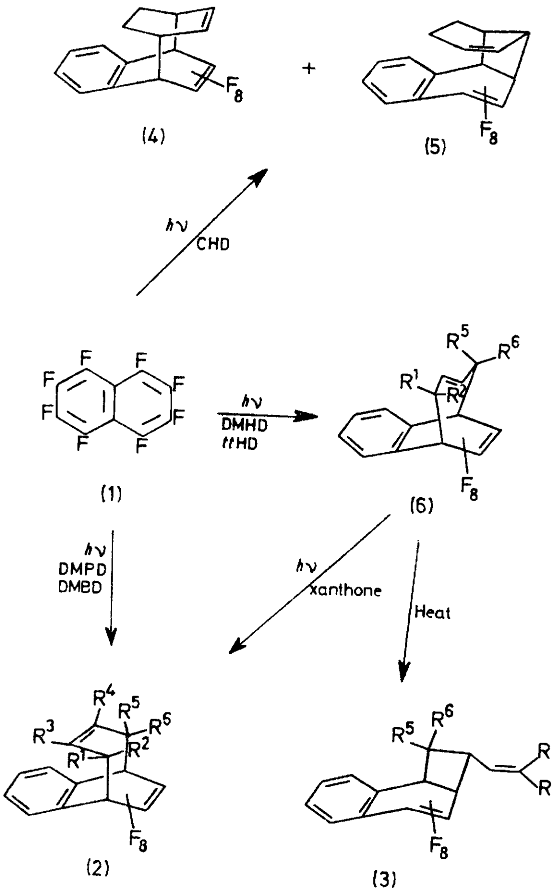
Dual Photochemical Behaviour of Octafluoronaphthalene towards Conjugated Dienes. An Example of a Solvent-induced Potential Surface Crossing

By JACQUELINE LIBMAN

(*Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot, Israel*)

Summary The photochemical behaviour of octafluoronaphthalene towards conjugated dienes is shown to exhibit a pronounced solvent dependence which is explained in terms of the formation of exciplexes in non-polar solvents and solvated charge-transfer complexes or ion pairs in polar solvents.

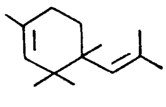
SPECTROSCOPIC and kinetic investigations by Weller[1] provided evidence for the formation of excited charge-transfer complexes, which are deactivated *via* exciplex emission in non-polar solvents, but *via* electron transfer in polar solvents. The behaviour of exciplexes[2] and the effect of solvent on the nature of exciplexes, their molecular composition,[3] electronic structure,[4] and physical deactivation modes[5] has since become a topic of increasing interest. An empirical equation for the relationship between ionic photodissociation of exciplexes and solvent polarity has recently been formulated.[6] Moreover a theoretical model has been described treating photochemical electron-transfer processes as potential energy surface crossing which may be solvent-assisted.[7] This communication deals with the dual photochemical behaviour of octafluoronaphthalene (**1**) in the presence of conjugated dienes in cyclohexane and acetonitrile solution.

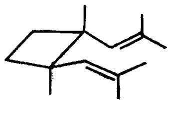


a; $R^1 = R^2 = R^4 = Me$; $R^3 = R^5 = R^6 = H$
b; $R^3 = R^4 = Me$; $R^1 = R^2 = R^5 = R^6 = H$
c; $R^1 = R^2 = R^5 = R^6 = Me$, $R^3 = R^4 = H$
d; $R^1 = R^6 = Me$; $R^2 = R^3 = R^4 = R^5 = H$

SCHEME

Irradiation of a solution of (**1**) (0·025 M) and 2,4-dimethylpenta-1,3-diene (DMPD) (0·5 M) in cyclohexane with a medium-pressure mercury lamp, Pyrex filter, at 10 °C yielded a 1 : 1 mixture of addition products (**2a**) (m.p. 141—143 °C) and (**3a**) (m.p. 78—79·5 °C) in 80% yield, which were isolated by chromatography and separated by fractionating crystallization. Octafluoronaphthalene (**1**) reacted under analogous conditions with cyclohexa-1,3-diene (CHD) to give addition products (**4**) (37%; m.p. 132—135 °C) and (**5**) (24%; m.p. 68—73 °C), and with 2,3-dimethylbuta-1,3-diene (DMBD) to give adduct (**2b**) (60%; m.p. 147—149 °C). 2,5-Dimethylhexa-2,4-diene (DMHD) and *trans,trans*-hexa-2,4-diene (*tt*HD) added to photoexcited (**1**) at −20 °C to give the labile products (**6c**) and (**6d**) respectively, which were characterized by their n.m.r. spectra at −20 °C. Adducts (**6c**) and (**6d**) underwent smooth Cope rearrangements to the bicyclic compounds (**3c**) (m.p. 112·5—113·5 °C) and (**3d**) (oil) respectively upon heating, and efficient *trans-cis*-isomerization to (**2c**) (m.p. 95—97 °C) and (**2d**) (m.p. 82—84 °C) upon photosensitization with xanthone.†


(7)


(8)

Irradiation of an acetonitrile solution of (**1**) (0·025 M) and DMPD (0·5 M) with a medium-pressure mercury lamp through a Pyrex filter at 5 °C resulted in slow conversion of (**1**) but rapid consumption of DMPD. Three photoproducts were isolated by chromatography on silica gel and preparative gas chromatography: the adduct (**2a**) (54%) and the diene dimers (**7**)‡ and (**8**) in an 8 : 1 ratio (53·5%). Pyrolysis of (**8**) at 185 °C for 12 h gave DMPD and the dimer (**7**).

