Mechanistic studies of pyrene-sensitized decomposition of *p*-butylphenyl azide: generation of nitrene radical anion through a sensitizer-mediated electron transfer from amines to the azide

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Pyrene-sensitized photolysis of *p*-butylphenyl azide (**1**) in acetonitrile containing diethylamine (DEA) gave a mixture of the 3*H*-azepine (**2**) and *p*-butylaniline (**3**). In order to reveal the mechanism of the formation of these photoproducts, the effects of the DEA or sensitizer concentration, solvents and various additives on the product distribution have been examined. Thus, it is proposed that the azepine **2** mainly originates from the singlet nitrene formed through the energy transfer from excited pyrene to the azide **1**, while the one-electron reduction of **1** with the pyrene radical anion produced through the electron transfer from DEA to singlet excited pyrene is involved in the formation of the aniline **3**.

The photochemistry of aryl azides has been the subject of great interest over the years.[1] It has been established that irradiation of phenyl azide in liquid solution gives singlet phenylnitrene, which immediately undergoes ring expansion to didehydroazepine in competition with intersystem crossing to triplet phenylnitrene. In the 1960s, Lewis and co-workers reported that the photodecomposition of organic azides could be sensitized by singlet or triplet sensitizers.[2] He observed an approximately linear relationship between sensitizer excited-state energy and the rate constant for energy transfer to the azide. He also pointed out that energy transfer from sensitizers having lower excited-state energy than the azide occurred more efficiently than expected for classical endothermic energy transfer. Recently, by the measurement of the rate constant for energy transfer from various sensitizers to phenyl azide, Platz and co-workers have determined its singlet and triplet energies as *ca.* 350 and *ca.* 290 kJ mol^{-1} ($\approx$83 and $\approx$70 kcal mol^{-1}), respectively.[3]

In contrast to this photophysical research, few studies of the chemical reactivities of the azides activated by energy transfer were reported. Schuster and co-workers presented the unique photochemical reactivities of the aryl or aroyl azides linked covalently to a sensitizer.[4,5] In their studies of acridine- or pyrene-sensitized photolysis of *p*-[(dimethylamino)carbonyl]-phenyl azide, they indicated that sensitization reactions of the azide in acetonitrile in the presence of alcohols gave the corresponding aniline which was not detected by direct irradiation. Though they explained the formation of the anilines in terms of electron transfer from excited singlet pyrene to the azide, the detailed mechanism has not yet been elucidated.

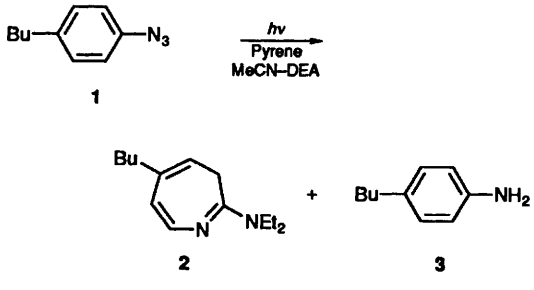
In the course of our studies on photochemistry of aryl azides,[6] we found that pyrene-sensitized photolysis of *p*-alkylphenyl azides in acetonitrile containing diethylamine (DEA) yielded the corresponding aniline together with the 3*H*-azepine derivative, while the latter was obtained as a sole product in direct irradiation of the azide. In this paper, we report our detailed mechanistic studies of pyrene-sensitized photoreactions of *p*-butylphenyl azide (**1**) in the presence of DEA, where the reaction scheme involving a competitive quenching of singlet excited pyrene by energy transfer to the azide and electron transfer from DEA could be established.

Results

Direct and pyrene-sensitized photolysis of *p*-butylphenyl azide 1

p-Butylphenyl azide (**1**) is a light yellow liquid, the absorption spectrum of which exhibits an intense transition with a maximum at 253 nm (log ε = 4.30 in acetonitrile) and a weak tailing to *ca.* 400 nm. Having significant absorption at 366 nm (log ε = 1.21 in acetonitrile), the azide **1** could be photolysed with light of a high-pressure mercury lamp filtered by the Corning glass filter #CS-052 (>350 nm). It is well known that in the absence of nucleophiles, the photoproducts of aryl azide are very complex because the didehydroazepine intermediate polymerizes or reacts with azide to produce an intractable tar.[1] Thus, irradiation (λ > 350 nm) of the azide **1** (6.3×10^{-3} mol dm^{-3}) in acetonitrile containing DEA (1.0 mol dm^{-3}) as a nucleophile gave 5-butyl-2-(diethylamino)-3*H*-azepine (**2**) in an almost quantitative yield. If other nucleophiles, such as alcohols, were employed instead of DEA, large amounts of tar were obtained and no azepine derivatives were detected, which was probably due to low electrophilicity of the didehydroazepine formed by the photolysis of the azide **1**.

On the other hand, under conditions identical to those described above with DEA, except for the presence of pyrene (2.3×10^{-2} mol dm^{-3}), irradiation of the azide **1** for 45 min, when 95% of the starting material was consumed, afforded *p*-butylaniline (**3**) in 59% yield, together with the azepine **2** (36%). Thus, it was found that the pyrene sensitization provided a new photochemical reactivity of *p*-alkylphenyl azides.



