Role of Excited Complexes in the Photochemical Sensitization of Hexa-2,4-dienes by Octafluoronaphthalene

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Summary The chemical behaviour of isomeric hexa-2,4-dienes upon photosensitization with octafluoronaphthalene demonstrates that charge-transfer interactions between octafluoronaphthalene and dienes do not result in enhanced intersystem crossing.

THE photochemical dimerization of conjugated dienes sensitized by octafluoronaphthalene (**1**) in acetonitrile solution has been demonstrated to involve charge-transfer processes where (**1**) acts as an electron acceptor and the dienes as electron donors.[1] The immediate precursor of the dimeric products may be either (i) a two-or three-component excited charge-transfer complex between OFN and the diene, or (ii) triplet state diene. The latter possibility has to be considered in view of the reported intersystem crossing of some charge-transfer complexes[2] and exciplexes[3] resulting in the formation of either component in the triplet state. In order to distinguish between these two possibilities the sensitization by (**1**) of each of the three isomeric hexa-2,4-dienes in comparison with the benzophenone triplet sensitization of these dienes in acetonitrile solution was investigated. These dienes were chosen as chemical probes since their behaviour in the excited singlet and triplet state is well established.[4]

TABLE

(a) Reactions of hexa-2,4-dienes with photoexcited octafluoronaphthalene (**1**)

Diene	Quenching constant $k_{q}\tau$/l mol^{-1} [a]		Quantum yields Φ		
			Disappearance of (**1**)[b,c]		Dimerization[b,c,d]
	C_6H_{12}	MeCN	C_6H_{12}	MeCN[e]	MeCN[e]
(**2a**)	26·6[f]	30·6[f]	0·43	0·09	0·155
(**2b**)	16	22	0·43	0·125	0·18
(**2c**)	12·3[f]	21	0·47	0·06	0·045

(b) Quantum yields, Φ, for isomerization in MeCN[e]

	Sensitization by (**1**)[b,c,d]	Sensitization by benzophenone[b,g,h]
(**2a**) → (**2b**)	0·53	0·47
(**2a**) → (**2c**)	<0·05	0·20
(**2b**) → (**2a**)	0·31	0·39
(**2b**) → (**2c**)	*ca.* 0·05	0·19
(**2c**) → (**2b**)	0·83	0·47
(**2c**) → (**2a**)	0·23	0·38

[a] The slope of the Stern–Volmer plot of the fluorescence quenching of (**1**) (5×10^{-4}); excitation wavelength 313 nm. [b] The quantum yields were determined on a merry-go-round apparatus with benzophenone–benzhydrol as actinometer: excitation wavelength 313 nm. [c] (**1**) concentration: 0·025 M; diene concentration: 0·5 M. [d] G.l.c. analysis with column a, 20% Carbowax on Chromosorb P, 1/8 in × 15ft. [e] 4% (v/v) methylcyclohexane as internal standard. [f] N. C. Yang and D. M. Shold, unpublished results. [g] Benzophenone concentration: 0·1M; diene concentration: 0·5M. [h] G.l.c. analysis with column b, 25% ββ′-oxydipropionitrile on chromosorb P, 1/8 in x 15ft.

Irradiation of solutions in MeCN of (**1**) (0·025 M) in the presence of either *trans,trans*-(**2a**), *trans,cis*-(**2b**), or *cis,cis*-hexa-2,4-diene (**2c**) (0·5 M) with a medium-pressure mercury lamp, Pyrex filter, at −5 °C resulted in rapid consumption of the dienes and slow conversion of (**1**). G.l.c. analysis in conjunction with mass spectral analysis of the crude irradiation products on column (a) (see footnotes to Table) showed the formation of different mixtures (A, B, and C) of diene dimers (M^+, *m/e* 164, base peak *m/e* 82) from each of the isomeric hexa-2,4-dienes. The mixtures A, B, and C were isolated and fully hydrogenated to give different mixtures (A′, B′, and C′) of hydrogenation products, each of the hydrocarbons exhibiting an M^+ peak at *m/e* 168. These *m/e* values demonstrate that the dimers are monocyclic compounds.†

G.l.c. analyses of the neat reaction mixtures on column (b) established the occurence of double bond isomerization in competition with diene dimerization. The quantum yields for the dimerization and isomerization of the dienes and for the consumption of (**1**) are summarized in the Table as are the quenching constants for the quenching of the fluorescence of (**1**) by these dienes.

