Photoinduced Coupling Reaction of Benzotriazole with Aromatic Hydrocarbons Sensitized by 9,10-Dicyanoanthracene (DCA) *via* an Electron-transfer Mechanism. A Simple Synthesis of 1-Arylbenzotriazole

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The photoinduced coupling reaction of benzotriazole with aromatic hydrocarbons (anisole, biphenyl and naphthalene) is sensitized by 9,10-dicyanoanthracene (DCA) to give 1-arylbenzotriazoles in moderate yields *via* an electron-transfer mechanism.

The use of a cosensitizer with an appropriate oxidation potential as a relay in the photoinduced electron-transfer process between a donor substrate and an acceptor sensitizer has received increasing attention recently.[1-5] Not only is rate acceleration of the SET reaction often observed, but in many cases, endothermic electron-transfer, which are not facile processes, are made feasible by the addition of a suitable cosensitizer. We report here the photoinduced electron-transfer reaction between 9,10-dicyanoanthracene (DCA) and benzotriazole (BTA) cosensitized by aromatic hydrocarbons and the subsequent addition reaction of the benzotriazolyl radical derived from the BTA cation radical to the cosensitizer hydrocarbons leading to the formation of the corresponding 1-arylbenzotriazoles.

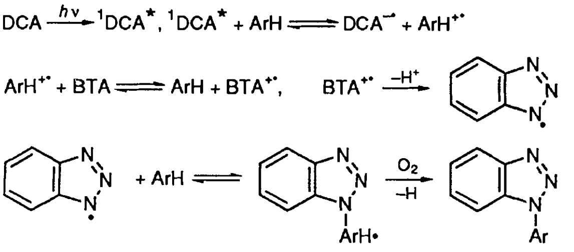
As an electron deficient heterocycle, BTA (E_i, 9.20 eV)[6] has an oxidation potential of *ca.* 2.56 V *vs.* standard calomel electrode (SCE) as estimated by the Miller empirical equation.[7] The electron transfer between BTA and singlet excited DCA has a free energy change ΔG_{ET} of 13.60 kcal mol^{-1} and is a largely endothermic process as calculated using the Weller equation.[8] In accordance with this, a fluorescence quenching experiment showed that BTA could not quench ^{1}DCA* in acetonitrile solution. The fluorescence intensity of the ^{1}DCA* (5×10^{-5} mol dm^{-3}) at λ 200–500 nm had no measurable change within experimental error with or without $\leqslant 1.6 \times 10^{-2}$ mol dm^{-3} of BTA. This observation, together with the calculated ΔG_{ET} value indicated that photoinduced electron transfer between ^{1}DCA* and BTA could not happen on direct irradiation.

However, it was found that when an aromatic hydrocarbon, *e.g.* biphenyl (BP), was added to a solution of DCA and benzotriazole in anhydrous acetonitrile, irradiation under an

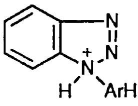
Table 1 Photoinduced coupling reaction of benzotriazole with aromatic hydrocarbons (ArH) sensitized by DCA[a]

ArH	$E^{ox}_{1/2}$ of ArH /V (SCE)	ΔG_{ET}[b] /kcal mol^{-1}	Irradiation time/h	Conversion (%)	Yield of 1-aryl-benzotriazole[c] (%)
BP	1.90	−1.61	46	47	41
Naphthalene	1.70	−6.23	10	100	39
Anisole	1.76	−4.84	22	51	77

[a] The light source is a 500 W medium pressure mercury lamp in a cooling water jacket surrounded by a layer of $NaNO_2$ filter solution (1 cm thickness, >400 nm). Solution of DCA (10^{-4} mol dm^{-3}), BTA (5×10^{-2}) and cosensitizer ArH (1×10^{-1} mol dm^{-3}) in dry acetonitrile placed in glass tubes was photolysed with continuous oxygen purging for the indicated time. The reaction mixture was concentrated *in vacuo* and chromatographed on a silica gel column. The crude products were further purified by recrystallization. [b] Refers to the SET process between $^1DCA^*$ and the ArH. [c] 1-(1-Naphthyl)benzotriazole and 1-(4-methoxyphenyl)benzotriazole were identified by comparing their spectra with that of authentic samples. Structure of 1-(4-biphenylyl)benzotriazole was determined by its spectroscopic and elemental analysis data, and was further proved by the fact that on direct photolysis, 1-(4-biphenylyl)benzotriazole gave the known 3-phenylcarbazole.



