3}$ s and hence, $k_c = 70\,s^{-1}$. From the Eyring equation we can obtain the free energy of activation at the coalescence temperature, $\Delta G^{\ddagger}_{233} = 4.57\,T(10.2 + \log T/k) = 11.4$ kcal/mol. The upfield signal (at 1.2 ppm) is little affected in this process, broadening appreciably only at the lowest temperatures.

Irradiation of the dimer (**6a**) at various wavelengths in 1,4-dioxane solution brings about precipitation of a single, high-melting, *isomeric* product to which we assigned the [1, 3] rearranged structure (**11a**) on the following rationale. Spectroscopic measurements showed an IR absorption at λ_{max} 1750 cm^{-1} (bridged CO) and UV spectrum: $\lambda_{max}(\epsilon)$ 253 (145,000), 277 (60,000); 297 (31,400). The latter was of diagnostic value after having compared it on one hand with phenanthrene:[11] $\lambda_{max}(\epsilon)$ 220 (23,000), 244 (51,000), 251 (67,000), 274 (14,600), 281, (11,400), 292 (14,800) and on the other hand with 9,10-dihydrophenanthrene:[12] $\lambda_{max}(\epsilon)$ 263 (18,000), 299 (4,750). At once we see that we deal with a molecule carrying two phenanthrene moieties and not with one of the possible (saturated) cage compounds analogous to **4** or **5**. Unfortunately the compound is too insoluble in any solvents for NMR spectroscopic measurements. It is nevertheless clear that, having assured the *endo* structure of **6a** by establishing its fluxional character due to the degenerate [3.3] Cope rearrangement and the presence of (two) phenanthrene moieties in its photoisomeric product, the latter can have only the centrosymmetric structure (**11a**), as a result of a 1,3-rearrangement of **6a**.

More surprising, though, was the finding that the same rearranged diketone (**11a**) was obtained also by *thermal* transformation of **6a**, e.g. in refluxing xylene. No decarbonylation could be observed to accompany this process, in contrast to the behaviour of all other known cyclopentadienone-dimers.[1,3,6]

The failure to isolate or detect the monomeric cyclopentadienone (**10a**) is not extended to its cycloaddition products (**12**, **13**), which are obtained from the reaction by the dimer (**6a**) with maleic anhydride or N-phenylmalemide, respectively, even at room temperature. Interestingly, the adduct **12** is also formed by refluxing a solution of maleic anhydride with the rearranged

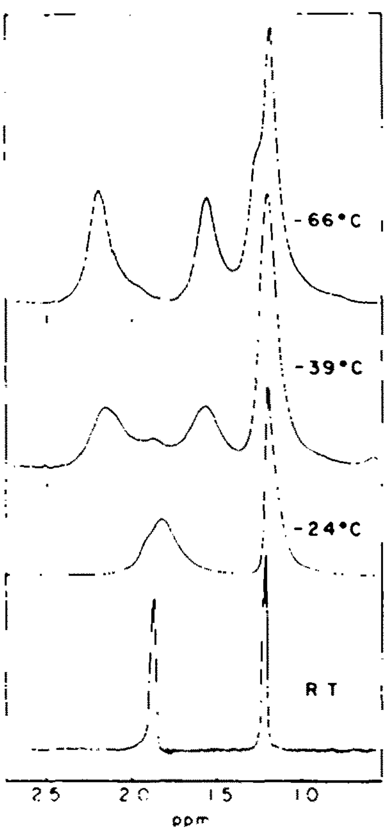
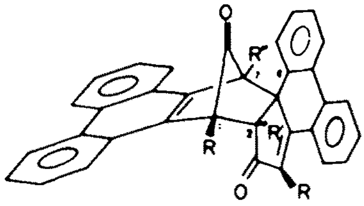


Fig. 1. Methyl/proton resonances in the NMR spectrum (100 MHz) of the dimer (**6a**).

diketone (**11a**) or with the acetate (**8a**), although the latter could not be induced to eliminate acetic acid to give the cyclopentadienone (**10a**) itself. Moreover, we were able to bring about a further cycloaddition process by warming (60°) a solution of equimolar amounts of the dimer **6a** and the *dissociating dimer* (**2**: Ar=Ph, R=Me) whereby we isolated quantitatively the "mixed dimer" (**14**), whose structure is wholly supported by spectroscopic data, in particular UV and NMR.