Curiously, when irradiation in the presence of pyrene was stopped after 10 min, when the conversion of the azide **1** was 26%, the yields of the azepine **2** and the aniline **3** were 50 and 45%, respectively, as measured on the basis of the reacted material. Thus, it was found that the distribution of the photoproducts was dependent on the irradiation time; the product ratio [**3**]:[**2**] increased as the photoreaction proceeded. In order to gain more detailed information on the dependence of the product distribution on the irradiation time, the change

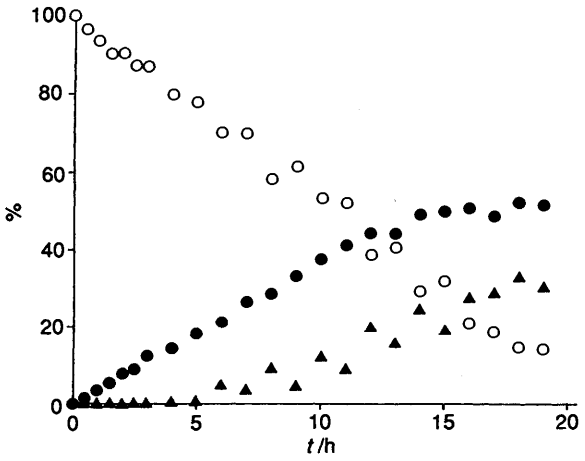


Fig. 1 Change in the concentration of the starting material **1** (○) and the photoproducts, the azepine **2** (●) and the aniline **3** (▲), with irradiation time in the pyrene-sensitized photolysis in acetonitrile containing DEA with a weaker light source (> 350 nm). [pyrene] = 2.3×10^{-2} mol, dm^{-3}, [DEA] = 1.0 mol dm^{-3}.

Table 1 Dependence of the photoproducts on solvent and DEA concentration in the pyrene-sensitized photolysis of the azide **1**[a]

		Yield (%)		
Solvent	[DEA]/mol dm^{-3}	**2**	**3**	[**3**]:[**2**]
Acetonitrile	1.0	36	59	1.6
Methanol	1.0	94	< 1	< 0.01
Dichloromethane	1.0	73	< 1	< 0.01
Cyclohexane	1.0	91	2	0.02
Acetonitrile	0.10	74	23	0.31
Acetonitrile	0.01	92	7	0.08

[a] [**1**] = 6.3×10^{-3} mol dm^{-3}, [pyrene] = 2.3×10^{-2} mol dm^{-3}. Conversion of the azide **1** was 70–95%.

Table 2 Dependence of the photoproducts on additives in the pyrene-sensitized photolysis of the azide **1** in acetonitrile in the presence of DEA (1.0 mol dm^{-3})[a]

		Yield (%)		
Additive	[Additive]/mol dm^{-3}	**2**	**3**	[**3**]:[**2**]
—	—	50	45	0.90
Et_3N	0.01	37	53	1.4
Et_3N	0.10	19	59	3.2
O_2	9.1×10^{-3}[b]	71	< 1	< 0.01
Piperylene	0.10	38	41	1.1

[a] [**1**] = 6.3×10^{-3} mol dm^{-3}, [pyrene] = 2.3×10^{-2} mol dm^{-3}. Conversion of the azide **1** was 20–30%. [b] Value for 1 atm pressure of O_2 from ref. 8.

in the concentration of the starting material and the photoproducts with irradiation time was closely examined by the use of a weaker light source. The result shown in Fig. 1 demonstrates the presence of an induction period in the formation of the aniline **3**, as well as the saturation in the formation of the azepine **2**. Thus, it seems likely that an independent mechanism involving different reactive intermediates operates in the formation of each photoproduct. Note also that a final product ratio [**3**]:[**2**] shown in Fig. 1 is estimated to be 0.60, which is quite different from the value 1.6, obtained using a more intense light source. This seems to be due to the prolonged induction period in the formation of the aniline **3** in the use of a weaker light source.

Table 3 Dependence of the photoproducts on additives in the pyrene-sensitized photolysis of the azide **1** in acetonitrile in the presence of DEA (0.01 mol dm^{-3})[a]

		Yield (%)		
Additive	[Additive]/mol dm^{-3}	**2**	**3**	[**3**]:[**2**]
—	—	99	< 1	< 0.01
Et_3N	0.10	26	61	2.4
Et_3N	1.0	14	64[b]	4.5
DMA[c]	0.10	13	54	4.0
MeOH	0.10	78	4	0.05
^iPrOH	0.10	90	5	0.06

[a] [**1**] = 6.3×10^{-3} mol dm^{-3}, [pyrene] = 2.3×10^{-2} mol dm^{-3}. Conversion of the azide **1** was 20–30%. [b] The additional product which was identified as *p*-butyl-*N*-ethylideneaniline (**4**) was obtained in 17% yield (see text). [c] *N*,*N*-Dimethylaniline.

In order to reveal the mechanism for the formation of the two products obtained in the pyrene-sensitized photolysis of the azide **1**, the dependence of the product distributions on the DEA or sensitizer concentration, solvents and various additives was examined. Since the product ratio was found to be dependent on the irradiation time and the light intensities as shown above, we were careful not to change the irradiation conditions in a series of experiments.

Effect of solvent and DEA concentration on the pyrene-sensitized photolysis of the azide 1

At first we examined the dependence of the product distribution on the solvent used in the pyrene-sensitized photolysis of the azide **1** (Table 1). The results showed that *p*-butylaniline (**3**) could not be produced in solvents other than acetonitrile.

