(E)-S-Phenyl 2-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]-3-hydroxythiohex-4-enoate (19) (oil, 80:20). ¹H NMR data for 19s: 4.31, 4.26, 3.3, 9.0. For 19a: 4.31, 4.31, 4.5, undet. IR: 3480, 1707 cm⁻¹. Anal. Calcd for C₁₈H₂₈O₃SSi: C, 61.32; H, 8.00. Found: C, 61.23; H, 8.07.

Synthesis of Methyl 2,3-Bis(phenylmethoxy)butanoate 20 from 9a. Compound 9a was converted (87% yield) into the corresponding methylester by treatment with $Cu(OAc)_2$ in re-fluxing methanol as described.⁸ Benzylation with benzyl bromide in the presence of Ag₂O in refluxing Et_2O afforded 20⁹ in 58% yield after flash chromatography with a 80:20 hexanes-Et₂O mixture as eluant.

Synthesis of Methyl 2,3-Dihydroxy-3-phenylpropanoate from 18s. Compound 18s was converted (60% yield) into the corresponding methylester as described above.⁸ Desilvlation with a few drops of 40% aqueous HF in acetonitrile at rt afforded compound 21 in 97% yield. The crude product was shown to be identical by ¹H NMR to the diol prepared by osmylation of (E)-methyl cinnamate.

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Photoinduced Electron-Transfer Reactions of 1-Substituted 2,3-Diphenylaziridines with 9,10-Dicyanoanthracene and Chloranil

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Introduction

An electron donor can be converted to the corresponding cation radical through a single electron transfer (SET) to an excited state of an electron acceptor. Back-electron transfer (BET) from the anion radical of the acceptor to the cation radical leads to unproductive decay, but rapid bond cleavage can compete with this energy-wasting process.¹ Aziridines are reactive substrates under photoinduced SET conditions since their cation radicals can undergo facile bond cleavage driven by the relief of the ring strain. Previous studies have demonstrated that 1,3-dipolar cycloaddition is involved in SET photoreactions of certain aryl-substituted aziridines with electron acceptors in the presences of dipolarophiles.² In these cases, cycloadducts are produced through dipolar additions between the dipolarophile and the ring-opened intermediates that have escaped from the geminate ion radical pairs. Interestingly, little information is available on the behavior of aziridine cation radicals in ion radical pairs.³ In this paper, we report the results of a study of the photoreactions of 1-substituted 2,3-diphenylaziridines (1) with electron acceptors 9,10-dicyanoanthracene (DCA) and chloranil (CL).⁴



Results

The DCA-sensitized photoreactions of cis 1-substituted 2,3-diphenylaziridines 1 were conducted in methylene chloride (entries 1-6 in Table I). To prevent decomposition of the initial products, irradiation was discontinued at 44-67% conversion of 1. ¹H NMR analysis of the reaction mixture obtained from the irradiation of cis-1benzyl-2,3-diphenylaziridine (1a) demonstrated that dibenzylamine (2a) and benzaldehyde (4) were the major products along with a small amount of benzalbenzylamine (3a). When cis-1-tert-butyl-2,3-diphenylaziridine (1b) was subjected to the similar reaction conditions, benzyl-tertbutylamine (2b), benzal-tert-butylamine (3b), and 4 were formed. The yield of 4 was nearly the same whether the reaction was conducted under a N2 or an O2 atmosphere (entries 1 and 2). This result suggests that the oxygen in 4 does not come from molecular oxygen. Since 2 and 4 appear to be formed through a formal hydrolysis of 1, a trace amount of H₂O in photolysis solutions must be responsible. Indeed, the yields of 2 increased when H_2O was added to the photolysis solutions (entries 3 and 6). Similarly, the yield of 2a increased when MeOH was present (entry 4).

These observations suggest that the addition of a nucleophilic species to intermediates in these processes is involved in product formation. To test whether a nucleophile was involved, DCA-sensitized photoreactions of 1a in methylene chloride were conducted in the presence of D_2O or MeOD. Under these conditions, we expected that one hydrogen at the benzylic position of 2a would be substituted by deuterium. Indeed, dibenzylamine obtained from the acidic extraction of the reaction mixtures was found (¹H NMR analysis) to be nearly quantitatively monodeuterated at the benzylic position (see Experimental Section).