We looked into the thermal and photochemical behaviour of **14** and were again surprised. While its solutions are clearly coloured indicating reversible dissociation, reflux of a xylene solution gave the 1,3-rearranged diketone (**15**), but irradiation ($\lambda > 340$ nm) yielded quantitatively an isomeric product (MS), having no phenanthrene moiety (UV) and no symmetry (NMR). Hence, we can not but assign it the cage structure (**16**). Irradiation at lower wavelengths led to photostationary states of **14** and **16**, in line with the known photoreactivity of cages of type **4**[1,3,5] towards reversal to the corresponding dimers (**2**). It may be worth mentioning that not only does the dimer **6a** fail to undergo such an intramolecular ($_{\pi}2 + {}_{\pi}2$) photo-cycloaddition but so is its $NaBH_4$ reduction product **17**. In previous instances,[1,3] this was a major route for attaining such photochemical cage (**4**) closures. Strangely enough, irradiation of **17** consistently provided a *ca.* 20% yield of the *centrosymmetric diketone* (**11a**). This was taken to arise following photodissociation of **17** and formation of **6a** which subsequently photorearranges.

The unusual behaviour of the dimer (**6a**) compelled us to study further cyclopentadienone-dimers bearing the o,o'-biphenylene moieties. We pursued this by preparing the dimer (**6b**) in the reaction sequence:



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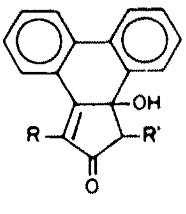
a: R = R' = R'' = Me
b: R = Me; R' = R'' = H
c: R = R' = Me; R'' = H



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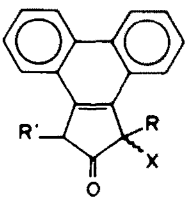
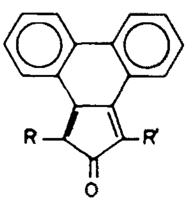


8: X = OAc
9: X = Cl



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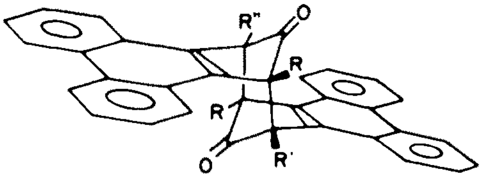

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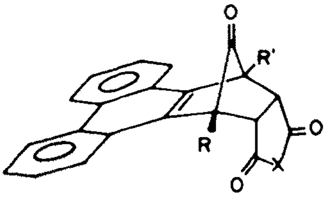
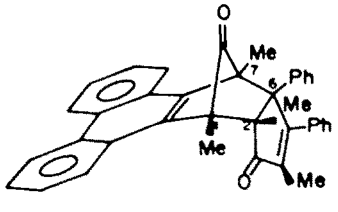


12: X = O
13: X = NPh



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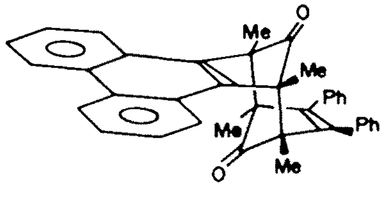

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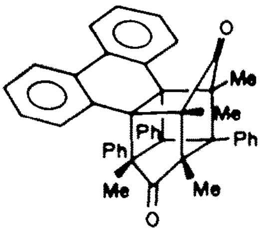

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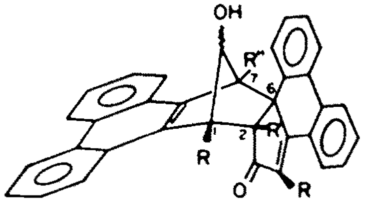

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phenanthraquinone + 2-butanone $\xrightarrow{OH}$ **7b** $\xrightarrow{AcCl}$ **9b** $\xrightarrow{KOH}$ **6b**. Another, "mixed dimer" (**6c**) was obtained exclusively, when equimolar amounts of the chlorides **9a** and **9b** were warmed at 80° in the presence of triethylamine (use of KOH in this case, leads to the isolation of the two normal dimers **6a** and **6b**). The *endo*-dimeric structure for **6b** and **6c** is fully corroborated by their spectroscopic data, and a full assignment of the methyl-proton resonances was made (Table 1) on the basis of a similar comparative NMR study in the 3,4-diphenylcyclopentadienone-dimer (**2**) series.[1,3]