Diene dimers were also obtained upon photolysis of (**1**) in the presence of CHD, DMBD, and *tt*HD in varying chemical and quantum yields. Naphthalene reacts photochemically with conjugated dienes to give addition products in ben-

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† All new compounds except the labile adducts (**6c**) and (**6d**) were characterized by their spectroscopic and analytical properties including their ^{19}F n.m.r. spectra, which will be described elsewhere.

‡ The ^{13}C n.m.r. spectra showed triplets for the methylene carbon atoms with higher order splitting indicating that the two methylene groups are adjacent to each other.

TABLE. Quenching of octafluoronaphthalene (**1**) fluorescence by conjugated dienes and quantum yields (Φ) for photoreaction of (**1**) with conjugated dienes

Diene	Ionization potential/eV of diene[a]	Solvent	Quenching constant $k_q\ \tau$/mol^{-1}	Φ for consumption of (**1**)[b]	Φ for diene dimerization[b]
DMHD	7·46	C_6H_{12}	42·6[c]	0·46[e]	—
		MeCN	44[c]	<0·01[e]	—
CHD	7·88	C_6H_{12}	26·6[c]	0·39[e]	<0·05[e]
		MeCN	25·3[c]	0·03[e]	0·46[e]
DMPD		C_6H_{12}	16[d]	0·47[e]	<0·05[e]
		MeCN	16[d]	0·10[e]	0·39[e]
*tt*HD	8·03	C_6H_{12}	30·6[c]	0·43[e]	<0·005[e]
		MeCN	26·6[c]	0·085[e]	0·17[e]
DMBD	8·54	C_6H_{12}	0·53[d]	0·24[f]	<0·05[f]
		MeCN	0·49[d]	0·24[f]	<0·05[f]

[a] D. A. Labianca, G. N. Taylor, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1972, **94**, 3679. [b] The quantum yields were measured on a merry-go-round apparatus with benzophenone–benzhydrol as actinometer; excitation wavelength 313 nm; concentration of (**1**) 0·025 M. [c] Ref. 10. [d] This work. The slope of the Stern–Volmer plot for the fluorescence quenching of (**1**) (5×10^{-4} M) by dienes; excitation wavelength 313 nm. [e] Diene concentration 0·5 M. [f] Diene concentration 2·0 M.

zene.[8] Irradiation of naphthalene with DMPD in acetonitrile gave also addition products accompanied by traces of diene dimers.

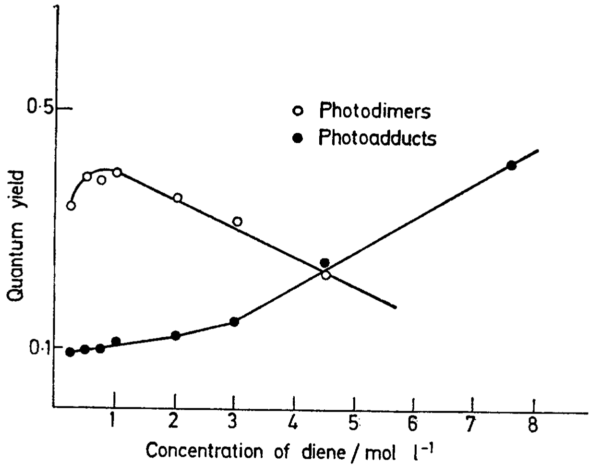

FIGURE. Photochemical reactions of (**1**) in the presence of DMPD. ○ Photodimers; ● photoadducts.

The efficiencies by which conjugated dienes quench the fluorescence of (**1**) are similar in cyclohexane and acetonitrile solution, while the efficiencies of the addition of conjugated dienes to photoexcited (**1**) depend strongly on the solvent (Table). Thus the quantum yields for the addition of dienes to photoexcited (**1**) are high in cyclohexane solution and do not vary appreciably with the dienes used, but they are lower in acetonitrile solution and decrease gradually as the ionization potentials of the dienes decrease. Furthermore, diene dimerization does not occur in cyclohexane solution (Φ <0·05), while becoming a process of increasing importance in acetonitrile solution as the ionization potential of the diene decreases. The concentration dependence of the addition and the dimerization reactions for the system (**1**)–DMPD in acetonitrile solution indicates that these two transformations are competitive processes involving different precursors (Figure)

The high efficiencies for the addition of dienes to (**1**) in cyclohexane and for the dimerization of dienes in acetonitrile under conditions where most of the fluorescence of (**1**) is quenched by the respective dienes indicate that the primary process in both transformations is the formation of collision complexes between the two components. In cyclohexane solution exciplex formation and subsequent chemical deactivation *via* bond formation may successfully compete with a variety of other deactivation modes to give addition products. The recently observed exciplex emission from the (**1**)–DMHD[10] system provides support for the possible intermediacy of excited complexes in these additions. The qualitative correlation between the quantum yield for the diene dimerization§ and the ionization potential of the diene in acetonitrile at the expense of diene addition to (**1**) suggest that the dimerization involves the intermediacy of solvated charge-transfer complexes or ion pairs. Their formation may be attributed to the occurence of a solvent-induced crossing between the covalent and ionic potential energy surface of the (**1**)-diene system in acetonitrile.[7]

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§ The failure of DMHD to form dimers in acetonitrile may be attributed to steric hindrance of the terminal methyl groups.

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