The dependence of the product ratio on the concentration of DEA in acetonitrile was examined next. As shown in Table 1, the product ratio was very dependent on the DEA concentration. Surprisingly, lowering the DEA concentration resulted in an increase in the yield of the azepine **2** at the expense of the aniline **3**, though the rate of the nucleophilic attack of DEA on the didehydroazepine to form the azepine **2** should be reduced in a low concentration of DEA. This finding suggested that DEA participated in the rate-determining step of the formation of the aniline **3**, which probably involved a single electron transfer from DEA to the excited pyrene. The solvent effect on the product distribution was consistent with this postulate.

Effect of additives in the pyrene-sensitized photolysis of the azide 1 in the presence of DEA

The dependence of the product distributions on the addition of various substances is shown in Tables 2 and 3. As mentioned before, the pyrene-sensitized irradiation of the azide **1** in acetonitrile containing DEA (1.0 mol dm^{-3}) gave both the azepine **2** and *p*-butylaniline (**3**) in comparable yields. Addition of triethylamine (TEA) caused a remarkable increase in the yield of the aniline **3** at the expense of the azepine **2** (Table 2). More strikingly, the aniline **3** could not be obtained in a low concentration of DEA (0.01 mol dm^{-3}), while **3** came to be produced in over 60% yield by the irradiation of the reactants in the presence of TEA (Table 3). Thus, it was found that TEA was more effective in the formation of the aniline **3** than DEA. This observation is in line with the assumption described in the previous section that the aniline **3** is formed by a mechanism involving a single electron transfer. As discussed in a subsequent section, it would be reasonable to think that the addition of TEA accelerates the electron transfer process because of its lower oxidation potential compared with DEA. Further support for this assumption was given by the addition of the more electron-donating amine, *N*,*N*-dimethylaniline (DMA), where

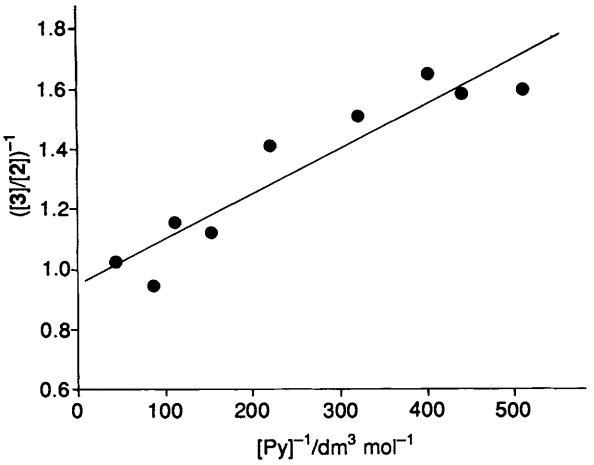


Fig. 2 Dependence of the product distribution [3]:[2] on the concentration of sensitizer in the pyrene-sensitized photolysis of the azide **1** in acetonitrile containing DEA (1.0 mol dm^{-3})

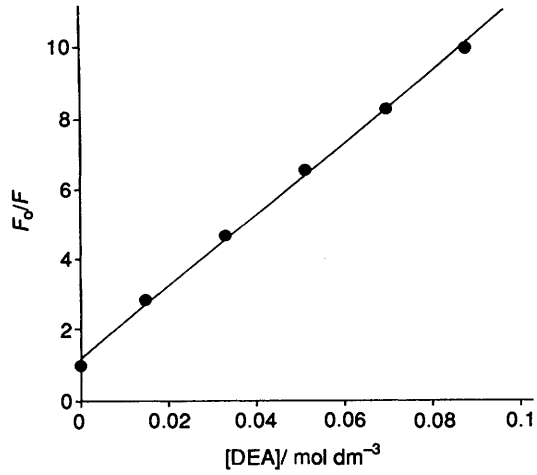


Fig. 3 Stern–Volmer plot for quenching of the fluorescence of pyrene by DEA in acetonitrile

a high product ratio [3]:[2] was achieved even at a low concentration of DMA (0.1 mol dm^{-3}).

Note that an additional product was detected in the photolysis in the presence of TEA. Though the isolation of this product from the irradiated mixture was unsuccessful, the product was identified as *p*-butyl-*N*-ethylideneaniline **4** on the basis of its GC–MS spectrum, which was identical to that of the product formed by the condensation of *p*-butylaniline **3** with acetaldehyde. The yield of the aldimine **4** was estimated to be 17% by GC in the pyrene-sensitized photolysis of the azide **1** with DEA (0.01 mol dm^{-3}) in acetonitrile containing 1.0 mol dm^{-3} of TEA (Table 3). At a low concentration of TEA (0.1 mol dm^{-3}), the aldimine **4** could be detected in high conversion of the starting azide **1**, where the yield of **4** was calculated to be *ca.* 5%. The formation of the aldimine **4** is consistent with electron transfer to produce a TEA radical cation, as discussed in a subsequent section.

As shown in Table 2, the yield of the aniline **3** was little affected by the addition of the triplet quencher, piperylene, while in the irradiation of the solution saturated with oxygen the formation of **3** was completely quenched.

Moreover, Table 3 shows that the addition of alcohols had much less effect on the production of the aniline **3** in the photolysis in a low concentration of DEA than the addition of the electron-donating amines. This observation seems to exclude the possibility that the failure to obtain the aniline **3** in a low concentration of DEA is simply due to the lack of a proton source.