Both the dimethyl dimer (**6b**) and the trimethyl "mixed dimer" (**6c**) do not dissociate to their monomers, but in this case they are expected not to, since they lack any substituent in position 7, in analogy to the known non-dissociating cyclopentadienone-dimers.[1,6] They do, however, react with maleic anhydride, **6b** giving the anhydride **12b** and **6c** giving both anhydrides **12a** and **12b**. The similarity to **6a** does not end here. On irradiation *or heating* of the dimers **6b** or **6c**, the centrosymmetric diketones (**11b**) and (**11c**) are obtained respectively. This process is irreversible and no decarbonylation products were again isolated. Finally, in contrast to **6b**, no [3.3] Cope rearrangement could be detected in **6b** and **6c**.

DISCUSSION

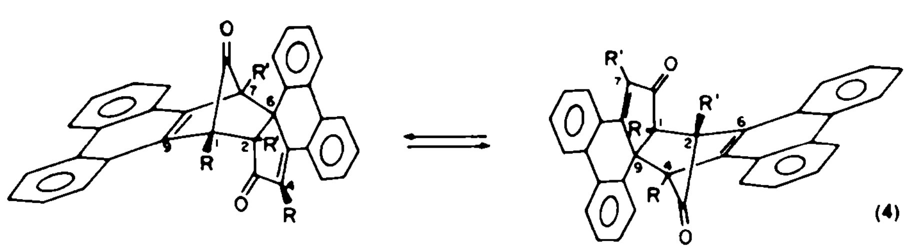
The above described behaviour of the various 3,4-(o,o'-biphenylene) cyclopentadienone-dimers has some apparent discrepancies with the well documented behaviour of dissociating and non-dissociating dimers of substituted cyclopentadienones.[1-6] For one, the tetramethyl derivative **6a** should be a dissociating dimer and yet, no monomeric cyclopentadienone (**10a**) can be spectroscopically detected although its Diels–Alder adducts are readily obtained. The degenerate Cope rearrangement in **6a**, indicates that the first step of the dissociative process, *viz* the C-6—C-7 bond cleavage is in fact built in, the second C-1—C-2 bond breaking being obviated

Table 1. ^{1}H-NMR chemical shifts of methyl protons in the 3,4-(o,o'-biphenylene)cyclopentadienone-dimers (**6a-c**)[a]

position / Comp	1		2	4		7
6a		1.2		2.2	1.86	1.6
6b	1.25			2.40		
6c	1.30		1.15	2.40		
14	1.40		0.70	2.20		2.05
2[b] (Ar Ph;R=Me)	1.25		0.58	2.25		1.65

a) Measured in $CDCl_3$/TMS at 60 MHz. Data are given in ppm.

b) This dissociating dimer[3] is given for the sake of comparison.



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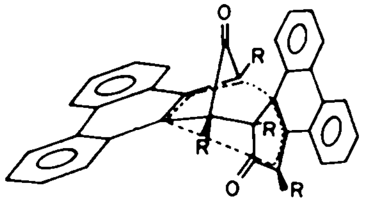

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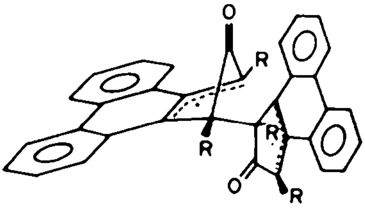

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precisely by the Cope fluxionality. The latter (eqn 4) appears to be a concerted pericyclic process in a system (**18**) with certain diradicaloid character which in the limiting case, on thermolysis or photolysis, actually reaches the level of a true diradical intermediate (**19**) on its way to the rearranged diketone (**11a**). Hence, we submit that the monomeric cyclopentadienone (**10a**) may indeed not prevail, while the cycloaddition processes leading to the adducts **12**, **13** or **14** actually start by attack of the respective dienophiles *on the dimer itself*, proceeding stepwise to the formation of the adducts by a 1,4-displacement mechanism. This is strengthened by the fact that the acetate (**8a**) as well as the rearranged diketone (**11a**) react with maleic anhydrides to give **12**, obviously without the intermediacy of **10a**. This mechanism is, in fact, bound to operate as well in the reactions between the other (*bona fide*) non-dissociating dimers **6b** and **6c** with maleic anhydride to give the corresponding adducts (**12**).[13] The failure to detect in **6b** and **6c** a [3.3] Cope rearrangement is readily understandable, since it would be a non-degenerate process in either case, in which a system (**6**) with a methyl group in the least hindered 4 position would exchange for one bearing the methyl in the most hindered 7 position and, what is even more important, the absence of the substituent in position 7 raising the barrier to C-6—C-7 bond cleavage beyond attainability at or around room temperature while at higher temperature another process, the [1,3] rearrangement takes over. Hence, this combination of thermodynamic and kinetic factors that prohibits the Cope rearrangement in **6b** and **6c**, and allows it in **6a**, is essentially a steric effect.

