The Photosensitized (Electron Transfer) [4e + 2e] Intramolecular Cycloaddition of 1,1,8,8-Tetraphenyl-1,7-octadiene; X-Ray Crystal Structure of 4a,9a-*trans*-4a,10-*trans*-1,2,3,4,4a,9,9a,10-Octahydro-9,9,10-triphenylanthracene

Dino Mangion,[a] **Robert M. Borg***[a] **and William Errington**[b]

[a] *Department of Chemistry, University of Malta, Msida, Malta MSD 06*
[b] *Department of Chemistry, University of Warwick, Coventry, UK CV4 7AL*

Irradiation of 1,1,8,8-tetraphenyl-1,7-octadiene in the presence of the electron transfer photosensitizer 1,4-dicyanobenzene results in the formation of a [4e + 2e] cycloadduct, the structure of which is determined by X-ray crystallographic analysis to be 4a,9a-*trans*-4a,10-*trans*-1,2,3,4,4a,9,9a,10-octahydro-9,9,10-triphenylanthracene.

Since its original discovery in 1973 by Neunteufel and Arnold,[1] the photoinduced intermolecular [4e + 2e] cycloaddition reaction of 1,1-diphenylethene has been extensively investigated. The proposed photosensitized electron transfer mechanism has been fully rationalized and the scope of the reaction has been extended to the use of several other photosensitizers and co-sensitizers as well as other aryl-alkenes and -alkynes.[2]

However, in sharp contrast to the 1,1-diarylethenes, it has been reported that 1,1-diphenylpropene does not undergo a [4e + 2e] cycloaddition reaction under similar conditions.[3a] This lack of reactivity has been attributed to the inability of the alkene to dimerize to a 1,4-radical cation as a consequence of steric hindrance caused by the methyl groups.[3b,c] We now report that 1,1,8,8-tetraphenyl-1,7-octadiene **1**, a molecule that possesses the essential structural elements of 1,1-diphenylpropene (and which would therefore presumably also exhibit a similar steric effect), *does* undergo such a [4e + 2e] cycloaddition reaction in high yield.

Irradiation of a 3:1 acetonitrile–benzene mixture of 1,1,8,8-tetraphenyl-1,7-octadiene **1**, (0.05 mol dm^{-3}) and 1,4-dicyanobenzene **2**, (0.10 mol dm^{-3}) for 30 h with a 400 W medium pressure mercury lamp through Pyrex (λ > 280 nm) under a nitrogen atmosphere, resulted in the complete conversion of **1** to a single product as indicated by GC monitoring. Hexane extraction of the photolysate after removal of solvent, followed by short column chromatography (silica gel) and recrystallization from propanol–water afforded a white crystalline material in 87% yield. The photosensitizer was recovered completely. Dark controls established the photochemical nature of the process. The photoproduct was identified as 4a,9a-*trans*-4a,10-*trans*-1,2,3,4,4a,9,9a,10-octahydro-9,9,10-triphenylanthracene **3** (Scheme 1) by spectroscopic techniques.† The stereochemistry was determined as *trans*, *trans* from selective homonuclear decoupling NMR experiments which established that proton 4a-H was coupled to 9a-H and 10-H with the large coupling constants (*ca.* 10–12 Hz) typical of antiperiplanar coupling.[4] However, because this assignment was not unequivocal, the stereochemical structure was confirmed by X-ray crystallographic analysis (Fig. 1).‡

In accordance with the established mechanism for the [4e + 2e] photocycloaddition of 1,1-diphenylethene,[1] we are suggesting that a photoinduced single electron transfer (SET) mechanism is also operative in this case (Scheme 2). Whether the initial SET step occurs from the first excited singlet of either **1** or **2** (^{1}**1*** or ^{1}**2*** respectively) is not clear since both sensitizer and diene absorb competitively under the reaction conditions. Presumably, both pathways contribute initially to the overall mechanism, though the SET step involving ^{1}**2*** probably dominates as the reaction proceeds and **1** is consumed. Evidence for an SET mechanism stems from the observation that the reaction requires the presence of a polar solvent (acetonitrile) to occur.§ Reactions carried out in non-polar benzene solution did not result in any formation of **3**. Unfortunately, direct evidence for the involvement of the first excited singlet state of the sensitizer could not be obtained from Stern–Volmer-type fluorescence quenching measurements due to complications arising from the above-mentioned competitive absorption by

