The Photoinduced Ring-opening Reaction of 1-(2-Naphthoyl)aziridine in Alcohols

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Photoreactions of 1-(2-naphthoyl)aziridine (**1**) in a series of alcohols have been studied at $\lambda_{ex.}$ 313 nm and room temperature under deaerated conditions. Irradiation of (**1**) in methanol gave *N*-(2-methoxyethyl)naphthalene-2-carboxamide (**2a**) selectively, while *N*-ethylnaphthalene-2-carboxamide (**3**) was produced in ethanol and propan-2-ol. The competitive formation of *N*-(2-t-butoxyethyl)-naphthalene-2-carboxamide (**2b**) and (**3**) occurred in t-butyl alcohol. These alcohols formed 1:1 hydrogen bonds with (**1**) in their ground states. The quantum yield for the fluorescence emission (Φ_F) of (**1**) increased and the red shift of the emission maximum was enhanced with the increase in hydrogen bonding ability of the alcohols. Penta-1,3-diene quenched the formation of (**3**) but not (**2a**) or (**2b**). The Stern–Volmer plot for quenching of the formation of (**3**) by penta-1,3-diene was linear in propan-2-ol, whereas it curved downward to approach a definite value in ethanol or t-butyl alcohol. The quantum yield of (**2b**) in t-butyl alcohol-containing mixed solvents tended to increase with the increased dielectric constant (ε).

We reported in a preliminary study that 1-(2-naphthoyl)-aziridine (**1**) undergoes a photochemical ring-opening reaction at the aziridine-ring moiety, typically giving a solvent-incorporated product *N*-(2-methoxyethyl)naphthalene-2-carboxamide (**2a**) in methanol or *N*-ethylnaphthalene-2-carboxamide (**3**) as a result of hydrogen abstraction from the solvent molecule in propan-2-ol.[1] It has been assumed that the nucleophilicity of alcohols determines the ring-opening mode of (**1**) in the electronically excited state, whether heterolysis as in the case of methanol or homolysis as in the case of propan-2-ol.

In this paper we report further details on the correlation between molecular properties of a series of alcohols employed as solvents and photochemical ring-opening modes of (**1**). The mechanism of photoinduced secondary amide formation is discussed on the basis of the behaviour of the alcohols in ground-state hydrogen bonding to (**1**), the fluorescence emission characteristics of (**1**), and quenching experiments with penta-1,3-diene.

Experimental

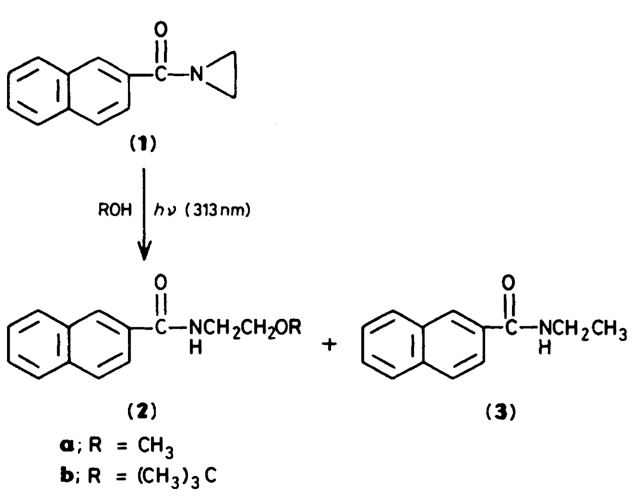
Materials.—1-(2-Naphthoyl)aziridine (**1**) was prepared and purified as reported.[1] 1-Acetylaziridine was prepared by the reaction of aziridine with acetyl chloride in the presence of triethylamine in diethyl ether and purified by distillation under reduced pressure (22.2 °C and 600 mPa). t-Butyl alcohol was refluxed and fractionally distilled over calcium hydride. Methanol, ethanol, propan-2-ol, benzene, and carbon tetrachloride were of spectroscopic grades and used without further purification. Acetonitrile was refluxed over phosphorus pentaoxide and then fractionally distilled. Penta-1,3-diene (*cis–trans* mixture) was distilled before use. Authentic *N*-(2-t-butoxyethyl)naphthalene-2-carboxamide (**2b**) was prepared by the reaction of (**1**) with t-butyl alcohol in the presence of BF_3–OEt_2 in a manner analogous to the preparation of (**2a**) described previously,[1] $\nu_{max.}$(KBr) 3 350s, 1 640s, 1 530s, and 1 090s cm^{-1}; δ (60 MHz; $CDCl_3$) 8.34br (1 H, s), 7.90br (4 H, s), 7.63 (2 H, m), 6.87 (1 H, m), 3.60br (4 H, s), and 1.22 (9 H, s) (Found: C, 75.1; H, 7.8; N, 5.1; O, 11.7. Calc. for $C_{17}H_{21}NO_2$: C, 75.3; H, 7.75; N, 5.2; O, 11.8%). Other reagents were used as received.

