The Dimer of 2,3-Dimethyl-3,4-(*o*,*o*′-biphenylene)cyclopentadienone: Thermal and Photochemical Transformations[1]

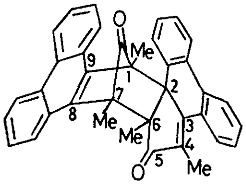
By Benzion Fuchs,* M. Pasternak, and G. Scharf
(*Department of Chemistry, Tel-Aviv University, Tel-Aviv, Israel*)

Summary The title compound (**1**) undergoes a degenerate Cope rearrangement which was studied within the n.m.r. time scale; further thermal and photochemical transformations of (**1**) are also presented.

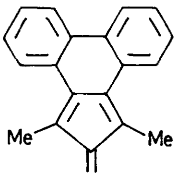
A recent report[2] on the synthesis of the cyclopentadienone dimer (**1**) and of some cycloaddition products of its monomeric unit (**2**), have prompted us to report some properties of (**1**).

The known hydroxy-ketone (**3**)[3] withstood any dehydration attempt[4] to (**2**) but gave with acetic anhydride the rearranged acetates (**4a**) and with acetyl chloride[2] or thionyl chloride the rearranged chlorides (**4b**). The latter underwent rapid and quantitative dehydrochlorination on treatment with alcoholic KOH to give the dimer of 2,5-dimethyl-3,4-(*o*,*o*′-biphenylene)cyclopentadienone (**1**).

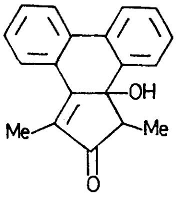
The properties and behaviour of (**1**) are very interesting. While the usual carbonyl absorptions occur as expected[5] at 1690 and 1765 cm^{-1}, it exhibits only two (instead of four[5]) methyl singlets in its n.m.r. spectrum, at τ 8·80 (6H) and 8·32 (6H). Barring the unlikely coincidence of accidental isochronism of two methyl pairs, there is only one explanation for this, a rapid exchange, relative to the n.m.r. time scale, between two methyl pairs. This is possible only by invoking a degenerate [3·3]Cope rearrangement in the *endo*-dimer (**1**), whereby bonds are ruptured and formed simultaneously between the carbons 1,2 and 4,8. We substantiated this hypothesis, by performing variable temperature (100 MHz) n.m.r. spectroscopic measurements of (**1**) down to $-75\,^{\circ}\text{C}$. The low field methyl signal gradually broadened until it was split into two well resolved singlets at τ 8·40 and 7·77 which coalesce at $T_c = 233$ K. The upfield signal at τ 8·80 underwent only appreciable broadening in this process. A comparison of these data with the methyl resonances in various other methyl substituted cyclopentadienone dimers[5] reveals that the above described low-temperature splitting represents exchange of the methyl groups in positions 1 and 4, as implied by the proposed [3·3]Cope rearrangement. Considering the case of the two non-interacting, equally populated sites and using the approximation[6] $\tau_c = \sqrt{2}/\pi\delta = 7{\cdot}2 \times 10^{-3}$ s the rearrangement rate $k_c = 70$ s^{-1} can be calculated. Applying the absolute reaction rate theory, $\Delta G^{\ddagger}_{233} = 4{\cdot}57\, T(10{\cdot}2 + \log T/k) = 11{\cdot}4$ kcal mol^{-1}.



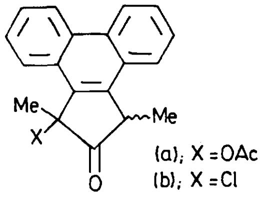
(1)



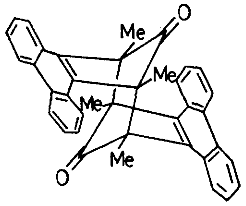
(2)



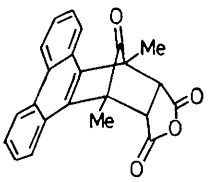
(3)



(4)



(5)



(6)

This behaviour is worthy of comparison with that of other, dissociating[5] and non-dissociating[7] cyclopentadienone dimers. In none of these cases was it possible to detect the thermal Cope rearrangement in the n.m.r. time scale. In the unsubstituted case it can be inferred from deuterium labelling experiments that such a process occurs slowly around 80 °C.

Direct and sensitized (acetone) irradiation of the dimer (**1**) at $\lambda > 300$ nm gives up to 94% of a highly insoluble product, m.p. 312 °C, ν_{max} 1750 cm^{-1}; λ_{max} 254 (ϵ 71,000), 277 (32,000) 296 (17,000) nm; *m/e* 516 (M^+), 258 ($M/2^+$, 100%). The insolubility of the product precluded any n.m.r. measurements but the above data indicate an isomer of (**1**) having bridged carbonyls and phenanthrene rather than biphenyl chromophores (as would be required by cage structures). Structure (**5**) is therefore assigned to this product. Interestingly, (**5**) is also exclusively formed by heating (**1**) at 80 °C and above. Evidently, (**5**) constitutes an energy well which may be reached from (**1**) either by photolysis *via* a triplet excited state or in a thermal ("forbidden") reaction which may indicate a diradical intermediate. This explains why no thermal dissociation of the dimer (**1**) to the monomer (**2**) is ever observed.[2] Moreover, (**1**) was not isolated on thermolysis of (**5**) although when the latter was heated with maleic anhydride the adduct (**6**) was slowly formed. The same anhydride (**6**) was obtained from the dimer (**1**) [or the acetate (**4a**) at higher temperature] with maleic anhydride. We feel compelled to conclude that the coplanar aromatic ring systems in (**1**) stabilize the biradicaloid transition state in positions 1 and 2 (or the allyl radicals 2,3,4 and 1,9,8) while minimizing steric interference[2] for the described rearrangement.

We thank Mrs. Sarah Weinman for technical assistance.

(*Received*, 16*th October* 1975; *Com.* 1162.)

---

[1] For previous papers in this series see, B. Fuchs and G. Scharf, *J.C.S. Chem. Comm.*, 1975, 244.

[2] D. W. Jones, *J.C.S. Chem. Comm.*, 1975, 199.

[3] F. L. C. Baramyovitz and J. E. Downes, B.P. 1,052,951 (*Chem. Abs.*, 1967, **66**, 94727e).

[4] C. F. H. Allen and J. A. Van Allan, *J. Amer. Chem. Soc.*, 1950, **72**, 5165; *J. Org. Chem.*, 1945, **10**, 33 and references therein.

[5] B. Fuchs, B. Pazhenchevsky, and M. Pasternak, *Tetrahedron Letters*, 1972, 3051.

[6] G. Binsch, *Topics Stereochem.*, 1968, **3**, 97.

[7] B. Pazhenchevsky and B. Fuchs, *Tetrahedron Letters*, 1972, 3047; U. Klinsman, J. Gauthier, K. Schaffner, M. Pasternak, and B. Fuchs, *Helv. Chim. Acta*, 1972, **55**, 2643.