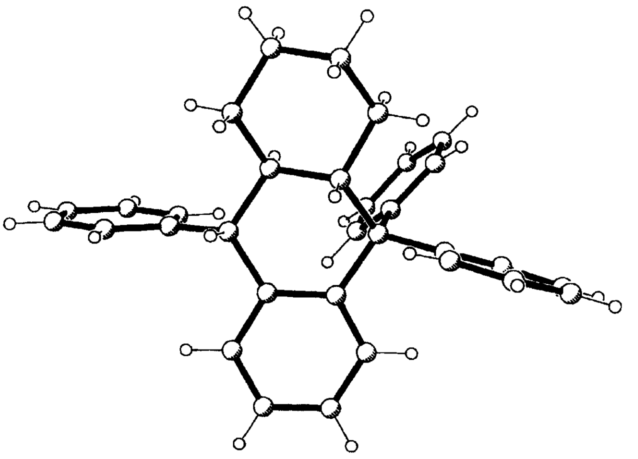
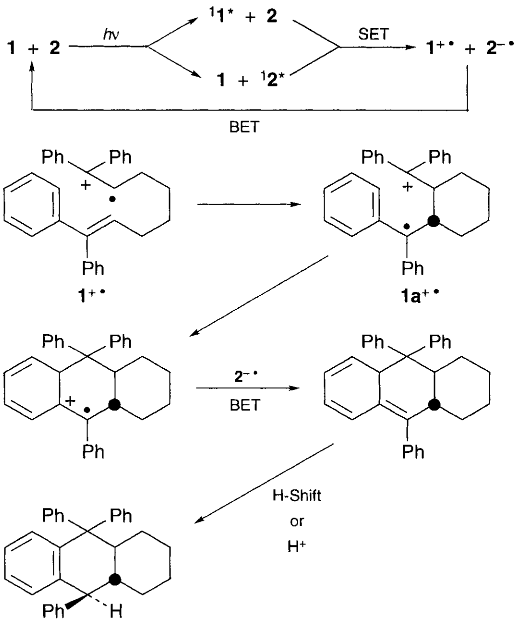
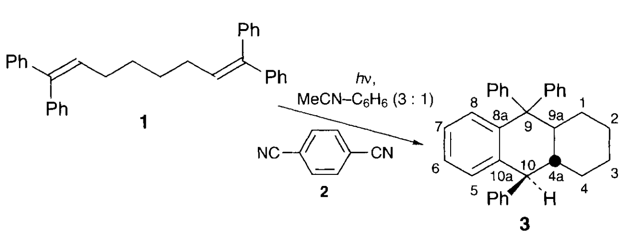


Fig. 1 X-ray crystallographic structure of **3**



Scheme 2



Scheme 1

the diene quencher. However, it should be noted that an SET mechanism should be feasible thermodynamically since the free-energy change (ΔG) for the photoinduced SET process is estimated, by means of the Rehm–Weller equation, to be exothermic (*ca.* -90 kJ mol^{-1}).[¶]

The possibility of an unsensitized mode of reactivity is ruled out by the observation that irradiation of **1** in the absence of **2** failed to give **3**. In fact, other well-known electron-acceptors such as 9,10-dicyanoanthracene, 1-cyanonaphthalene and 2-cyanonaphthalene have also been found to sensitize the reaction, though not as efficiently as **2**. These results also eliminate the possibility of a mechanism involving singlet–singlet *energy* transfer, since these sensitizers possess lower first excited singlet state energies than that of **1**.

A key step is the cyclization of the 1,2-radical cation of **1** to give the 1,4-radical cation $\mathbf{1a}^{+\cdot}$ in a *trans* fashion.[||] This then undergoes a second ring closure *via* electrophilic attack on an aromatic ring. Back electron transfer (BET), followed by re-aromatization (either *via* a hydrogen shift, or acid catalysis) leads to the final product. It is noteworthy that of four possible diastereoisomers, only one is formed. This stereoselectivity has interesting mechanistic implications and ongoing studies in our laboratories are focusing on this aspect.[**]