Spectroscopic Measurements.—I.r. spectra were measured with a JASCO A-302 spectrophotometer. For the determination of hydrogen-bonding interactions, the O–H (or O–D) stretching-vibration band of 5mM-alcohols (or methan[^{2}H]ol) in the presence of 40mM-(**1**) in carbon tetrachloride was recorded at room temperature using KBr sealed cells (1.0 mm optical path length). ^{1}H N.m.r. measurements were performed by a JEOL PMX-60 spectrometer with tetramethylsilane as internal standard. Electronic absorption spectra were recorded on a Shimadzu UV-220S spectrophotometer. Fluorescence spectra were measured at room temperature with a JASCO FP-550A fluorescence spectrophotometer ($\lambda_{ex.}$ 313 nm), in which the spectral response was corrected.[2] The fluorescence quantum yield (Φ_F) was determined by reference to a standard solution of 5mM-quinine sulphate in aqueous sulphuric acid (0.5M),[3] in which the refractive index of the solution was corrected. The fluorescence lifetimes (τ_F) of 0.5mM-(**1**) in several solvents were determined by a single-photon time coincidence method with a PRA system and a Hitachi multichannel analyser (half-duration of the pulsed light was *ca.* 2 ns, $\lambda_{ex.}$ 337 nm). The fluorescence response functions were obtained as the sum of two exponentials $[A\exp(-t/\tau_F) + A'\exp(-t/\tau'_F)]$ by computer-aided deconvolution of the observed decays. Both the photostationary-state and time-resolved fluorescence measurements were carried out for solutions deaerated by repeated freeze–pump–thaw cycles under reduced pressure (< 13 mPa).

Analyses.—Conversion of (**1**) and the product yields were determined by h.p.l.c. analysis with a TOYO SODA HLC-802UR h.p.l.c. using the conditions reported[1] but not the combination of columns (G 2000H, 600 mm × 7.5 mm × 2).

Preparative Photolysis.—Solutions of (**1**) (0.5 g) in ethanol and t-butyl alcohol (120 ml) were divided into six portions, placed in the Vycor glass tubes (19 mm diameter), and then irradiated using a merry-go-round apparatus equipped with a 400 W high-pressure mercury arc (Eiko-sha 400). After irradiation, the resulting reaction mixture was concentrated with a rotary evaporator and chromatographed on a silica gel column. The starting aziridine (**1**) was eluted with benzene and an amide (**3**) with 20% v/v benzene–$CHCl_3$ in both reaction systems. Further elution with 50% v/v $CHCl_3$–ethyl acetate gave (**2b**) in the case of the t-butyl alcohol system. The ^{1}H n.m.r. spectra and h.p.l.c. elution volumes of (**2b**) and (**3**) thus isolated were identical with those of authentic samples.

Reaction Quantum Yield.—Monochromatic light at 313 nm was isolated from a 100 W high-pressure mercury arc with an



Scheme 1.

Table 1. Quantum yields ($\Phi_R{}^0$) for photoreactions of 0.85mM-(1) in deaerated alcohols[a]

Alcohol	Conversion $10^3\Phi_R{}^0(-1)$	Product[b] $10^3\Phi_R{}^0(2)$	$10^3\Phi_R{}^0(3)$
CH_3OH	7.0	6.8 [(**2a**)]	0
CH_3CH_2OH	3.2	0	2.9
$(CH_3)_2CHOH$	2.6	0	2.6
$(CH_3)_3COH$	2.5	0.7 [(**2b**)]	0.8

[a] On irradiation at λ_{ex} 313 nm and room temperature. [b] Another product detected was ring-opened oligomer of (**1**).

aqueous solution filter containing 0.020% K_2CrO_4 and 3% K_2CO_3.[4] This solution filter had a maximum transmittance of 73% at 313 nm and half band-pass width of 27 nm. The intensity of incident light was determined as 2.08×10^{-7} einstein ml^{-1} min^{-1} with a ferrioxalate actinometer ($\Phi_{Fe(II)}$ 1.24 at 313 nm).[5] In a typical run, a solution of 0.85mM-(**1**) in alcohol (5 ml) placed in a finger glass tube attached to an optically flat quartz cell (1 mm path length) was deaerated by repeated freeze–pump–thaw cycles, sealed off, and then irradiated with the 313 nm mercury line at room temperature. The solution irradiated for an appropriate time was evaporated under reduced pressure and the resulting photoproduct was subjected to h.p.l.c. analysis. The reaction quantum yield ($\Phi_R{}^0$) was obtained as the ratio of the number of specified product to that of quanta absorbed by (**1**) over the period of irradiation resulting in a conversion of less than 10% of the aziridine. For quenching studies, solutions of 0.85mM-(**1**) in deaerated alcohols with varying concentrations of penta-1,3-diene were irradiated at λ_{ex} 313 nm.