The product distributions from photoreactions in MeCN were different from those in methylene chloride, and the yields were relatively low (entry 7 in Table I). While H_2O had little influence on the product yields (entry 8), MeOH significantly increased the yields of 2a and 4 (entry 9). Moreover, 2a was not detected when LiClO₄ was present in the photolysis solution (entry 10). The absence of 2a is not due to decomposition, since more than 87% of 2a was recovered when DCA-sensitized photoreactions of 2a were performed under similar conditions.

In contrast, when a methylene chloride solution of 1a (0.043 M) and CL (0.044 M) was irradiated for 60 min, tetrachlorohydroquinone (CLH₂) was formed in 82% based on consumed 1a. Products 3a (82%) and 4 (74%) were also detected by ¹H NMR analysis of the photolysate at 81% conversion of 1a. Thus, photoreactions of 1a with CL lead to consumption of the acceptor. Results from studies of the photoreactions of 1a and CL (ca. 0.5 equiv) under various conditions are notable in that 2a is not formed under any of the reaction conditions used (Table II). In both methylene chloride and acetonitrile, H_2O and MeOH had little effect on the yield of 3a (entries 2, 3, 5, and 6), and appreciable amounts of the dimethyl acetal

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⁽⁴⁾ Mattay, first reported that benzaldehyde benzylimine was formed in the photoreaction of cis-2,3-diphenylaziridine sensitized by chiral 1,1'-binaphthalene-2,2'-dicarbonitrile. However, the reaction mechanism as not explained in detail. Vondenhof, M.; Mattay, J. Chem. Ber. 1990, 123. 2457.

Table I. DCA-Sensitized Photoreactions of Cis 1-Substituted 2,3-Diphenylaziridines 1^a

							product yields"/%			
entry	solvent	1	atm	additive	time/min	conversion ^b /%	2	3	4	
1	CH ₂ Cl ₂	1 a	N ₂		15	59	63	17	68	
2	CH_2Cl_2	la	O_2		15	67	48	18	66	
3	CH ₂ Cl ₂	1 a	N_2	H ₂ O	15	63	78	8	68	
4	CH ₂ Cl ₂	1 a	N_2	MeOH	15	66	88	8	82	
5	CH_2Cl_2	1 b	N_2		30	44	52	11	43	
6	CH ₂ Cl ₂	1 b	N_2	H ₂ O	30	55	82	11	55	
7	MeČN	1 a	N_2	-	15	62	21	26	23	
8	MeCN	1 a	N_2	H ₂ O	15	57	35	11	14	
9	MeCN	1 a	N_2	MeOH	15	56	86	13	82	
10	MeCN	1 a	N_2	LiClO ₄	15	64	0	17	28	

^a Conditions: irradiation ($\lambda > 360$ nm); [1] = 3.4-3.6 × 10⁻² M, [DCA] = 4.0-4.4 × 10⁻⁴ M. ^b The product yields were determined by ¹H NMR based on the conversion of 1.

Table II. Photoreactions of 1-Benzyl-2,3-diphenylaziridine (1a) with CL^a

				product yields ^b /%		
entry	solvent	additive	conversion ^b /%	3a	4	
1	CH ₂ Cl ₂	·	46	91	83	
2	CH ₂ Cl ₂	H ₂ O	49	84	61	
3	CH ₂ Cl ₂	MeOH	45	82	60 (33)°	
4	MeČN		52	65	85	
5	MeCN	H ₂ O	51	76	75	
6	MeCN	MeOH	43	86	26 (74)°	
7	MeCN	LiClO ₄	49	63	94	

^aConditions: irradiation ($\lambda > 340$ nm) for 15 min under N₂; [1a] = $3.5-3.7 \times 10^{-2}$ M, [CL] = 1.8×10^{-2} M. ^bThe product yields were determined by ¹H NMR based on the conversion of 1a. ^cValues in parentheses are the yields of benzaldehyde dimethyl acetal.

of 4 were obtained when photoreactions were conducted in the presence of MeOH (entries 3 and 6). The yield of **3a** was not greatly affected by the addition of $LiClO_4$ (entry 7). Since a mechanism for formation of 3a involving the reaction of 2a and CL was possible, the photochemistry of 2a and CL was explored. However, the yield of 3a from 2a was less than 15% under the similar irradiation conditions used for reaction of 1a.

