

## Photosensitized (Electron Transfer) [2e + 4e] Cross-cycloaddition of Alkylated Olefins to Phenylated Olefins

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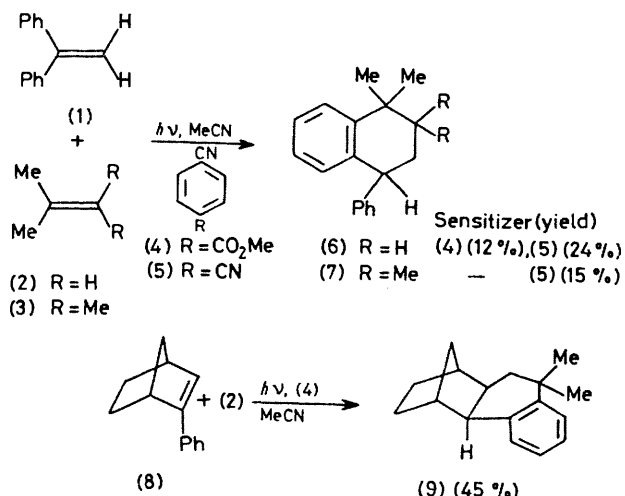
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*Summary* The [2e + 4e] cross-cycloaddition products are formed when an acetonitrile solution of 1,1-diphenylethylene or 2-phenylnorbornene and isobutene or 2,3-dimethylbut-2-ene is irradiated in the presence of the photosensitizers (electron transfer) methyl *p*-cyano-benzoate or 1,4-dicyanobenzene.

CYCLODIMERIZATION of phenylated olefins occurs *via* [2e + 4e] cycloaddition when the phenylated olefins are irradiated in the presence of an electron acceptor sensitizer.<sup>1</sup> There are few examples of cross-photocycloaddition and all of them proceed *via* [2e + 2e] cycloaddition.<sup>2</sup> We here describe the first examples of [2e + 4e] cross-cycloaddition

involving an alkylated and a phenylated olefin *via* photo-sensitization (electron transfer).

Irradiation† of an acetonitrile solution of 1,1-diphenylethylene (1) or 2-phenylnorbornene (8), saturated with isobutene (2), in the presence of methyl *p*-cyanobenzoate (4) or 1,4-dicyanobenzene (5), gave the cross-cycloadducts (6)‡ and (9)‡, respectively. Similarly, irradiation of (1) and



2,3-dimethylbut-2-ene (excess) (3) in acetonitrile and in the presence of (5) yielded (7).‡ This reaction also gave 1,1,4-triphenyl-1,2,3,4-tetrahydronaphthalene (19%), a small amount of the [2e + 2e] cycloaddition product, 1,1,2,2-tetramethyl-3,3-diphenylcyclobutane‡ (6%), 2,3-dimethyl-5,5-diphenylhex-2-ene‡ (4%), and 2% of a 4:1 mixture of 2,3,6,7-tetramethylocta-2,6-diene and 2,3,3,4,4,5-hexamethylhexa-1,5-diene. The sensitizer (5) was largely consumed in this case to give 2,3-dimethyl-1-(4-cyanophenyl)but-2-ene‡ (34%) and 2,3-dimethyl-3-(4-cyanophenyl)but-1-ene‡ (22%).

The structural assignments for the new compounds were based on analysis of their spectra (i.r., n.m.r., and mass). In the case of (9) the analysis of the <sup>13</sup>C n.m.r. spectrum was

particularly useful. Signals at 29.8 and 29.5 p.p.m., assigned to C-5 and C-6 may be compared to the corresponding nuclei of norbornane (29.7 p.p.m.). Since it is known that the presence of *endo* alkyl substituents in the 2- and 3-positions cause considerable shielding at C-5 and C-6, we conclude that the junction with the norbornane system in the cross-cycloadduct (9) is *exo-exo*.<sup>3</sup>

The mechanism we propose for these [2e + 4e] cross-photocycloadditions is similar to that suggested for the dimerization of (1).<sup>1a</sup> The key step involves electron transfer from the phenylated olefins (1) or (8) to the singlet excited state of the sensitizers (4) or (5). Attack by the radical cation of the phenylated olefin on the alkylated olefin is followed by closure to a strain-free, delocalized radical cation. Back electron transfer from the sensitizer radical anion and rearomatization complete the sequence.

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

Sensitizer	Singlet energy/ kJ mol <sup>-1</sup>	$\Delta G_{\text{calc}}/\text{kJ mol}^{-1a}$			
		(1)	(2)	(3)	(8)
(4)	398	-59	-98	+20	-44
(5)	408	-78	-117	-0	-64

<sup>a</sup> Using the Weller equation (D. Rehm and A. Weller, *Israel J. Chem.*, 1970, **8**, 259):  $\Delta G = 96.4[E(D/D^+)_{\text{v}} - E(A/A^-)_{\text{v}} - e^2/\epsilon a] - \Delta E_{0,0}/\text{kJ mol}^{-1}$ . The oxidation potentials of (1) and (8) and the reduction potentials of (4) and (5) were taken from A. J. Maroulis, Y. Shigemitsu, and D. R. Arnold, *J. Amer. Chem. Soc.*, 1978, **100**, 535. The oxidation potentials of (2) and (3) were calculated from their ionization potentials with the aid of the equation:  $E_{1/2}^{\text{ox}} = 0.827 \text{ I.P.} - 5.40 \text{ V}$  (W. C. Nerkam, G. R. Dimeler, and M. M. Desmond, *J. Electrochem. Soc.*, 1964, **111**, 1190).

Electron transfer from the phenylated olefins to the sensitizer singlet is favourable in every case (see Table). The poorer yield of cross-photocycloaddition product and the consumption of photosensitizer<sup>4</sup> observed with (3) in contrast to (2) may result from reactions of the radical cation of (3), since the electron transfer process is also favourable in this case.

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† The irradiation source was a 1 kW medium pressure mercury vapour lamp with a Pyrex filter. The temperature was kept at 10 °C. Products were isolated by column and semi-preparative vapour phase chromatography.

‡ New compounds; satisfactory combustion analyses or exact mass measurements were obtained.

<sup>1</sup> (a) R. A. Neunteufel and D. R. Arnold, *J. Amer. Chem. Soc.*, 1973, **95**, 4080; (b) T. Asanuma, M. Yamamoto, and Y. Nishijima, *J.C.S. Chem. Comm.*, 1975, 608.

<sup>2</sup> T. S. Cantrell, *Chem. Comm.*, 1970, 1633; R. G. Solomon and J. K. Kochi, *J. Amer. Chem. Soc.*, 1974, **96**, 1137.

<sup>3</sup> J. B. Stothers, C. T. Tan, and K. C. Teo, *Canad. J. Chem.*, 1973, **51**, 2893.

<sup>4</sup> A. Yashino, K. Yamasaki, and T. Yonezawa, *J.C.S. Perkin I*, 1975, 735.