Following this train of thought, one may ask, why then does the 2,5-dimethyl-3-4-diphenylcyclopentadienone-dimer (**2**: Ar=Ph, R=Me)[3] neither undergo the [3.3] Cope-nor the [1,3] rearrangement *as* **6a** *does*, and dissociates instead to its monomers (**1**: Ar=Ph, R=Me), *as* **6a** *does not*? The effect of determining the outcome of this competition between two possible reaction paths is this time, electronic: the 2,5-dimethyl-3,4-(o,o'-biphenylene) cyclopentadienone (**10a**) with its phenanthroquinonoid electronic structure is evidently much more unstable than its 3,4-diphenyl counterpart (**1**: Ar=Ph, R=Me) on one hand and with respect to phenanthrenic structures like **6a**, **11a** or **12a** on the other hand. By the same token, a diradicaloid structure of type **19** is bound to be relatively stabilized due to the electron-delocalization into the phenanthrene moieties. These same arguments hold for the fact that the hydroxyketones **7** do not eliminate water but rearrange to **8** or **9** instead, as well as for the complete lack of thermal or photochemical decarbonylation of any (**6**). In fact, we also attribute the lack of cage (type **4**) formation in the irradiation ofthe dimers (**6**) to the successful competition of C-6—C-7 cleavage because of the above enhanced (bi)radical stabilization. In accord with that, irradiation of the mixed dimer (**14**) led only to the cage product (**16**).

To conclude, the peculiar o,o'-biphenylenecyclopentadienone-dimers can be understood after all, by being aware of the subtle interplay between electronic and steric effects which determine their behaviour. The latter becomes then an integral part of the fascinating behaviour of cyclopentadienones and their dimers, in their ground and excited states.[1–6]

EXPERIMENTAL

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 a Jeol JNM-C-60 HI. and Brucker WH-90 spectrometers in $CDCl_3$ solutions 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 oxygen-free nitrogen or argon.

The synthetic work is described below in the form of general procedures for groups of compounds, whenever possible.

4-Hydroxy-2-methyl-3,4-(o,o'-biphenylene)cyclopent-2-enones (7b)

9,10-Phenanthraquinone (10 g) was dissolved in a solution of KOH (0.7 g) in methanol (50 ml). 2-Butanone (26 ml) were added slowly with stirring at room temperature. The reaction mixture was stirred for another 40 hr after which the solid was collected and recrystallized from ether/dichloromethane. Yield: 8 g (64%) m.p. 190°; *m/z* 262 (M^+); ν_{max} 3420 (OH), 1685 (CO); δ (D_2O) 2.1 (s, 3H), 3.15 (d, 2H) 7.2–8.2 (m, 8H).

The 2,5-dimethyl derivative (**7a**) was prepared by the same procedure and showed similar properties also in accord with literature reports.[7-9] The 2-acetoxy-3,4-(o,o'-biphenylene)cyclopent-3-enones (**8**) were obtained by treating 120 mg hydroxyketone (**7**) with 1 ml freshly distilled acetic anhydride and one drop of H_2SO_4 conc. with stirring at room temperature. After another 4 hr, the precipitate was collected and washed with methanol/ether. Tlc (silica gel/$CHCl_3$) and NMR spectra show two isomeric components in the product. No attempts at resolution were made. **7a**:[7,13] m.p. 160–1°; *m/z* 316 (M^+); ν_{max} 1765, 1730; **7b**: m.p. 245–8°; *m/z* 302 (M^+); ν_{max} 1760, 1730 (CO).