Results and Discussion

Characteristics of the Photoreaction of (**1**) *in Several Alcohols.*—On irradiation of a solution in alcohols at λ_{ex} 313 nm, (**1**) underwent α-cleavage at the aziridine-ring moiety to give *N*-(2-alkoxyethyl)naphthalene-2-carboxamide (**2**) and/or *N*-ethylnaphthalene-2-carboxamide (**3**) (Scheme 1). Under these conditions the naphthalene chromophores of (**1**) uncomplexed and complexed with a solvent alcohol molecule, but neither of the solvents are photoexcited in the primary step of the ring-opening reactions (see below). Table 1 summarizes the quantum yields of the products [$\Phi_R{}^0(2)$ and $\Phi_R{}^0(3)$] together with that for the overall conversion of (**1**) [$\Phi_R{}^0(-1)$].

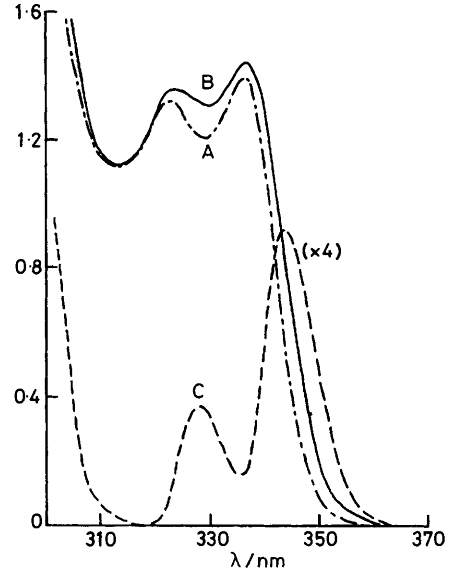


Figure 1. Electronic absorption spectra of 1.1mM-(**1**) in acetonitrile A, without and B, with 9.8mM-methanol, and the difference absorption spectrum between acetonitrile solutions of the (**1**)–methanol mixture (sample solution) and the single component (**1**) (reference solution)

The $\Phi_R{}^0(-1)$ value increased on varying the solvent alcohols in the order t-butyl alcohol $\lesssim$ propan-2-ol < ethanol < methanol. Moreover, it is clear in Table 1 that the selectivities of (**2**) and (**3**) depend on the alcohols employed. Thus, photolyses of (**1**) led to the selective formations of (**2a**) in methanol and (**3**) in propan-2-ol, respectively, in accord with the previous observation.[1] Similarly, (**3**) was produced selectively in ethanol with almost the same quantum yield as in propan-2-ol. In contrast to these solvents, t-butyl alcohol gave rise to simultaneous formation of (**2b**) and (**3**) along with larger amounts of oligomer of (**1**). The quantum yields of (**2b**) and (**3**) in this case were nearly equal.

Hydrogen-bond Formation between (**1**) *and Alcohols in the Ground State.*—Figure 1 illustrates the representative electronic absorption spectra of 1.1mM-(**1**) in the absence and presence of 9.8M-methanol in acetonitrile. The absorption band with the maxima at 337 and 323 nm observed without alcohols (Figure 1A) is assigned to π–π* ($S_0 \longrightarrow S_1$) transition of the naphthalene chromophore of (**1**).[1,2] The difference absorption spectrum measured between acetonitrile solutions of the (**1**)–methanol mixture (sample solution) and the single component (**1**) (reference solution) is also shown, in Figure 1C, demonstrating the appearance of new absorption maxima at 343 and 328 nm. The absorbance at this red-shifted band increased upon increasing the concentration of methanol. These spectral data indicate the complex formation between (**1**) and methanol in their ground states. Essentially identical results were obtained with the other alcohols. A pair of maximal frequencies of the red-shifted band ($\tilde{\nu}_{c,1}$ and $\tilde{\nu}_{c,2}$), which have been observed in each acetonitrile solution with alcohol, are listed in Table 2. It is obvious that the magnitude of red shift, as measured by the difference between the lower-frequency maxima of uncomplexed ($\tilde{\nu}_{0,1}$ 29 790 cm^{-1}) and complexed (**1**), is relatively small and does not significantly change; *i.e.* $\tilde{\nu}_{0,1} - \tilde{\nu}_{c,1}$ 630—690 cm^{-1}.

Table 2. Ground-state complex formation of (**1**) with alcohols in acetonitrile solution at room temperature

Alcohol	$\tilde{\nu}_{c.1}{}^{a}$/cm^{-1}	$\tilde{\nu}_{c.2}{}^{a}$/cm^{-1}	$\Delta\tilde{\nu}_1{}^{b}$/cm^{-1}	K^c/ l mol^{-1}
CH_3OH	29 100	30 480	690	0.14
CH_3CH_2OH	29 110	30 500	680	0.061
$(CH_3)_2CHOH$	29 110	30 500	680	0.020
$(CH_3)_3COH$	29 160	30 510	630	0.009

[a] Frequencies of the electronic absorption maxima of the complex band. [b] Frequency shift relative to free (**1**) in acetonitrile, $\Delta\tilde{\nu}_1 = 29\,790 - \tilde{\nu}_{c.1}$. [c] Equilibrium constant for ground-state complex formation.