Effect of pyrene concentration

As mentioned in the previous section, the azide **1** could be photolysed efficiently with the filtered light (> 350 nm) to give the azepine **2** in an almost quantitative yield. Therefore, it might be possible that the azepine **2** obtained in the presence of pyrene also originates from the directly excited azide **1***. In order to reveal the origin of the azepine **2**, the dependence of the product distribution on the sensitizer concentration was examined. If the efficiency with which excited pyrene py* leads to the azepine **2** and the aniline **3** is represented by φ_{PZ} and φ_{PA}, respectively, and the directly excited azide **1*** gives **2** with the efficiency φ_{DZ} in the pyrene-sensitized photolysis of the azide **1**, then the ratio of the photoproducts [3]:[2] is given by eqn. (1), where [py*] and [**1***] are the concentrations of excited pyrene and azide,

$$\frac{[3]}{[2]} = \frac{\varphi_{PA}[py^*]}{\varphi_{PZ}[py^*] + \varphi_{DZ}[\mathbf{1}^*]} \quad (1)$$

respectively. Assuming that the ratio of the excited species [**1***]/[py*] is equal to that of the product of the molar absorptivity and concentration of each species, eqn. (1) may be rearranged to eqn. (2). Thus, the reciprocal of the product ratio

$$\left(\frac{[3]}{[2]}\right)^{-1} = \frac{\varphi_{PZ}}{\varphi_{PA}} + \frac{\varphi_{DZ}}{\varphi_{PA}} \times \frac{\varepsilon_D[\mathbf{1}]}{\varepsilon_P[py]} \quad (2)$$

is expected to be dependent linearly on the reciprocal of the sensitizer concentration [py]. The dependence of the product distribution on the pyrene concentration obtained under the defined conditions ([**1**] = 6.3 × 10^{-3} mol dm^{-3}, [DEA] = 1.0 mol dm^{-3}; conversion of the azide **1** was 20–30%) is illustrated in Fig. 2. In accordance with eqn. (2) a plot of ([3]/[2])$^{-1}$ *versus* [py]$^{-1}$ gives a straight line (correlation coefficient 0.938). If the molar absorptivities determined at 366 nm in acetonitrile are defined as ε_D and ε_P in eqn. (2),† we obtain $\varphi_{PZ}/\varphi_{PA}$ and $\varphi_{DZ}/\varphi_{PA}$ as 0.951 and 3.23, respectively, by the least-squares analysis of the plot. Thus, the fraction of the azepine **2** originating from the directly excited azide **1***, which is expressed as $\varphi_{DA}[\mathbf{1}^*]/(\varphi_{PZ}[py^*] + \varphi_{DZ}[\mathbf{1}^*])$, is calculated to be 0.06 under our initial irradiation conditions ([py] = 2.3 × 10^{-2} mol dm^{-3}). This finding has revealed that most of the azepine **2** obtained in the pyrene-sensitized photolysis of the azide **1** is derived from excited pyrene. In other words, an excitation-energy transfer from pyrene to the azide **1** is involved in the formation of the azepine **2**.

Quenching of pyrene fluorescence by DEA

It is important to identify the species which quenches the excited state of the sensitizer in the pyrene-sensitized photolysis of the azide **1** in the presence of DEA. For the purpose of quantitative analysis, quenching of the fluorescence of pyrene by DEA was examined in acetonitrile at room temperature. Stern–Volmer treatment of the quenching data shown in Fig. 3 gave the value of $k_q\tau_0$ = 1.02 × 10^{-2} dm^3 mol^{-1}. The lifetime of pyrene fluorescence in acetonitrile was reported to be 303 ns.[7] Thus, the rate constant of quenching of singlet excited pyrene by DEA is k_q = 3.4 × 10^8 dm^3 mol^{-1} s^{-1}. This value is one order of magnitude lower than the rate of quenching by TEA, which was reported to be 1.8 × 10^9 dm^3 mol^{-1} s^{-1}.[7] *N*,*N*-Dimethylaniline (DMA) is expected to quench the singlet excited state

† The molar absorptivities of the azide **1** and pyrene at 366 nm were determined to be 1.61 × 10 and 2.15 × 10^2 dm^{-3} mol^{-1} cm^{-1} in acetonitrile, respectively.

of pyrene at a rate two orders of magnitude greater than DEA, since the quenching rate constant of *N*,*N*-dimethylaniline has been reported to be 1.0×10^{10} dm^3 mol^{-1} s^{-1} in toluene.[8]

Platz and co-workers reported quenching of the fluorescence of various aromatic hydrocarbons by phenyl azide in benzene.[3] On the basis of the plot of the quenching rate against singlet energy of the hydrocarbons, the rate constant of energy transfer from singlet excited pyrene to phenyl azide is calculated to be *ca.* 6×10^9 dm^3 mol^{-1} s^{-1}. This value could be applied to the rate constant of quenching of singlet excited pyrene by the azide **1** in acetonitrile, since either the alkyl substituent on the benzene ring or the solvent polarity seems to have little effect on the rate constant for energy transfer from excited pyrene to phenyl azide.‡

Thus, semi-quantitative analyses based on these kinetic data reveal that the singlet excited state of pyrene is preferentially quenched by DEA under the initial conditions employed in our experiments ([**1**] = 6.3×10^{-3} mol dm^{-3}, [DEA] = 1.0 mol dm^{-3}, [pyrene] = 2.3×10^{-2} mol dm^{-3} in acetonitrile), though an excitation-energy transfer from pyrene to the azide **1** could be fast enough to compete with quenching by DEA. When the concentration of DEA was reduced to 0.01 mol dm^{-3}, singlet excited pyrene is expected to be quenched by the azide **1** in preference to DEA. On the other hand, in the presence of the electron-donating amines such as TEA and DMA, these amines even in a low concentration quench the singlet excited state of pyrene more effectively than the azide **1**.

