Isolation, Spectral Properties, and Photochemistry of Unstable Substituted Cyclopentadienones

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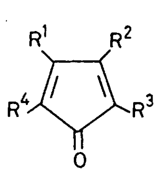
Summary A new approach to the isolation of unstable cyclopentadienones from dissociating dimers is described; 2,5-dimethyl-3,4-diphenylcyclopentadienone (**1d**) and two other derivatives, (**1e**) and (**1f**), were obtained in crystalline state and their spectral properties were investigated, and irradiation of (**1d**) in the crystal quantitatively gave the cage-product (**3**).



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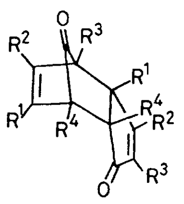
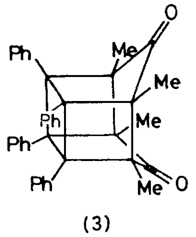


(2)

	R^1	R^2	R^3	R^4
a;	H	H	H	H
b;	Ph	Ph	Ph	Ph
c;	H	Bu^t	H	Bu^t
d;	Ph	Ph	Me	Me
e;	C_6H_4Me-*p*	C_6H_4Me-*p*	Me	Me
f;	Ph	Ph	Et	Me



(3)

THE cyclopentadienone unit (**1**) is primarily known as a building block of interesting structures, *e.g.* the dimers (**2**).[1,2] The compounds (**2**) are known to exist as reversibly dissociating or non-dissociating dimers depending on whether or not the starting monomers (**1**) bear substituents in both 2- and 5-positions, the effect being largely a steric one.[2]

The peculiar electronic structure of cyclopentadienone[3,4] imparts to it and many of its derivatives pseudo-antiaromatic character and frustrating elusiveness under ordinary laboratory conditions. That is why the only known stable derivatives of cyclopentadienone exist by virtue of both electronic and steric stabilization brought about by tetrasubstitution, such as in tetracyclone (**1b**),[2] or purely steric hindrance to dimerization caused by bulky substituents, such as in 2,4-di-t-butylcyclopentadienone (**1c**).[4] Recently, the parent molecule (**1a**) was prepared at −196 °C and its i.r. spectrum was measured;[5] its dimerisation to (**2a**) is complete at −80 °C.

In the course of our studies of thermal and photochemical transformations of cyclopentadienone dimers[6,7] we became intrigued by the fact that, on heating in solution, dissociating dimers like (**2d**) are seen to yield the corresponding monomers, but the latter have actually never been isolated or studied. We now report the isolation of pure 2,5-dimethyl-3,5-diphenylcyclopentadienone (**1d**) by sublimation *in vacuo* (150 °C, 0·01 Torr) of the corresponding dimer (**2d**). The red compound (**1d**), λ_{max} (Bu^{t}OH, 40 °C) 254 (ϵ19,900), 292 (9,000), 404 (400), 423 (420), and 446 (300) nm; ν_{max} (KBr) 1705 (C=O) cm^{-1}; τ (C_4Cl_6, 160 °C) 8·30 (s, 6H), and 3·1 (m, 10H), can be stored indefinitely as a solid even at room temperature. At 80 °C it undergoes smooth dimerization to (**2d**) apparently in the course of a phase transition. Two other closely related cyclopentadienones, (**1e**) and (**1f**), were isolated similarly.

Irradiation of crystals of (**1d**) in any of its (u.v. or visible) absorption bands results in efficient and quantitative cycloaddition to give the cage product (**3**).[7,8] We first thought that this provided the solution to a mechanistic puzzle that we had encountered in previous work;[7,9] namely the formation of (**3**) by irradiation of the dimer (**2d**) in solution. However, subsequent observations compelled us to conclude that a dual mechanism was operative. Solutions of (**1d**) failed to show any photochemical reaction in the range −20 to −70 °C.[9]

The photo-cycloaddition of (**1d**) in the solid can be envisaged either as an eight-centre one-step reaction or, more plausibly, a series of two cycloadditions: ${}_{\pi}4 + {}_{\pi}4$ followed by ${}_{\pi}2 + {}_{\pi}2$, or two consecutive ${}_{\pi}2 + {}_{\pi}2$.

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