Table 3. Frequencies of the O–H stretching vibration of 5mM-alcohols in the presence of 40mM-(**1**) in carbon tetrachloride at room temperature

Alcohol	$\nu_0(OH)^a$/ cm^{-1}	$\nu_c(OH)^b$/ cm^{-1}	$\Delta\nu(OH)/\nu_0(OH)^c$
CH_3OH	3 662	3 528	0.0366
CH_3CH_2OH	3 636	3 515	0.0333
$(CH_3)_2CHOH$	3 624	3 512	0.0309
$(CH_3)_3COH$	3 613	3 505	0.0299

[a] Monomeric free OH. [b] OH hydrogen-bonded to (**1**). [c] Relative frequency shift, $\Delta\nu(OH) = \nu_0(OH) - \nu_c(OH)$.

As reported previously,[1] the carbonyl n–π^* band for (**1**) lies behind the intense π–π^* bands of the naphthalene chromophore. For an understanding of the behaviour of the carbonyl n–π^* band related to the ground-state complex formation, the electronic absorption spectra of 3.0mM-1-acetylaziridine in acetonitrile and in these alcohols were also measured. In each alcohol solution the characteristic n–π^* absorption maximum of 1-acetylaziridine was observed at a wavelength shorter than that in acetonitrile (239 nm). The magnitude of the blue shift (cm^{-1}) changed considerably in contrast to the red-shifted band of the 1:1 complex between (**1**) and alcohol, increasing in the order t-butyl alcohol (400) < propan-2-ol (560) < ethanol (760) < methanol (1 020). In view of these results, it seems reasonable to predict that the red-shifted band as in Figure 1C is attributable to π–π^* transition of the naphthalene chromophore of complexed (**1**).

According to the previous procedure[2] based on the Benesi–Hildebrand equation,[6] the equilibrium constant (K) was evaluated by assuming a 1:1 complexation of (**1**) with each alcohol [reaction (1)].

$$(1) + ROH \overset{K}{\rightleftharpoons} (1)\cdot ROH \qquad (1)$$

Figure 2 shows the typical Benesi–Hildebrand plots for a fixed concentration (1.1mM) of (**1**) with varying concentrations of alcohols, which are consistent with the 1:1 complex formation as in the above equilibrium. From such linear plots at three different wavelengths the average K values were derived as listed in Table 2. Comparing the K values thus obtained with the spectroscopic data for 1-acetylaziridine described above, a trend is evident that the abilities of alcohols to form the ground-state complex with (**1**) and to enhance the n–π^* blue shift of 1-acetylaziridine increase in the same sequence; *i.e.* t-butyl alcohol < propan-2-ol < ethanol < methanol.

On the other hand, the i.r. spectra of 5mM-alcohols in CCl_4 solution demonstrated that the presence of 40mM-(**1**) gives rise to a new OH stretching-vibration band at lower frequency [$\nu_c(OH)$] in addition to the original monomeric band [$\nu_0(OH)$] as listed in Table 3. This characteristic frequency shift is attributable to hydrogen bonding of a given alcohol to (**1**), revealing the character of the 1:1 ground-state complex.

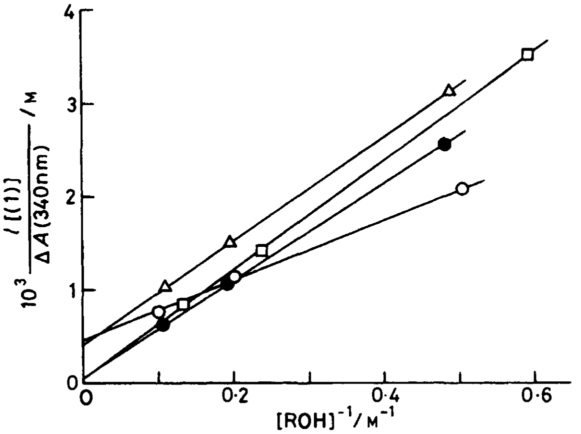


Figure 2. Benesi–Hildebrand plots for 1:1 complex formation of (**1**) with alcohols (ROH) in acetonitrile solution at room temperature: ○, methanol; △, ethanol; ●, propan-2-ol; □, t-butyl alcohol. ΔA (340 nm) is the apparent absorbance of the complex band at 340 nm derived from the difference absorption spectrum and l is the light-path length (1 cm)

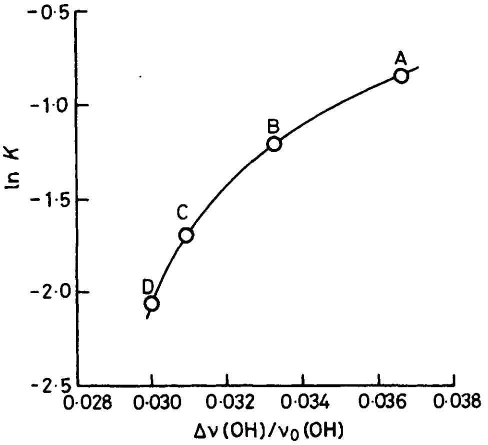


Figure 3. Relationship between logarithm of the equilibrium constant for (**1**)–alcohol complex formation (ln K) and relative frequency shift of the O–H stretching vibration of alcohols [$\Delta\nu(OH)/\nu_0(OH)$]: A, methanol; B, ethanol; C, propan-2-ol; D, t-butyl alcohol