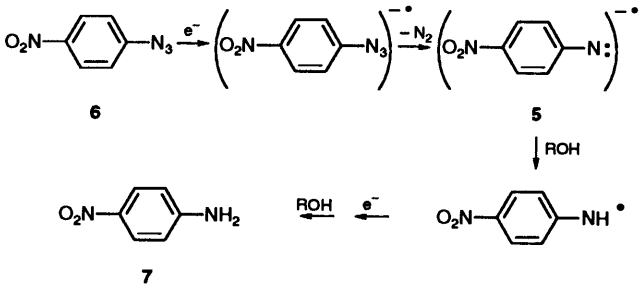
Discussion

A mixture of the 3*H*-azepine derivative **2** and the aniline **3** was obtained in pyrene-sensitized photolysis in acetonitrile containing DEA. The aniline **3** could not be detected in the direct irradiation of the azide **1**. Thus, the pyrene sensitization opens up a new channel of photochemical reaction of *p*-alkylphenyl azides. The mechanism for the formation of both products in the sensitized photolysis is now discussed.

Mechanism for the formation of *p*-butylaniline 3

There are two possible mechanisms for the formation of the aniline **3** in the pyrene-sensitized photolysis of the azide **1**; (*i*) hydrogen abstraction by the triplet nitrene and (*ii*) sequential proton and hydrogen abstraction by the nitrene radical anion. It has been established that anilines formed by the photolysis of aryl azides are derived from triplet nitrenes.[1] However, it is very unlikely that the triplet nitrene is involved in the pyrene-sensitized irradiation in the presence of DEA. The failure of piperylene to quench the formation of the aniline **3** has ruled out the participation of the triplet excited state of pyrene in the formation of **3**. Furthermore, the remarkable dependence of the product ratio on the DEA or sensitizer concentration described in the previous section cannot be explained by the triplet mechanism, since the rate of intersystem crossing of the singlet nitrene to the triplet state is not expected to be largely affected by the change in the concentration of DEA or sensitizer.

It therefore seems likely that the aniline **3** arises from the nitrene radical anion, which could be formed by the extrusion of dinitrogen from the azide radical anion produced by the one electron reduction of the azide **1**. The production and reactivity of the phenylnitrene radical anion have been studied in the gas phase.[9] Recently, Herbranson and Hawley established the formation of the *p*-nitrophenylnitrene radical anion **5** in solutions by the electrochemical reduction of the corresponding azide **6**.[10] They found that the electrolysis of the azide **6** in the presence of a proton donor gave *p*-nitroaniline (**7**) quantitatively, the mechanism of which was explained in terms of a two-electron reduction of **6** through the radical anion **5** as a transient intermediate (Scheme 1). The participation of radical anion **5**



Scheme 1

was also postulated by Liang and Schuster in the formation of the aniline **7** in the photolysis of the azide **6** in the presence of *tert*-butyldimethylamine, where the authors claimed that the radical anion **5** was produced by electron transfer from the amine to the triplet nitrene.[11]

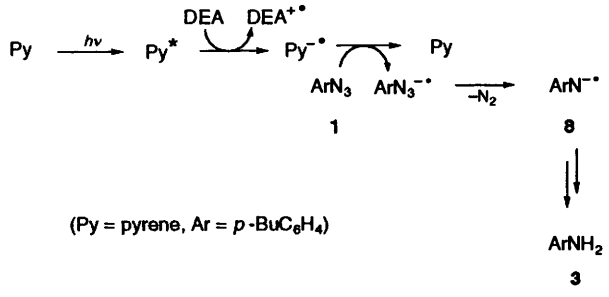
In the pyrene-sensitized photolysis of the azide **1** in the presence of DEA, there are two potential intermediates participating in the one-electron reduction of **1**; (*i*) the singlet excited pyrene (py*) and (*ii*) the pyrene radical anion (py$^{\bullet-}$) formed by the electron transfer from DEA to py*. For the following four reasons, we propose that the pyrene radical anion (py$^{\bullet-}$) operates as an electron donor to the azide **1**. First, it is found that the singlet excited state of pyrene is quenched by DEA with the rate constant of 3.4×10^8 dm^3 mol^{-1} s^{-1} in acetonitrile. Considering the quenching rate constant and the concentration of *p*-butylphenyl azide (**1**) and DEA, it is reasonable to think that the singlet excited state of pyrene is preferentially quenched by DEA in our irradiation conditions. Secondly, the addition of the electron-donating amines, *e.g.* TEA and DMA, increases the yield of the aniline **3** considerably. The rate of quenching of singlet excited pyrene by TEA and DMA is found to be one order and two orders of magnitude greater than by DEA, respectively. The variation in the rate constants of these quenchers appears to reflect the difference in their oxidation potentials and imply that electron transfer contributes predominantly to the quenching process. In fact, the free energies for electron transfer from these amines to singlet excited pyrene are calculated by the Rehm–Weller equation[12] to be 22, −12 and −72 kJ mol^{-1} for DEA, TEA and DMA, respectively.§ Thus, the remarkable increase in the yield of the aniline **3** caused by the addition of TEA or DMA is reasonably explained in terms of an acceleration of electron transfer to produce the pyrene radical anion (py$^{\bullet-}$). Thirdly, in a low concentration of DEA, where the singlet excited state of pyrene (py*) appeared to be quenched by the azide **1**, the aniline **3** could not be practically obtained. This observation clearly demonstrates the participation of DEA in the rate-determining step of the aniline formation. If the nitrene radical anion is formed through the direct electron transfer from

‡ In general, a contribution of electron transfer to the overall rate of quenching of the singlet excited state of aromatic hydrocarbons by aryl azides having no electron-withdrawing substituents is considered small. Thus, a large acceleration of quenching of the singlet excited state of pyrene by the azide **1** would not be expected in a change of solvent from benzene to acetonitrile.

