Redox-photosensitised Cleavage of Indene Dimers Using Aromatic Hydrocarbon–Dicyanobenzene Systems; Catalysis by the Cation Radical of Aromatic Hydrocarbons

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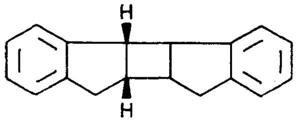
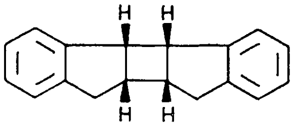
Summary Selective photoexcitation of phenanthrene in the phenanthrene–dicyanobenzene–indene dimer–acetonitrile system resulted in the cleavage of indene dimer to give indene in a limiting quantum yield of 8·2; a mechanism is suggested involving catalysis by the cation radical of phenanthrene.

Cycloreversions of cyclobutane compounds are of current interest with regard to the conservation of orbital symmetry,[1] 1,4-biradical intermediates,[2] solar energy utilisation,[3] and photoreactivation of damaged DNA.[4] Cleavage of the cyclobutane ring is usually carried out by means of thermolyses or photolyses and occasionally by metal ion catalyses. We describe here a novel type of photosensitised cleavage of indene dimers which occurs in a chain mechanism. We call photosensitisation using aromatic hydrocarbon–dicyanobenzene systems redox-photosensitisation, since excited aromatic hydrocarbons may act as redox-carriers.[5,6]



(1)



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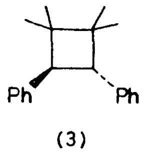

(3)

Irradiation of an acetonitrile solution containing phenanthrene (P), 1,4-dicyanobenzene (*p*-DCNB), and *anti* head-to-head indene dimer (**1**) at 313 nm gave indene in 75—80% yield,† with no change in the amounts of either P or *p*-DCNB. In the absence of either P or *p*-DCNB, no photoreaction occurred. 1,2- and 1,3-Dicyanobenzene can be used in place of *p*-DCNB.

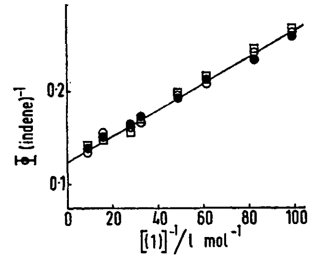

Figure 1. Plots of ϕ(indene)$^{-1}$ *vs.* $[(\mathbf{1})]^{-1}$. Degassed acetonitrile solutions, 313 nm irradiation with light intensities of $2·7 \times 10^{-8}$ (○), $1·2 \times 10^{-7}$ (●), and $6·4 \times 10^{-7}$ (□) einstein min^{-1}; [P] = 0·01 M, [*p*-DCNB] = 0·1 M.

The quantum yields for the formation of indene were independent of the intensity of the incident light (Figure 1). Strikingly, the limiting quantum yield was 8·2, thus demonstrating the occurrence of a chain reaction. As discussed by us[5] and others,[6] the photoreaction is apparently initiated by the electron transfer from excited singlet P (^{1}P*) to *p*-DCNB, since the fluorescence of P was quenched by *p*-DCNB at a diffusion-controlled rate but not at all by (**1**), *i.e.* $^1\mathrm{P}^* + p\text{-DCNB} \longrightarrow \mathrm{P}^{+\cdot} + p\text{-DCNB}^{-\cdot}$.

On the basis of these results, we suggest a mechanism involving the catalytic cleavage of (**1**) by $\mathrm{P}^{+\cdot}$; cleavage of

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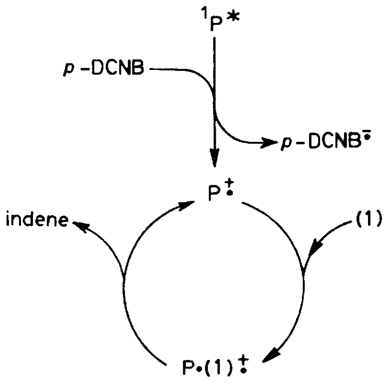
† Yields were determined by g.l.c. on the basis of the formation of 2 mol of indene per mol of (**1**) consumed.

(**1**) would occur *via* a π-complex cation radical $P\cdot(\mathbf{1})^{+\cdot}$, resulting in the formation of two neutral indene molecules and the regeneration of $P^{+\cdot}$ (Scheme). This novel type of mechanism is different from the cation radical mechanism discussed for cyclodimerisations of *N*-vinylcarbazole and related olefins,[7] and for the ring opening of 1,2-*trans*-dicarbazylcyclobutane[8] by electron transfer. Complete hole transfer from $P^{+\cdot}$ to (**1**) is very unlikely, since the oxidation potential of P ($E_{1/2}$ 1·25 V)‡ is much lower than that of (**1**) ($E_{1/2}$ 1·35 V). In accord with this, indene was the only initial product even when the photoreaction was carried out in acetonitrile–methanol (3:1) solution, while 2-methoxyindane was formed at a later stage as conversions increased (Figure 2). This clearly demonstrates that 2-methoxyindane is a secondary product which arises from the redox-photosensitised addition of methanol to initially formed indene.[5] Moreover, methanol adducts of (**1**) could not be detected. These results require that the redox-photosensitised cleavage of (**1**) must occur by a mechanism which involves neither $(\mathbf{1})^{+\cdot}$ nor $(\text{indene})^{+\cdot}$, since the addition of methanol to cation radicals of the styrene chromophore is well documented[9] and, indeed, the redox-photosensitised reaction of indene gave 2-methoxyindane by the addition of methanol to $(\text{indene})^{+\cdot}$;[5] *i.e.* $P^{+\cdot} + (\mathbf{1}) \not\longrightarrow P + (\mathbf{1})^{+\cdot}$ and $P + \text{indene} + (\text{indene})^{+\cdot}$.



Scheme

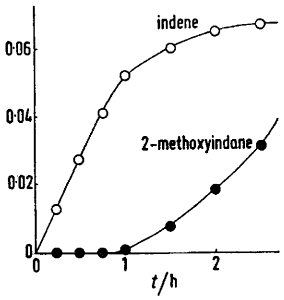


Figure 2. Formation of indene (○) and 2-methoxyindane (●) [mol per mol of (**1**)] *vs.* irradiation time. Degassed 3:1 acetonitrile–methanol solutions, 313 nm irradiation.

Similarly, (**2**) was efficiently cleavage by redox-photosensitisation, while cleavage of (**3**) did not occur. Since (**3**) is apparently less strained than (**1**) and (**2**), and possesses a higher oxidation potential ($E_{1/2}$ 1·53 V) than those of (**1**) and (**2**), strain energies and/or oxidation potentials are likely to be important factors in the redox-photosensitised cleavage. In this regard, it should be noted that the photosensitised cleavage of (**1**) and (**2**) took place if napthalene ($E_{1/2}$ 1·32 V) was used in place of P, but not chrysene ($E_{1/2}$ 1·17 V) or pyrene ($E_{1/2}$ 0·90 V).

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‡ Half peak potentials *vs.* Ag/Ag^{+} in acetonitrile using $Et_4N^{+}BF_4^{-}$ as supporting electrolyte; 0·2 V s^{-1} scan speed.

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