Previously we[7] and others[8–11] suggested the use of the similar O–D stretching-frequency shift of methan[^{2}H]ol, $\Delta\nu(OD)$ (cm^{-1}) = $\nu_0(OD) - \nu_c(OD)$, as a measure of hydrogen-bond donor (or Lewis) basicity. In a comparative measurement with methan[^{2}H]ol, we observed the red shift from $\nu_0(OD)$ 2 689 to $\nu_c(OD)$ 2 602 cm^{-1} in the presence of (**1**) in CCl_4. By reference to the compiled data,[7,11] the frequency shift $\Delta\nu(OD)$ 87 cm^{-1} relative to CCl_4 was found to be comparable to those for ketones rather than amines and even amides. Thus, although (**1**) has two possible types of basic site, one may expect that the carbonyl oxygen is more favourable than the aziridinyl nitrogen for the hydrogen-bond complexation with alcohols. This is clearly consistent with the blue shift of the carbonyl n–π^* transition band of 1-acetylaziridine in hydrogen-bonding alcohols.[12]

Figure 3 shows the increase in ln K with the relative frequency shift [$\Delta\nu(OH)/\nu_0(OH)$] for the series of hydrogen-bonded complexes between (**1**) and alcohols. Assuming that the entropy change (ΔS) in the complex formation remains constant or varies linearly, the relationship in Figure 3 implies that the heat

Table 4. Fluorescence emission characteristics of 0.4mM-(**1**) in deaerated alcohols and acetonitrile at room temperature

Solvent	$\tilde{\nu}_f{}^a$/cm^{-1}	$\Delta\tilde{\nu}_f{}^b$/cm^{-1}	$\Phi_F{}^c$	Lifetime^d A	τ_F/ns	A'	τ_F'/ns	$k_F{}^e$/s^{-1}
CH_3OH	25 870	2 280	0.15	1.00	0.7			2×10^8
CH_3CH_2OH	26 080	2 070	0.10	1.00	0.6			2×10^8
$(CH_3)_2CHOH$	26 250	1 900	0.08	1.00	0.6			1×10^8
$(CH_3)_3COH$	26 640	1 510	0.07	0.99	0.7	0.01	14.0	1×10^8
CH_3CN	28 150^f	0	0.02	0.98	0.4	0.02	11.0	5×10^7

[a] Frequency of fluorescence emission maximum. [b] Frequency shift relative to acetonitrile (reference solution). [c] Quantum yield for fluorescence emission. [d] Fluorescence response function is represented as $F(t) = A\exp(-t/\tau_F) + A'\exp(-t/\tau'_F)$. [e] Rate constant of fluorescence emission $[k_F = \Phi_F]$. [f] Distinct shoulders were also observed at 29 570 and 26 760 cm^{-1}.

of complex formation (ΔH) increases as the $\Delta\nu(OH)/\nu_0(OH)$ value increases.[13,14]

Fluorescence Characteristics of (**1**) *in Several Alcohols*.—Changes in the fluorescence spectra of 0.4mM-(**1**) in deaerated alcohols relative to the acetonitrile solution were more distinct than those in the corresponding electronic absorption spectra. Although the vibrational structures were observed in the fluorescence spectra of (**1**) in acetonitrile as well as benzene,[2] the spectra in alcohols were commonly broad and structureless. Moreover, enormous red shifts of the fluorescence emission band occurred in alcohols, which could not be interpreted in terms of usual polarity effect of (aprotic) solvents on the fluorescence spectra.[15] The magnitude of the red shift relative to the acetonitrile solution (Table 4) is seen to increase with the increase in hydrogen-bonding ability of the alcohols as indicated by the $\Delta\nu(OH)/\nu_0(OH)$ values. Thus, it is most likely that the lowest excited $^1(\pi,\pi^*)$ state of the naphthalene chomophore of (**1**) forming a hydrogen bond with a solvent alcohol, the energy level of which should be increasingly lowered as the hydrogen bond becomes stronger, is reponsible for the red-shifted fluorescence emission. Obviously there are two possible routes to such a hydrogen-bonded $^1(\pi,\pi^*)$ state, *i.e.* direct excitation of the ground-state complex and excitation of uncomplexed (**1**) followed by hydrogen bonding of an alcohol to the resulting excited (**1**).

Table 4 also shows the quantum yields for the fluorescence emission (Φ_F) and the fluorescence lifetimes (τ_F). The Φ_F value was significantly enhanced in alcohols compared with in aprotic acetonitrile, possibly as a result of hydrogen-bond formation. Furthermore, a trend is evident that the increase in Φ_F parallels to the magnitude of the red shift [*i.e.* the lowering of the energy level of hydrogen-bonded $^1(\pi,\pi^*)$ state]. In contrast to the Φ_F, the τ_F values * in the series of alcohols were mutually very close while they became longer than in acetonitrile. From these Φ_F and τ_F values we evaluated the rate constants of fluorescence emission ($k_F = \Phi_F/\tau_F$) as listed in Table 4.