Discussion

The results described above clearly demonstrate that two typical fragmentation products, 2 and 3, are produced from the SET-induced photoreactions of 1 with acceptors. While 2 is a major product formed under DCA-sensitized conditions, only 3 is obtained in photoreactions with CL. However, in both cases, SET from 1 to an excited state of the acceptor appears to initiate the reactions. The fact that the oxidation potentials $(E_p^{ox}, V \text{ vs SCE})^5$ of 1a and 1b are 1.64 and 1.55, respectively, indicates that these substrates can be readily oxidized by SET to the excited singlet of DCA (E^{red} , ca. 2.0 V)⁶ or the excited triplet of CL (E^{red} , ca. 2.7 V).⁷ Indeed, it is reported that both 1a and 1b efficiently quench the DCA fluorescence $(k_q =$ $8.5-8.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$).^{2c}

Based on previous studies² and the results obtained here, a plausible reaction mechanism for the DCA-sensitized photoreactions of 1a can be formulated (Scheme I). Initial SET between 1a and the excited singlet of DCA is followed



by carbon-carbon bond cleavage of the cation radical of 1a (5). The deuterium-labeling experiment clearly demonstrates that a negative charge is generated at C_2 or C_3 in the reaction of 1a. Thus, it is reasonable to assume that BET from the DCA anion radical to azomethine ylide cation radical 6 gives azomethine ylide 7. Ylide 7 can react with H_2O to produce α -amino acohol 8, which is the precursor of 2a and 4.8

According to this mechanism, interruption of BET between the DCA anion radical and cation radical 6 pair decreases the yield of 2. Since the yields of contact ion radical pairs are higher in less-polar solvent than those in more-polar solvents,¹ it makes sense that the yields of 2a and 4 are higher in methylene chloride than in acetonitrile. The addition of LiClO₄ should also result in the interruption of BET between 6 and the DCA anion radical, as has been observed earlier.⁹ Finally, the enhancing effect of the polar protic substances H₂O and MeOH on the yield of 2a can be explained by the interception of 7 by pro-

⁽⁵⁾ Oxidation potentials $(E_p^{ox} \vee sSCE)$ of 1 were obtained by cyclic voltammetry (Pt electrode, scan rate 100 mV/s) in MeCN containing tetrabutylammonium perchlorate (0.1 M). The generous assistence of Professor Masaki Kamata (Faculty of Education, Niigata University) in

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⁽⁸⁾ Intermediate 8 has not yet been detected. However, when a similar irradiation of 1a and DCA was conducted in CD_2Cl_2 containing MeOH (ca. 1%) and ¹H NMR analysis was performed without workup, three diagnostic singlet peaks were observed at 3.35, 3.68, and 4.68 ppm. Relative intensities of these peaks were approximately 3, 4, and 1. Notably, when this solution was concentrated and again analyzed by ${}^{1}H$ NMR in CDCl₃ (usual procedure), those three peaks had decreased while the peaks of 2a and 4 had increased. Thus, these singlets are tentatively assigned to the structure of N-(methoxyphenylmethyl)dibenzylamine that

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tonation-addition, which can compete with return to the aziridine ground state.

In contrast to the DCA-sensitized photoreactions, the photoreaction of 1a and CL produced 3a, 4, and CLH₂. The overall reaction mechanism proposed for the CL processes is shown in Scheme II. The lack of formation of 2a suggests that, in this case, the reaction 6 with H_2O to form 9 is faster than BET to form 7. Slow BET in triplet ion radical pairs such as 6 and the CL anion radical is consistent with the above observation. Thus, the small effect of LiClO₄ on the product yields in the CL case can be radionalized by the rapid fragmentation of 6, which is assisted by the combination of the CL anion radical and H_2O in the triplet-ion radical pair. In the ion radical pair, protonation of the basic CL anion radical by H₂O would occur.¹⁰ This protonation assists the nucleophilic addition of H_2O to 6. Then, fragmentation of the formed free radical 9, assisted by hydrogen abstraction by 10, gives 3a, 4, and CLH_2 . Alternatively, SET from 9 to 10 followed by fragmentation of 11 involving ptoton transfer to 12 can also produce the observed compounds.

Summary

We have found that the photoinduced electron-transfer reaction of 1-substituted 2,3-diphenylaziridines 1 with DCA affords secondary amines and benzaldehyde, and the reaction of 1 with CL gives imines and benzaldehyde. The release of aziridine ring strain drives rapid bond cleavage of the cation radicals and may overcome the relatively lower electron-donating ability of azirizines compared to amines.¹¹ The results obtained in this study and related studies^{2,3,12} indicate that aziridines should be reactive substances in other chemical or biological electron-transfer reactions.