§ The oxidation potentials (E_{ox}) of DEA, TEA and DMA were estimated to be 1.51, 1.15 and 0.53 V *vs.* SCE, respectively. The value for DEA was calculated from E_{ox} *vs.* Ag/Ag$^+$ as reported in ref. 13. The other values came from ref. 8. For the calculation of the free energies for electron transfer, 321 kJ mol^{-1} (76.9 kcal mol^{-1}) and −2.09 V *vs.* SCE were employed for the excited singlet energy (E_s) and the reduction potential (E_{red}) of pyrene, respectively. The Coulomb term was assumed to be 4 kJ mol^{-1}.

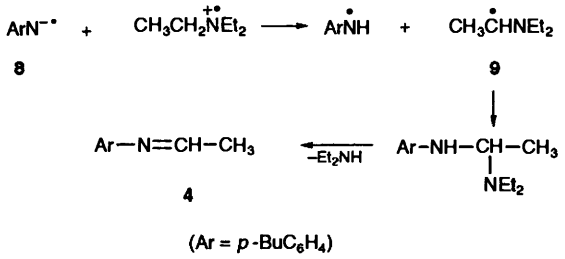
py* to the azide **1**, this observation would be explained in terms of the decrease in the rate of proton abstraction of the nitrene radical anion owing to a low concentration of DEA and the addition of alcohol, which is known to be a good proton donor to nitrene radical anions,[4,10] would largely enhance the production of the aniline **3**. This is not the case as shown in Table 3. Thus, it is reasonable to think that a nitrene radical anion cannot be produced in a low concentration of DEA. Finally, we observed complete quenching of the formation of the aniline **3** in the solution saturated with O_2 (Table 2), which can be explained in terms of the effective quenching of the radical anion intermediates by O_2.[14]

The mechanism which we propose for the formation of the aniline **3** in the pyrene-sensitized photolysis of the azide **1** in the presence of DEA is illustrated in Scheme 2. The nitrene radical



Scheme 2

anion **8** formed through the electron transfer would undergo proton and hydrogen-atom abstraction to give the final product **3**. When TEA was used as an electron donor, the additional product identified as *p*-butyl-*N*-ethylideneaniline (**4**) was detected. Under this condition, the electron transfer from TEA to py* should occur to produce the TEA radical cation. Therefore, the formation of the aldimine **4** is reasonably explained in terms of the proton transfer from the TEA radical cation to the radical anion **8**, followed by the coupling of the resulting α-amino radical **9** with the arylaminyl radical and the elimination of DEA (Scheme 3). The generation of the radical **9** in the



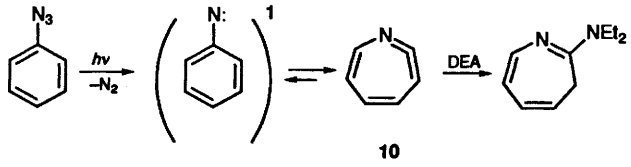
Scheme 3

photoinduced electron transfer from TEA to *o*-quinones has been reported.[15]

As mentioned in the previous section, the product ratio [**3**]:[**2**] was dependent on the irradiation time; the prolonged irradiation which led to a high conversion of the starting material **1** resulted in an increase in the product ratio. Moreover, as illustrated in Fig. 1, the induction period in the formation of the aniline **3** is observed in the irradiation of the reaction mixture with a weak light source. The profile shown in the figure implies that a steady state cannot be achieved in the concentrations of the intermediates which are involved in the formation of the aniline **3**. Though it is possible that quenching of $py^{\bullet-}$ by the residual O_2 and the acceleration of the formation of the aniline **3** by the participation of photoproducts in the electron transfer process are responsible for these observations, a definitive conclusion concerning the origin of the induction period cannot be drawn at the present stage.

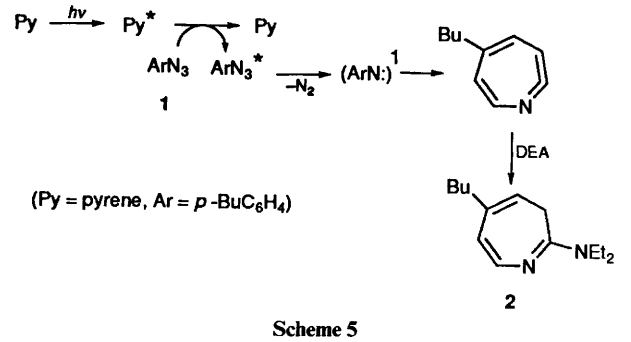
Mechanism for the formation of the azepine 2

It is well established that irradiation of phenyl azide in a solution containing DEA gives 2-(diethylamino)-3*H*-azepine.[1] Recent spectroscopic studies have revealed that this reaction proceeds through didehydroazepine (**10**), which is formed directly from singlet nitrene in solutions (Scheme 4).[16]