Quenching of the Formation of (**3**) *by Penta*-1,3-*diene*.—The effect of penta-1,3-diene, which is a well known quencher for both the excited singlet and triplet states of a variety of reactants,[16] on the two modes of ring-opening reaction of (**1**) in alcohols was also determined. Figure 4 shows the Stern–Volmer plots of $\Phi_R{}^0/\Phi_R$ against [penta-1,3-diene] for the formations of (**2**) and (**3**). In the propan-2-ol system the $\Phi_R{}^0(3)/\Phi_R(3)$ value increased linearly upon increasing the diene concentration up to 13mM. From the slope of the straight line the Stern–Volmer constant (K_{SV}) was evaluated as 420 l mol^{-1}. Since the product of the diffusion-controlled rate constant (k_{diff} 2.7×10^9 l mol^{-1} s^{-1} at 20 °C)[17] and the fluorescence lifetime τ_F (0.6 ns) in propan-2-ol is negligibly small compared with this K_{SV} value, it is reasonable to predict that the formation of (**3**) in propan-2-ol proceeds almost exclusively *via* the lowest excited $^3(\pi,\pi^*)$ state[2] of (**1**).

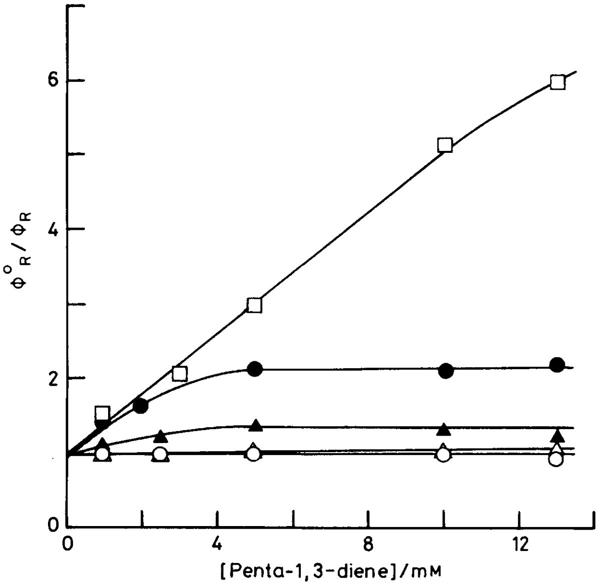


Figure 4. Stern–Volmer plots for quenchings of (**2a**) formation: ○, in methanol, (**2b**) formation: △, in t-butyl alcohol, (**3**) formation: ●, in ethanol; □, in propan-2-ol; ▲, in t-butyl alcohol by penta-1,3-diene on irradiation of 0.85mM-(**1**) at $\lambda_{ex.}$ 313 nm and room temperature under deaerated conditions

In both the ethanol and t-butyl alcohol systems, however, the $\Phi_R{}^0(3)/\Phi_R(3)$ value increased in a downward curve to approach constant limits upon increasing the diene concentration. Such a profile of the Stern–Volmer plot is characteristic of kinetics in which reaction occurs from both the excited singlet and triplet states of a reactant but only the triplet state is quenched.[18] Similar to the propan-2-ol solution, the failure to quench the excited singlet state would be accounted for by the very short fluorescence lifetimes (0.6—0.7 ns). Thus, we concluded that not only the $^3(\pi,\pi^*)$ state, as is predominant in propan-2-ol system, but also the $^1(\pi,\pi^*)$ state of (**1**) can lead to (**3**) in ethanol and t-butyl alcohol. According to this aspect, the limiting $\Phi_R{}^0(3)/\Phi_R(3)$ values at higher diene concentrations (>5mM) provide the estimates of the $\Phi_{TR}{}^0/\Phi_{SR}{}^0$ ratios as 1.2 in ethanol and 0.4 in t-butyl alcohol, in which $\Phi_{TR}{}^0$ and $\Phi_{SR}{}^0$ refer to the