2-*Chloro-3,4-(o,o'-biphenylene)cyclopent-3-enones* (**9**).

The hydroxyketone (**7**) was treated with a ten-fold excess of acetyl chloride with stirring at 0°. After 30 min the solid was collected and washed with ether. The yields were in both cases 86–87%. (The same procedure using thionyl chloride gave inferior yields.) Tlc and NMR showed two isomeric components in each case, which were not separated. **9a**:[2a] m.p. 125°; *m/z* 294, 296 (M^+); ν_{max} 1760 (CO); **9b**: m.p. 130°; *m/z* 280, 282 (M^+); ν_{max} 1755 (CO).

Preparation of the 3,4-(o,o'-biphenylene)cyclopentadienone-dimers (**6a**-c and **14**)

A solution of the diastereomeric mixture of chloroketone (**9**) (0.03 mol) in dichloromethane or benzene (100 ml) was added dropwise to ethanolic KOH (2 g/70 ml) at 0°. The mixture was stirred for another 30 min and treated afterwards with dilute HCl until neutral. The aqueous layer was well extracted with dichloromethane or benzene and the unified organic fractions were washed with water, dried and evaporated. The products were crystallized from benzene/ethanol. **6a**[2,8] yield: 90%; m.p. 305° (d); *m/z* 516 (M^+), 258 ($M/2^+$); ν_{max} 1770, 1690 (CO); λ_{max} (ϵ) 254 (83.800), 297 (21.100), 312 (14,100); NMR, see Table 1. **6b**: Yield 75% (an additional product was obtained and therefore the mixture was separated by chromatography on alumina); m.p. 274 (d); *m/z* 488 (M^+), 244 ($M/2^+$); ν_{max} 1770, 1680 (CO); λ_{max} (ϵ) 254 (88,100), 297 (21,600), 308 (17,300); NMR, see Table 1. (Found: C, 87.81, H 4.91. Calc. for $C_{36}H_{24}O_2$: C 88.52, H 4.92%).

A mixture of the chloroketones (**9a**) and (**9b**) (0.005 moles each) was added to a solution of triethylamine (0.025 mol) in benzene (50 ml). The solution was refluxed for 22 hr, cooled and filtered off the precipitated salt. The solvent was evaporated and the residue crystallized from benzene/ethanol. **6c**: Yield: 76%; m.p. 296 (d); *m/z* 502 (M^+), 258, 244 ($M/2^+$); ν_{max} 1770, 1680 (CO); λ_{max}(ϵ) 254 (86,400), 298 (20,500), 310 (15,500); NMR, see Table 1. (Found: C 87.93, H 5.21. Calc. for $C_{37}H_{26}O_2$: C 88.45, H 5.18%). An equimolar mixture of the dimers (**6a**) and (**2**: Ar=Ph, R=Me)[3] in chloroform (50 ml), was refluxed over night, evaporated to dryness and crystallized from benzene/ethanol to give exclusively the "mixed dimer" **14**, yield 82%, m.p. 312 (d) (phase transition at 225); *m/z* 518 (M^+), 260, 258 ($M/2^+$) 1765, 1690 (CO); λ_{max} (ϵ) 257 (82,800), 280 (29,100); NMR, see Table 1. (Found: C 87.35, H 5.96. Calc. for $C_{38}H_{30}O_2$: C 88.03, H 5.79%).

Reactions of the dimers (**6a**-c, **14**) *with maleic anhydride*

A solution of the dimer (0.001 mol) and maleic anhydride (0.005 mol) in benzene (50 ml) was refluxed for 24 hr. After concentration and cooling, the precipitated adducts were collected. **12a**: Yield: 96%; m.p. 325 (d); *m/z* 356 (M^+); ν_{max} 1865, 1780 (CO); **12b**: yield: 49%; m.p. 280 (d); *m/z* 342 (M^+); ν_{max} 1860, 1780 (CO).