Scheme 1



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oxygen atmosphere with light λ >400 nm where DCA is the only absorbing species led to continuous consumption of BTA and the formation of 1-arylbenzotriazole. As an example, irradiation of an acetonitrile solution of DCA (1×10^{-4}), BTA (5×10^{-2}) and BP (1×10^{-1} mol dm^{-3}) yielded 1-(4-biphenylyl)benzotriazole in 41% yield (based on consumed BTA, see Table 1). Naphthalene and anisole served as cosensitizers similarly in the DCA–BTA system and upon irradition under the same conditions, 1-(1-naphthyl)benzotriazole and 1-(4-methoxyphenyl)benzotriazole were formed respectively (Table 1).

These reactions were found to be very sensitive to the polarity of the solvents and were extremely slow in less polar solvents, *e.g.* dichloromethane and could not proceed in the nonpolar solvent, benzene. The presence of oxygen is necessary for the reactions because no reaction was observed when the irradiation was conducted with continuous argon purging. Presumably the aromatic hydrocarbons acted as a relay to induce the otherwise very unfavourable endothermic electron transfer between $^1DCA^*$ and BTA, taking advantage of the fact that $ArH^{+\bullet}$ has a much longer lifetime than $^1DCA^*$ and hence can more readily accept an electron from BTA. All the cosensitizers used have $E^{ox}_{1/2} \leqslant 2$ V (SCE) and the SET reactions between each of them and $^1DCA^*$ are exothermic processes with negative ΔG_{ET} values (Table 1).

The reaction mechanism is proposed as in Scheme 1. The cation radical of BTA is a strong acid, which loses a proton quickly once formed to give the benzotriazoylyl radical, thus effectively suppressing the back electron transfer between ArH and $BTA^{+\bullet}$. The addition of the benzotriazoylyl radical to a neutral aromatic hydrocarbon molecule gives the addition radical, dehydrogenation of which by dissolved oxygen gives the final product 1-arylbenzotriazole. Besides the significant solvent polarity effect, the electron transfer character of the above reactions was further proved by the observation of the characteristic nine line ESR signal of $DCA^{-\bullet}$[9] and the ESR signal of the BTA radical trapped by phenyl *tert*-butyl nitrone on irradiation of a deaerated acetonitrile solution of DCA (10^{-4}), BTA (5×10^{-2}) and BP (5×10^{-2} mol dm^{-3}).†

The above reaction serves to illustrate the potential of suitable cosensitizers in expanding the application of photoinduced SET reactions to rather electron deficient compounds with high oxidation potential. It also provides a straightforward one-step synthesis in moderate yield directly from BTA and the corresponding aromatic hydrocarbons for the 1-arylbenzotriazoles, which are important starting materials in the synthesis of carbazole derivatives by the Graebe–Ullmann reaction through thermal[10] or photochemical[11,12] extrusion of nitrogen.

The application of other aromatic hydrocarbons as the cosensitizer in the above mentioned reactions for the synthesis of other 1-arylbenzotriazoles and the investigation of the details of the reaction mechanism are underway.

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References

1 T. Majima, C. Pac, A. Nakasone and H. Sakurai, *J. Am. Chem. Soc.*, 1981, **103**, 4499.
2 A. P. Schaap, S. Siddiqui, G. Prasad, E. Palomino and L. Lopes, *J. Photochem.*, 1984, **25**, 167.
3 A. P. Schaap, S. Siddiqui, S. D. Gagnon and L. Lopes, *J. Am. Chem. Soc.*, 1983, **105**, 5149.
4 S. C. Shim and H. J. Lee, *J. Photochem. Photobiol., A. Chem.*, 1989, **46**, 59.
5 N. Ichinose, K. Mizuno, T. Tamai and Y. Otsuji, *J. Org. Chem.*, 1990, **55**, 4079.
6 O. Thorstad and K. Undheim, *Chem. Scr.*, 1974, **6**, 222.
7 L. L. Miller, G. D. Nordblom and E. A. Mayeda, *J. Org. Chem.*, 1972, **37**, 916.
8 D. Rehm and A. Weller, *Isr. J. Chem.*, 1976, **8**, 259.
9 J. Happ and E. G. Jansen, *J. Org. Chem.*, 1976, **35**, 96.
10 C. Graebe and F. Ullmann, *Justus Liebigs Ann. Chem.*, 1896, 291; W. Borsche and M. Feise, *Chem. Ber.*, 1907, **40**, 378.
11 H. Murai, M. Torres and O. P. Strausz, *J. Am. Chem. Soc.*, 1980, **102**, 1421.
12 J. J. Kulagowski, C. J. Moody and C. W. Rees, *J. Chem. Soc., Perkin Trans 1*, 1985, 2725.

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† Another mechanism, in which direct coupling of $ArH^{+\bullet}$ with BTA in a π-complex to give **4** followed by deprotonation leads to the addition radical BTA–ArH˙ without the formation of a discrete BTA cation radical, although this is not consistent with the observation of the BTA radical ESR spectrum, could be a possible parallel reaction pathway.