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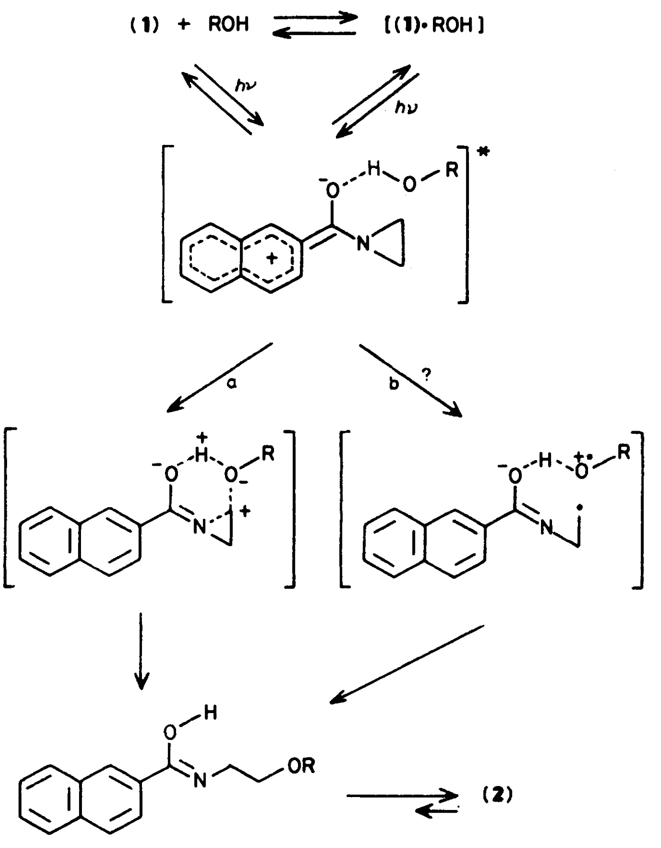
* Although the best-fit response function for the time-resolved fluorescence emissions in t-butyl alcohol and acetonitrile were represented by the sum of two exponentials, they can be safely approximated by the single exponential because of the minor contribution of the longer decay term.



Scheme 2.

quantum yields for singlet and triplet reactions to produce (3) in the absence of the diene.[18]

In contrast to the formation of (3), the quantum yields of the alcohol-incorporated products (**2a** and **b**) were not or little affected by penta-1,3-diene. This suggests that the formations of (**2a** and **b**) occur almost exclusively *via* the $^1(\pi,\pi^*)$ state of (1).

Mechanism of the Photoinduced Ring-opening Reaction of (1) *in Alcohols*.—The spectroscopic data presented above are consistent with 1:1 hydrogen-bond formation between (1), the possible basic site of which is the carbonyl oxygen, and each of the alcohols in their ground states. The hydrogen-bonding ability of the alcohols increases in the order t-butyl alcohol < propan-2-ol < ethanol < methanol. The initial steps of the ring-opening reaction are clearly the π–π^* electronic transitions of the naphthalene chromophores of both free and hydrogen-bonded (1), while the latter contribution should be minor because of the small K value. The red shift of the π–π^* band of (1) due to hydrogen bonding indicates that the base strength of the carbonyl oxygen increases[12] upon exciting the naphthalene chomophore of not only hydrogen-bonded but also free (1). Thus the hydrogen bonds of the series of alcohols to the excited state (1) should be stronger than those to the ground state one.

It is reasonable to expect that the enhanced hydrogen bonding of an alcohol to (1) in the lowest $^1(\pi,\pi^*)$ state favours heterolyses of the O–H bond of alcohol and the aziridinyl C–N bond of (1) to produce (2) as in Scheme 2 (path a). Presumably, this is the case for the formation of (**2a**) in methanol which has the greatest ability to form a hydrogen bond to (1) among the alcohols studied. Such a reaction pathway would become less important with lowering of the hydrogen-bonding ability as in the cases of ethanol and propan-2-ol. Following this aspect, however, it is particularly surprising that the least hydrogen bonding, t-butyl alcohol, gave rise to (**2b**). In this connection we have also noted the fact that the formation of (**2b**) is strongly dependent on the solvent polarity. Thus, on irradiation of 0.85mM-(1) in mixed solvents containing 25 vol % t-butyl alcohol, the yield of (**2b**) increased with dielectric constant of the solvent but that of the co-product (3) was roughly invariant (Table 5). Although an unambiguous explanation cannot be drawn at present, we postulated tentatively that local electron transfer[*] (or charge transfer) from the t-butyl alcohol oxygen to the aziridinyl carbon of (1) occurs in the hydrogen-bonded transition state within the reaction co-ordinate (Scheme 2, path b). The resulting cation radical form is expected to facilitate dissociation of proton from t-butyl alcohol, thereby producing the corresponding alkoxyl radical so as to incorporate into the aziridine-ring moiety of (1). In addition, the increased solvent polarity would become more favourable for such an electron-transfer reaction.

Table 5. Photoreactions of 0.85mM-(1) in several solvents containing 25 vol % t-butyl alcohol[a]

Solvent[b]	ε[c]	Quantum yield of product	
		$10^3\Phi_R{}^0$(**2b**)	$10^3\Phi_R{}^0$(3)
C_6H_6	4.82	0	0.6
$(CH_3CH_2)_2O$	6.37	0	1.0
$CH_3CO_2CH_2CH_3$	7.63	<0.04[d]	0.8
CH_3CN	30.08	0.4	0.9

[a] On irradiation at $\lambda_{ex.}$ 313 nm and room temperature under deaerated conditions. [b] Mixed with 25 vol % t-butyl alcohol. [c] Dielectric constant of mixed solvent [ε $0.75\varepsilon' + 0.25 \times 12.47$, where ε' is the dielectric constant of a given solvent]. [d] Upper limit.