Scheme 4

In the pyrene-sensitized photolysis of the azide **1** in the presence of DEA, the 3*H*-azepine derivative **2** was obtained in a comparable yield to *p*-butylaniline (**3**). On the basis of the effect of concentration of the sensitizer on the product distribution (Fig. 2), it is concluded that an excitation-energy transfer from pyrene to the azide **1** is involved in the formation of the azepine **2** in the sensitized photolysis. Once the singlet nitrene is generated through an excitation-energy transfer from pyrene, it isomerizes to the didehydroazepine derivative, which is captured by DEA to give the azepine **2**. There are two possible mechanisms for the generation of singlet nitrene; (*i*) electron transfer involving the singlet excited sensitizer and the azide to afford the nitrene radical anion, followed by back electron transfer from the nitrene radical anion to the counter radical cation and (*ii*) singlet energy transfer from the singlet excited sensitizer to the azide, followed by the extrusion of dinitrogen. Although Zhu and Schuster proposed the former mechanism for the generation of the nitrene in the sensitized photolysis of aroyl azides,[5] this mechanism can be ruled out in the pyrene-sensitized photolysis of the azide **1** for the following reasons. If the singlet nitrene is generated by the back electron transfer, the nitrene radical anion **8**, which is formed through the one-electron reduction of the azide **1** with $py^{\bullet-}$ as shown in Scheme 2, would be a common precursor of both photoproducts, the azepine **2** and the aniline **3**. However, this postulate cannot explain the observation that the formation of the aniline **3** alone was effectively quenched in a low concentration of DEA, as well as in the solution saturated with O_2. Thus, it is probable that the azepine **2** obtained in the pyrene-sensitized photolysis of the azide **1** is mainly formed through the singlet energy transfer from excited pyrene to **1**. The total mechanism is illustrated in Scheme 5.



Scheme 5

The rate constant for quenching of pyrene fluorescence by the azide **1** is estimated to be *ca.* 6×10^9 dm^3 mol^{-1} s^{-1}. Therefore, in our initial irradiation conditions ([**1**] = 6.3×10^{-3} mol dm^{-3}, [DEA] = 1.0 mol dm^{-3}), the energy transfer to the azide **1** could not be a major process for quenching of pyrene in the

singlet excited state (py*). Nevertheless, the azepine **2** was obtained in a comparable yield to the aniline **3** derived from quenching by the electron transfer from DEA (Scheme 2), which would be a predominant process for quenching of py*. This observation is explained in terms of a difference in efficiency to give a final product between two quenching processes. A high efficiency cannot be expected for the pyrene radical anion $py^{\bullet-}$ to reduce the azide **1**, since back electron transfer between DEA radical cation and $py^{\bullet-}$ to produce the ground-state reactants should compete with the chemical reaction which leads to the aniline **3**. On the other hand, it is reported that azides activated by energy transfer decompose with a comparable efficiency to azides excited directly.[2c] Moreover, decomposition of the azide **1** in solutions containing DEA gives the azepine **2** in an excellent yield, as mentioned in the direct irradiation of **1**. Thus, the singlet energy transfer from excited pyrene to the azide **1** would lead efficiently to the formation of the azepine **2**.

Conclusions

Pyrene-sensitized photolysis of *p*-butylphenyl azide (**1**) in acetonitrile containing DEA (1.0 mol dm^{-3}) gave a mixture of 5-butyl-2-(diethylamino)-3*H*-azepine (**2**) and *p*-butylaniline (**3**). We propose that the azepine **2** is mainly derived from the singlet nitrene produced through the singlet energy transfer from excited pyrene to the azide **1**, while the one-electron reduction of **1** with pyrene radical anion formed through the electron transfer from DEA to singlet excited pyrene is involved in the formation of the aniline **3** (Schemes 2 and 5). Our observation concerning the formation of the aniline **3** provides a new type of photodecomposition process of aryl azides, where nitrene radical anions are generated through a sensitizer-mediated electron transfer from electron-donating amines to the azides. Furthermore, it is possible to apply this reaction to construct a new class of donor–chromophore–reactive acceptor molecules used to study the effects of distance and orientation in energy and electron transfer, design and preparation of which are ongoing in our laboratory.

Experimental

General methods

^{1}H NMR spectra were recorded on a JEOL JNM-EX-270 spectrometer; *J* values in Hz. UV–VIS spectra were obtained with a JASCO V-560 spectrophotometer. Fluorescence spectra were recorded on a Hitachi MFP-2A spectrophotometer. GC–MS spectra were recorded on a Shimadzu QP-1000 mass spectrometer with a GC column prepared from 5% Silicone OV-17 on Diasolid L (5.0 mm × 1.0 m). The GC analyses were performed on a Yanagimoto instrument, Model G-80. The GC column was prepared from 5% Silicone OV-17 on Diasolid L (5.0 mm × 1.0 m). Gel permeation liquid chromatography (GPLC) was carried out on a JASCO HLC-01 high-pressure liquid chromatograph equipped with a Shodex GPC H-2001 column. Column chromatography was carried out on Fuji Davison silica gel BW-127ZH.

p-Butylphenyl azide (1)