The reaction of maleic anhydride with **6c** gave, according to NMR and MS an equimolar mixture of the adducts **12a** and **12b**. The reaction of maleic anhydride with **14** gave, according to NMR and MS an equimolar mixture of **12a** and the known 2,5-dimethyl-3,4-diphenylcyclopentadienone adduct.[6]

Reduction of the dimer (**6a**) *to the hydroxyketone* **17**

A mixture of the dimer (**6a** 0.5 g) and $NaBH_4$ (1 g) in 1,4-dioxane/ethanol (4:3) was stirred at room temperature for 16 hr. The solvents were evaporated in vacuo, water was added and the aqueous mixture was neutralized and extracted with chloroform. After washing, drying and evaporation to dryness, the residue was crystallized from ethanol to give **17** (0.47 g). Yield 94%; m.p. 280° (phase transition at 183°); *m/z* 518 (M^+); ν_{max} 3420 (OH), 1675 (CO); δ (D_2O) 1.0 (s, 3H), 1.6 (s, 3H), 2.22 (s, 3H), 2.32 (s, 3H, 6.1 (d, 1H), 6.8–8.9 (m, 16 H).

Thermal reactions of the dimers (**6a**-c, **14**)

A solution of the dimer (0.1 g) in xylene (50 ml) was refluxed over night. The precipitated product was collected and triturated with ether to give practically insoluble solids (this precluded NMR spectral measurements and lowered the accuracy of the ϵ values). **11a**: Yield 97%; m.p. 315 (d); *m/z* 516 (M^+), 258 ($M/2^+$); ν_{max} 1750 (CO); λ_{max} (ϵ) 253 (145,000), 277 (60,000), 297 (31,000). (Found: C 87.91, H 5.50; Calc. for $C_{38}H_{28}O_2$: C 88.37, H 5.43%). **11b**: Yield: 8%; m.p. 324 (d); *m/z* 488 (M^+), 244 ($M/2^+$); ν_{max} 1755 (CO); λ_{max} (ϵ) 253 (95,000), 274 (40,000), 296 (20,000). **11c**: Yield: 16%; m.p. 312 (d); *m/z* 502 (M^+), 258, 244 ($M/2^+$); ν_{max} 1750 (CO); λ_{max} (ϵ) 253 (92,000), 275 (40,000), 296 (21,000). **15**: Yield: 28%, m.p. 334 (d); *m/z* 518 (M^+), 258, 260 ($M/2^+$); ν_{max} 1750 (CO); λ_{max} (ϵ) 253 (94,500), 275 (37,000); 297 (15,000). (Found: C 87.36, H 5.45. Calc. for $C_{38}H_{30}O_2$: C 88.03, H 5.79%).

Irradiations of the dimers (**6a**-c)

A solution of the dimer (0.001 mol) in 1,4-dioxane (100 ml) was deoxygenated by sweeping it thoroughly with nitrogen and irradiated at 350 nm in pyrex, to exhaustion of starting material. The product (**11**) invariably precipitated and variable amounts of ill-defined by-products were found in the mother liquor and were not further investigated. **6a** $\xrightarrow{h\nu}$ **11a** (yield 78%); the same product was obtained by irradiating at different wavelengths and by sensitization (each for 16 hr for comparison), as follows: at 300 nm—52%, at 254 nm—52%, at 300 nm in acetone 94% (**11a**). **6b** $\xrightarrow{h\nu}$ **11b** (Yield 95%); **6c** $\xrightarrow{h\nu}$ **11c** (Yield 76%).

Irradiation of the "mixed dimer" (**14**)

A solution of the "mixed dimer" (**14**) (0.3 g) in 1,4-dioxane (100 ml) was deoxygenated by sweeping with nitrogen and irradiated at 350 nm through pyrex and a cut-off (solution) filter transmitting above $\lambda > 340$ nm,[5] for 96 hr. The solvent was evaporated and the residue crystallized from isopropanol to give **16** (0.23 g) yield: 77%, m.p. 297° (phase transition at 247°); *m/z* 518 (M^+); ν_{max} 1750 (CO); λ_{max} (ϵ) 252 (22.100), 285 (8100); δ 0.45 (s, 3H), 1.06 (s, 3H), 1.45 (s, 3H), 1.58 (s, 3H), 6.5–8.0 (m, 18H). (Found: C 87.37, H 5.88. Calc. for $C_{38}H_{30}O_2$: C 88.03, H 5.79). Irradiation (350 nm) of the hydroxyketone **17** gave invariably a 20% yield of **11a**. The mother liquor was not further investigated.

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[13] One should recall at this point, that "classical" non-dissociating dimers[6] consistently failed to give adducts of type **12** in their reaction with maleic anhydride. This was adequately discussed in Ref. 1.