

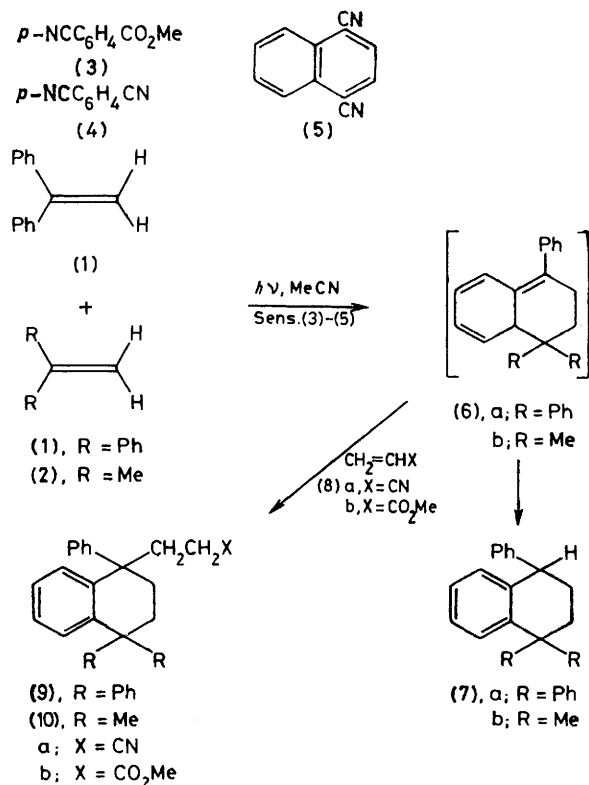
Photosensitized (Electron Transfer) [2e + 4e] Dimerization and Cross-cycloaddition of Phenylated Olefins: Trapping the Intermediate

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Summary If the photosensitized (electron transfer) dimerization of 1,1-diphenylethylene or cross-cycloaddition of 1,1-diphenylethylene with methylpropene is carried out in the presence of acrylonitrile or methyl acrylate, alkylated tetrahydronaphthalenes are obtained, consistent with trapping of the intermediate triene *via* an 'ene' reaction.

THE photosensitized (electron transfer) [2e + 4e] cyclo-dimerization¹ of phenylated olefins and the related cross-cycloaddition² of phenylated and alkylated olefins have been reported. In the mechanism proposed^{1,2} for these reactions, the triene (6) (Scheme) is an intermediate which gives the tetrahydronaphthalene derivative (7) upon re-aromatization. We have attempted to 'trap' (6) with the electron-poor eneophiles acrylonitrile (8a), and methyl acrylate (8b).



SCHEME

Sensitizer	% Yield			
	(9a)	(9b)	(10a)	(10b)
(3)	34	37	10	14
(4)	—	40	8	11
(5)	45	45	—	—

† Medium pressure Hg lamp, 1 kW (G.E.), Pyrex filter.

‡ New compounds; elemental analyses $\pm 0.3\%$.

When we irradiated† solutions of 1,1-diphenylethylene (1) and (8a or b) in acetonitrile, in the presence of a photosensitizer (electron transfer), little of the cyclodimerization product 1,1,4-triphenyltetrahydronaphthalene (7a) was formed.¹ Instead, a new crystalline product (9a or b)‡ was isolated (column chromatography on silica gel) in good

TABLE 1. Calculated free energy change for the electron transfer process.

Sensitizer (Acceptor)	Singlet energy /kJ mol ⁻¹	ΔG_{calc}^a for electron transfer /kJ mol ⁻¹			
		(1)	(2)	(8a)	(8b)
(3)	398	-58	+21	+146	+117
(4)	408	-79	ca. 0	+125	+96
(5)	361	-63	+17	+142	+113

^a Using the Weller equation (D. Rehm and A. Weller, *Isr. J. Chem.*, 1970, **8**, 259): $\Delta G = 96.4 [E(D/D^+)_{\text{v}} - E(A/A^-)_{\text{v}} - e^2/\epsilon a] - \Delta E_{0,0}$ /kJ mol⁻¹.

yield. Similarly, irradiation of a solution of (1) and (8a or b) in acetonitrile, saturated (excess) with methylpropene (2), afforded (10a or b)‡ as a colourless oil. Traces of the cross-adduct 1,1-dimethyl-4-phenyltetrahydronaphthalene² (7b) were also produced. The sensitizer was largely recovered in all cases.