In contrast to (**2a**) derived from the hydrogen-bonded $^1(\pi,\pi^*)$ state of (1), the formation of (3) in propan-2-ol is characteristic of the ring opening in the $^3(\pi,\pi^*)$ state. From the $\Phi_{TR}{}^0(3)/\Phi_{SR}{}^0(3)$ ratios and the overall yields $\Phi_R{}^0(3)$, the $\Phi_{TR}{}^0(3)$ values corresponding to triplet reactions in ethanol and t-butyl alcohol can be estimated as 1.6×10^{-3} and 0.2×10^{-3}, respectively. Thus, it is seen that the reactivity of alcohols toward the $^3(\pi,\pi^*)$ state of (1) increases in the order t-butyl alcohol [relative reactivity based on $\Phi_{TR}{}^0(3)$, 1] < ethanol (8) < propan-2-ol (13). This order agrees with the increased radical reactivity[†] of alcohols as observed in the conventional oxidation, suggesting a mechanism involving homolysis of the aziridinyl C–N bond of (1) in the $^3(\pi,\pi^*)$ state and hydrogen abstraction from alcohols. It seems also plausible that the hydrogen-bonding interaction makes a minor contribution to such a homolysis. Concerning the formation of (3) *via* $^1(\pi,\pi^*)$ state of (1) in ethanol and t-butyl alcohol, we have not yet obtained any mechanistic evidence.

Further studies on the formation of (**2b**) in t-butyl alcohol and that of (3) in ethanol and t-butyl alcohol *via* singlet photoreactions of (1) are being continued.

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[*] Ionization potentials (eV) of these alcohols were reported to decrease in the order: methanol (10.85) > ethanol (10.46) > propan-2-ol (10.29) > t-butyl alcohol (9.97) (C. J. Danby, B. J. Cocksey, and J. H. D. Eland, *J. Chem. Soc. B*, 1971, 790).

[‡] For instance, rate constants of hydroxyl radical reactions in aqueous solution (pH 7) are as follows: t-butyl alcohol (2.5×10^8 l mol^{-1} s^{-1}, relative value 1.0) < ethanol (1.1×10^9, 4.4) < propan-2-ol (3.9×10^9, 16) (G. E. Adams, J. W. Boag, J. Currant, and B. D. Michael, in 'Pulse Radiolysis,' eds. J. H. Baxendale, M. Ebert, J. P. Keene, and A. J. Swallow, Academic Press, London, 1965, p. 131).

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References

1 S. Nishimoto, T. Izukawa, and T. Kagiya, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 1484.
2 S. Nishimoto, T. Izukawa, and T. Kagiya, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1147.
3 W. H. Melhuish, *J. Phys. Chem.*, 1961, **65**, 229.
4 For instance, P. J. Wagner and E. J. Siebert, *J. Am. Chem. Soc.*, 1981, **103**, 7329.
5 J. G. Calvert and J. N. Pitts, Jr., 'Photochemistry,' Wiley, New York, 1966, p. 784.
6 H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, 1949, **71**, 2703.
7 T. Kagiya, Y. Sumida, and T. Inoue, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 767.
8 W. Gordy, *J. Chem. Phys.*, 1939, **7**, 93; 1941, **9**, 215; W. Gordy and S. C. Stanford, *ibid.*, 1940, **8**, 170; 1941, **9**, 204.
9 E. M. Arnett, *Prog. Phys. Org. Chem.*, 1963, **1**, 223.
10 I. A. Koppel and U. A. Palm, in 'Advances in Linear Free Energy Relationships,' eds. N. B. Chapman and J. Shorter, Plenum Press, London, 1972, ch. 5.
11 A. G. Burden, G. Collier, and J. Shorter, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1627.
12 G. C. Pimentel, *J. Am. Chem. Soc.*, 1957, **79**, 3323.
13 M. D. Joesten and R. S. Drago, *J. Am. Chem. Soc.*, 1962, **84**, 3817.
14 M. R. Basila, E. L. Saier, and L. R. Cousins, *J. Am. Chem. Soc.*, 1965, **87**, 1665.
15 N. Matag and T. Kubota, 'Molecular Interactions and Electronic Spectra,' Marcel Dekker, New York, 1970, ch. 8.
16 F. S. Wettack, G. D. Renkes, M. G. Rockely, N. J. Turro, and J. C. Dalton, *J. Am. Chem. Soc.*, 1970, **92**, 1793; R. G. Brown and D. Phillips, *ibid.*, 1974, **96**, 4784; D. A. Labianca, G. N. Taylor, and G. S. Hammond, *ibid.*, 1972, **94**, 3679; A. A. Lamola, in 'Technique of Organic Chemistry,' eds. P. A. Leermakers and A. Weissberger, Wiley, New York, 1969, vol. 14, p. 96.
17 J. G. Calvert and J. N. Pitts, Jr., 'Photochemistry,' Wiley, New York, 1966, p. 627.
18 J. C. Dalton and N. J. Turro, *Mol. Photochem.*, 1970, **2**, 133.

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