To a solution of 1.0 g (6.7 mmol) of commercially available *p*-butylaniline (**3**) in 50 cm^3 of dioxane was added 50 cm^3 of 3 mol dm^{-3} sulfuric acid. The mixture was cooled to 0–5 °C and a solution of 460 mg (6.7 mmol) of sodium nitrite in 10 cm^3 of water was added to the solution. After stirring for 2 h at this temperature, a solution of 870 mg (13.4 mmol) of sodium azide in 20 cm^3 of water was added dropwise to the solution. After the addition, the reaction mixture was stirred for 3 h at room temperature. The organic material was extracted with dichloromethane, and the extract was dried over sodium sulfate. The solvent was removed under reduced pressure, and the residue was developed on a silica gel column (2.8 cm in diameter, 20 cm in length) with hexane to give 870 mg (74%) of the azide **1**. (**WARNING:** the azide **1** is explosive. It is advisable to keep the temperature below 40 °C in the evaporation of its solutions and most inadvisable to attempt to distil the azide **1**.) The identity and purity of the azide **1** were established by ^{1}H NMR spectrum. **1**: oil; δ_H(270 MHz; $CDCl_3$) 0.92 (3 H, t, *J* 7.3), 1.30–1.38 (2 H, m), 1.52–1.63 (2 H, m), 2.58 (2 H, t, *J* 7.8), 6.94 (2 H, d, *J* 8.6) and 7.16 (2 H, d, *J* 8.6); ν_{max}(NaCl)/cm^{-1} 2930, 2850, 2100, 1610, 1580, 1500, 1280, 1120 and 830; λ_{max}(MeCN)/nm 253 [log(ε/dm^3 mol^{-1} cm^{-1}) 4.30], 280sh (3.60) and 290sh (3.42).

p-Butyl-*N*-ethylideneaniline (4)

To 2.0 g (13 mmol) of *p*-butylaniline (**3**) was added 0.74 cm^3 (13 mmol) of freshly distilled acetaldehyde dropwise at 0 °C. The reaction mixture was shaken for 15 min and warmed to room temperature. Potassium hydroxide pellets were added and the mixture was allowed to stand until separation into two layers was complete. The upper layer was separated, which was composed of the residual starting material **3** and the aldimine **4**. The conversion of the amine **3** was *ca.* 60%, which was estimated by the integration of each characteristic peak of the ^{1}H NMR spectrum (**3**, δ_H 6.62; **4**, δ_H 7.14) in the crude reaction mixture. Though attempts to purify the aldimine **4** were not successful because of its instability, **4** could be identified by ^{1}H NMR spectroscopy and GC–MS. **4**: δ_H(270 MHz; $CDCl_3$) 0.92 (3 H, t, *J* 7.3), 1.29–1.40 (2 H, m), 1.51–1.65 (2 H, m), 2.17 (3 H, d, *J* 5.0), 2.59 (2 H, t, *J* 7.6), 6.96 (2 H, d, *J* 8.3), 7.14 (2 H, d, *J* 8.3) and 7.90 (1 H, q, *J* 5.0); *m/z* 175 (M^+, 20%), 160 (7, M − CH_3), 149 (10), 132 (100, M − C_3H_7) and 106 (65).

Photolysis

Irradiation was carried out at room temperature with a 300 W high-pressure mercury lamp through the Corning glass filter #CS-052. For analytical experiments, a solution of the azide **1** (6.28×10^{-2} mol dm^{-3}, 2 cm^3) in acetonitrile containing pyrene, DEA and additives, the concentrations of which were described in Tables 1–3 and Figs. 1 and 2, was placed in a Pyrex tube (10 mm od) and purged with nitrogen for 10 min. The tube was placed in a Pyrex vessel containing water and irradiated. The distance between the lamp and the sample tube was *ca.* 5 cm. The consumption of the azide **1** and the yield of products were determined by GC on the basis of the reacted material. For the data shown in Table 1, the photolysis was carried out for 45 min, when 70–95% of the azide **1** was consumed. On the other hand, for the data shown in Tables 2 and 3 and Fig. 2, the photolysis was stopped at an early stage of the reaction, when the conversion of the azide **1** was determined to be 20–30%. For the concentration profile shown in Fig. 1, the irradiation was carried out on a merry-go-round apparatus with the lamp described above. The distance between the lamp and the samples was *ca.* 8 cm, and the lamp was surrounded with thick paper, part of which was fitted with a window (3.5 cm × 3.5 cm) for the Corning glass filter #CS-052. Thus, the light intensity for the photolysis was considerably decreased, so that the rate of the consumption of the starting material **1** was reduced to *ca.* 3% of that under the initial irradiation conditions. The azepine **2** was isolated by GPLC with chloroform eluent in a preparative scale irradiation, and characterized spectroscopically. 5-Butyl-2-(diethylamino)-3*H*-azepine (**2**): oil, δ_H(270 MHz; $CDCl_3$) 0.86 (3 H, t, *J* 7.1), 1.14 (6 H, t, *J* 7.1), 1.17–1.30 (2 H, m), 1.35–1.46 (2 H, m), 2.16 (2 H, t, *J* 7.4), 2.58 (2 H, br s), 3.35–3.43 (4 H, m), 4.88 (1 H, t, *J* 6.9), 5.67 (1 H, d, *J* 8.3) and 7.04 (1 H, d, *J* 8.3); *m/z* 220 (M^+, 84%), 205 (58, M − CH_3), 191 (57, M − C_2H_5), 177 (78, M − C_3H_7), 149 (100) and 107 (62). Identification of

the aniline **3** and the aldimine **4** was established by comparing GC–MS spectra with those of authentic samples.

Fluorescence quenching studies

Solutions of pyrene (1.19×10^{-5} mol dm^{-3}) in acetonitrile containing various amounts of DEA were placed in 10 mm quartz tubes, degassed by four freeze–thaw cycles and sealed under vacuum. Fluorescence spectra were measured at room temperature on excitation at 340 nm. Relative fluorescence intensities (F_0/F) were determined by measuring the peak heights for the maxima.

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