Experimental Section

General Procedures.¹³ 9,10-Dicyanoanthracene and chloranil were sublimed before use. Methylene chloride was distilled from calcium hydride after being treated with sulfuric acid, aqueous

sodium hydroxide, and calcium chloride. Acetonitrile was distilled first from phosphorus pentoxide and then from calcium hydride. Aziridines 1a and 1b were prepared in three steps from transstilbene oxide.¹⁴ 1a: mp 56-56.5 °C (lit.¹⁵ mp 52.5-53.5 °C); ¹H NMR (CDCl₃) δ 3.03 (s, 2 H), 3.85 (s, 2 H), 7.00–7.40 (m, 15 H). 1b: mp 97–98 °C (lit.¹⁶ 92–93 °C); ¹H NMR (CDCl₃) δ 1.15 (s, 9 H), 3.14 (2 H, s), 7.02-7.18 (m, 10 H).

Photolyses were performed in Pyrex tubes in a water bath with a 500-W Xe-Hg lamp with glass cut-off filters (Toshiba L-39 for DCA, Toshiba UV-37 for CL). The photoproducts were identified by direct comparison of their ¹H NMR spectra with those of authentic samples.

DCA-Sensitized Photoreactions of 1. Aziridine 1 (0.10-0.11 mmol) was dissolved in 3 mL of a methylene chloride or an acetonitrile solution of DCA (4.0-4.4 \times 10⁻⁴ M). The appropriate additive (H₂O, 0.1 mL; MeOH, 0.1 mL; LiClO₄, 0.53 mmol) was added if necessary, and then the solution was purged with nitrogen or oxygen for 15 min. Then, the solution was irradiated ($\lambda > 360$ nm). Concentration of the photolysate at ambient temperature afforded a residue, which was subsequently analyzed by ¹H NMR with triphenylmethane as an internal standard.

Deuterium-Labeling Experiments in DCA-Sensitized Photoreactions of 1a in Methylene Chloride. D₂O (99.8% D, 0.1 mL) or MeOD (99.5% D, 0.1 mL) was added to a methylene chloride (3 mL) solution of 1a (0.17-0.18 mmol) and DCA (0.0013 mmol). This solution was purged with nitrogen and irradiated for 40 min. the photolysate was extracted with 1 N HCl. The aqueous layer was basified with 2 N NaOH and subsequently extracted with methylene chloride. The extract was dried over anhydrous Na_2SO_4 and concentrated. Then, the ratio of the ¹H NMR peak integration of the aromatic protons to the benzylic protons of dibenzylamine was obtained. Ratios for D₂O and MeOD reactions were 3.4 and 3.3, respectively. In control experiments, H₂O or MeOH was added to the solution before irradiation, and D₂O or MeOD was added to the photolysate before workup. Ratios for these experiments were about 2.6.

Photoreactions of 1a with CL. 1a (0.10-0.11 mmol), CL (0.054 mmol), and the additive were dissolved in 3 mL of methylene chloride or acetonitrile. This solution was purged with nitrogen for 15 min and then irradiated ($\lambda > 340$ nm) for 15 min. The product yields were obtained by ¹H NMR after concentration of the photolysate.

To isolate tetrachlorohydroquinone, a methylene chloride (11 mL) solution of 1a (0.48 mmol) and CL (0.48 mmol) was purged with nitrogen and then irradiated for 60 min. Concentration of the phoyolysate was followed by the addition of chloroform. The solid obtained by filtration was identified as tetrachlorohydroquinone by comparing the IR spectrum of the product with that of an authentic sample.¹⁷ The filtrate was concentrated and analyzed by ¹H NMR. The conversion of 1a was 81%, and the yields of tetrachlorohydroquinone, 3a, and 4 were 66%, 71%, and 60%, respectively.

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A Cyclic Sulfate Route to Methylenecyclopropanes

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Hypoglycine A, an unusual amino acid, (+)- α -amino-2methylenecyclopropanepropionic acid (1), found in the unripe ackee fruit (Blighia sapida), has been implicated in the Jamaican vomiting sickness.¹ The actual causative

⁽¹⁰⁾ It is reported that quinone anion radicals are more basic than the DCA anion radical. Mattes, S. L.; Farid, S. J. Am. Chem. Soc. 1986, 108, 7356.

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