We are also evaluating the effect of the methylene chain length on the reactivity of the alkadienes. Preliminary investigations involving 1,1,7,7-tetraphenyl-1,6-heptadiene indicate that this alkadiene undergoes an analogous cycloaddition reaction when photosensitized by **2**. This is an intriguing result since other workers have reported that the 9,10-dicyanoanthracene-sensitized irradiation of this heptadiene does not lead to the formation of a cyclic 1,4-radical cation.[3c]

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Footnotes

[†] *Spectroscopic data* for **3**: mp 185 °C (decomp.); ^{1}H NMR (250 MHz, C_6D_6) δ 0.53 (m, 3ax-H), 0.91 (m, 4ax-H), 1.09 (m, 2ax-H), 1.29 (m, 1ax-H), 1.32 (m, 3eq-H), 1.51 (m, 2eq-H), 1.67 (m, 4eq-H), 1.76 (m, 4a-H), 1.88 (m, 1eq-H), 2.72 (t of d, 9a-H), 3.73 (d, 10-H), 6.73–7.55 (m, aromatic H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 25.8 (t), 26.7 (t), 28.8 (t), 33.8 (t), 39.7 (d), 47.2 (d), 56.0 (d), 58.2 (s), 125.9 (d), 126.0 (d), 126.1 (d), 126.2 (d), 126.3 (d), 126.4 (d), 127.8 (d), 128.4 (d), 129.4 (d), 129.8 (d), 129.9 (d), 130.7 (d), 132.8 (d), 140.4 (s), 143.3 (s), 144.1 (s), 146.0 (s), 146.8 (s); IR (NaCl) ν_{max}/cm^{-1} 3055, 3025, 2930, 2850, 1600, 1490, 1445, 1220, 1035, 755; MS (GC/ITD) *m/z* (rel. int.) 414(29), 332(100), 255(96), 179(18), 165(19), 91(44).

[‡] *Crystal data* for **3**: $C_{32}H_{30}$, $M = 414.56$, triclinic, $a = 9.503(7)$, $b = 9.543(5)$, $c = 13.885(9)$ Å, $\alpha = 77.38(5)°$, $\beta = 71.65(5)°$, $\gamma = 75.78(5)°$, $U = 1144.8(13)$ Å^3 (by least-squares refinement on diffractometer angles for 17 automatically centred reflections), $T = 220(2)$ K, $\lambda = 0.71073$ Å, space group $P\bar{1}$, $Z = 2$, $D_c = 1.203$ Mg m^{-3}, $F(000) = 444$. Colourless block with dimensions $0.21 \times 0.15 \times 0.11$ mm, μ(Mo-Kα) = 0.068 mm^{-1}. Data were collected using a Siemens P3R3 diffractometer in the range $4 < 2\theta < 46°$. Refinement was by full-matrix least-squares on F^2 for all data (3217) using SHELXL-93.[5] Anisotropic temperature factors were used for all carbon atoms; H-atoms were given isotropic temperature factors equal to 1.2 times the equivalent isotropic displacement parameter of the atom to which they are attached. Conventional R [for $I > 2\sigma(I)$] = 0.0781 and $wR2$ = 0.2010 (all data). Largest difference peak and hole 0.204 and -0.239 e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

[§] A 3 : 1 acetonitrile–benzene mixture is used rather than acetonitrile alone due to the low solubility of **1** in the latter solvent.

[¶] Determined by means of the Rehm–Weller equation: $\Delta G = 96.5\ (E_{\frac{1}{2}ox} - E_{\frac{1}{2}red} - \Delta_{o,o})$ kJ mol^{-1}.[6] $E_{\frac{1}{2}ox}$ (**1**) can be assumed to be similar to that of 1,1,7,7-tetraphenyl-1,6-heptadiene (1.29 V *vs.* Ag/Ag$^+$ in MeCN).[3c] $E_{\frac{1}{2}red}$ (**2**) = -2.00 V (*vs.* Ag/Ag$^+$ in MeCN),[7] $\Delta_{o,o}$ (**1**) $\approx$ $\Delta_{o,o}$ (**2**) $\approx$ 4.25 V.

[||] The initial ring closure in a *trans* fashion of the radical cations of similar dienes has been reported elsewhere.[3c]

[**] A stepwise stereoselective [2e + 2e] cycloaddition of dienes *via* a 1,4-radical cation has been reported recently.[8]

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