Photolysis of (**1**) in cyclohexane solution in the presence of either (**2a**), (**2b**), or (**2c**) under analogous conditions yielded addition products of the dienes to (**1**), but no dimerization was observed.

Irradiation of solutions in MeCN of benzophenone (0·1 M) in the presence of either diene (**2a**), (**2b**), or (**2c**) (0·5 M) with the same light source (Pyrex filter) resulted in rapid isomerization (Table) of the dienes and sluggish formation of diene dimers. The reaction mixtures were analysed by g.l.c. (columns a and b) at time intervals of between 2 and 4 h until the photostationary state of the isomerization process had been reached. The g.l.c. traces (column a) showed the formation of similar mixtures of diene dimers, independent of the diene used and of the percentage of diene converted.

On the basis of kinetic investigations it had been suggested that the photodimerization of conjugated dienes induced by (**1**) proceeds *via* the intermediacy of excited charge-transfer complexes or ion pairs.[1] The formation of different dimers upon sensitization by (**1**) of isomeric hexa-2,4-dienes in contrast to the formation of identical dimers upon benzophenone triplet sensitization demonstrates that different intermediates are involved in these two sensitization processes. This conclusion is confirmed by the observation that the relative efficiencies for the formation of either of the two isomers from each of the hexa-2,4-dienes are different with sensitization by (**1**) and benzophenone. Thus triplet-state diene does not play an important role in the dimerization of dienes induced by (**1**) and, if charge-transfer complexes are formed between (**1**) and the dienes, intersystem crossing does not constitute a significant relaxation mode for these systems. The formation of different mixtures of hydrocarbons upon hydrogenation of photodimers derived from the isomeric hexa-2,4-dienes (**2a**), (**2b**), or (**2c**) illustrates that the geometry of the diene is partially retained during the dimerization and determines the structure of the products.

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† The diene dimers were not fully characterized owing to the difficulty in separating the mixtures on a preparative scale.

The photochemical dimerization of conjugated dienes induced by (**1**) might be visualized to occur by reaction of a two-component (**1**)–diene charge-transfer complex with a second diene molecule to give a three-component complex[5,6] which deactivates *via* bond formation between the dienes. Alternatively, the two-component (**1**)–diene complex may decay to give the octafluoronaphthyl radical anion and diene radical cation. The latter may undergo electron exchange with any suitable electron donor to regenerate a diene molecule with or without concurrent bond rotation resulting in net double bond isomerization.

The recently observed formation of 1:1 exciplexes in benzene solution, but 1:2 exciplexes in acetonitrile solution between 9,10-dichloroanthracene and 2,5-dimethylhexa-2,4-diene[6] renders the involvement of a three-component excited complex in these dimerization processes an attractive possibility.

Anodic oxidation of either (**2a**), (**2b**), or (**2c**) (0·05 M) in acetonitrile solution (Bu_4NCl electrolyte) at a platinum electrode (1·76 V *vs.* SCE) resulted in *cis–trans* isomerization of the diene in competition with polymerization. No formation of photodimers was observed by g.l.c. (column a). These electrochemical results demonstrate that diene radical cations may be involved in the photochemical *cis–trans* isomerization, but are unlikely to be the intermediates in the photochemical dimerization.[7]

I thank Professor J. Menassen for helpful suggestions in the electrochemical work, Mr. Y. L. Freilich for technical assistance in the mass spectral analysis, and Professor N. C. Yang for discussions and information on his preliminary results.

(*Received, 4th February* 1976; *Com.* 116.)

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