The proof for the structures of these new compounds rests predominantly on their i.r., ¹H n.m.r., and ¹³C n.m.r. spectra, interpreted by comparison with the spectra of (7a and b). In the ¹H n.m.r. spectra of (9) and (10), the bis-benzylic proton of (7) (τ , δ 4.1, J 4–5 Hz) is replaced by a complex multiplet (δ 2.0–2.8), and the aliphatic carbon region of the uncoupled ¹³C n.m.r. spectra, which shows two triplets, one doublet, and a singlet for (7) [as well as an

TABLE 2. Half-wave oxidation and reduction potentials.

Compound	$-E_{\frac{1}{2}}^{\text{Red}}/\text{V}$	$E_{\frac{1}{2}}^{\text{Ox}}/\text{V}$
(3)	2.1 ^a	—
(4)	2.0 ^a	—
(5)	1.7 ^a	—
(1)	—	1.5 ^{a,b}
(2)	—	ca. 2.3 ^{c,d}
(8a)	2.7 ^{a,b}	ca. 3.6 ^{c,e}
(8b)	2.6 ^{a,b}	ca. 3.3 ^{c,e}

^a Cyclic voltammetry on Pt electrode, tetraethylammonium perchlorate (TEAP, 0.1M) in acetonitrile solution, vs. Ag/0.1M AgNO₃. Taken as 0.028 V before the anodic peak potential and 0.029 V before the cathodic peak potential (R. S. Nicholson and I. Shain, *Anal. Chem.*, 1964, **36**, 706.) ^b The electron-transfer process was irreversible. ^c Obtained from the ionization potentials by the use of $E_{\frac{1}{2}}^{\text{Ox}} = 0.827 \times \text{I.P.} - 5.40$ V (W. C. Nerkam, G. R. Dimeler, and M. M. Desmond, *J. Electrochem. Soc.*, 1964, **111**, 1190). ^d I.P. from T. S. Cantrell, *J. Org. Chem.*, 1977, **42**, 4238. ^e I.P. from M. A. M. Meester, H. van Dam, D. J. Stufkens, and A. Oskam, *Inorg. Chim. Acta*, 1976, **20**, 155.

additional pair of quartets for (**7b**), has four triplets and two singlets for (**9**) and (**10**). These structures are also consistent with elemental analysis and mass-spectra data.

Considering the complexity of the mechanistic scheme for the formation of (**9**) and (**10**), it is noteworthy that (**8a** and **b**) apparently do not become involved at some stage except for the trapping of the methylene cyclohexadiene (**6**). This is consistent with the positive calculated free energy change for the electron-transfer process between the excited singlet of the photosensitizers (acting as electron acceptors) and (**8a** or **b**) (Table 1). Since the reduction potentials of (**8a** and **b**) are greater (*i.e.* more negative) than those of the sensitizers (Table 2), it is unlikely that the radical anion of any of the latter will transfer an electron to

(**8a** or **b**). The proposed 'ene' reaction, and the lack of formation of a Diels-Alder adduct, has analogy in a closely related system.³

In conclusion, we point out that, in view of the reasonable yields of (**9a** and **b**) and the simplicity of the procedure, and since this type of compound is not readily available by other methods, this reaction has synthetic utility.

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¹ R. A. Neunteufel and D. R. Arnold, *J. Am. Chem. Soc.*, **1973**, **95**, 4080.

² A. J. Maroulis and D. R. Arnold, *J. Chem. Soc., Chem. Commun.*, **1979**, 351.

³ R. W. R. Humphreys and D. R. Arnold, *J. Chem. Soc., Chem. Commun.*, **1979**, 793