tube 1. A third irradiation, involving (a new) tube 3, was carried out.

Finally, the white solids deposited in tubes 1-3 were washed out with cold anhydrous Et_2O (drybox), triturated several times with additional ether, and then recrystallized from CH_3CN/Et_2O. The final $Cy_3C_3^+Cl^-$, 140 mg, was dried under vacuum. The yield is ~60%, based on decomposed diazirine (see Results).

For $Cy_3C_3^+Cl^-$, we observed mp 89-90 °C; IR (KBr) 3080 (m), 3010 (s), 1425 (s), 1400 (sh), 1330 (m), 1060 (s), 1040 (s), 900 (s), 875 (sh) cm^{-1}. The UV and NMR spectra are discussed in the Results.

Anal. Calcd for $C_{12}H_{15}Cl$: C, 74.0; H, 7.77; Cl, 18.2. Found: C, 74.1; H, 7.82; Cl, 18.0.

Other $Cy_3C_3^+$ Salts. Fluoroborate. $Cy_3C_3^+Cl^-$ (70 mg, 0.36 mmol) was dissolved in 5 mL of dry CH_3CN. To this solution was added 70 mg (0.36 mmol) of $AgBF_4$ in 5 mL of CH_3CN. An immediate precipitate of AgCl formed and was filtered. The filtrate was stripped of solvent on the rotary evaporator and the white residue was recrystallized from CH_3CN/Et_2O to give 70 mg (0.285 mmol, 79%) of $Cy_3C_3^+BF_4^-$, mp 137-140 °C (lit.[12] mp 141-142 °C). NMR spectra are discussed under Results.

Hexafluoroantimonate. $Cy_3C_3^+SbF_6^-$ was prepared in 74% yield from the chloride salt exactly as described for the fluoroborate, except that $AgSbF_6$ was used in place of $AgBF_4$: mp 213-215 °C; IR (KBr) 3070 (w), 3010 (w), 1445 (s), 1330 (m), 1300 (s), 1060 (s), 1030 (m), 1010 (m), 910 (s), 740 (m), 640 (s) cm^{-1}. The density of crystalline $Cy_3C_3^+SbF_6^-$ was 1.81 g/cm^3 as determined by the flotation method in a $CHBr_3/CCl_4/n\text{-}C_6H_{14}$ mixture. The X-ray crystal structure is presented under Results; cf. Table II and Figures 1 and 3.

1,2-Dicyclopropyl-3-phenylcyclopropenium Fluoride ($Cy_2PhC_3^+F^-$, 1c). 3-Fluoro-3-phenyldiazirine[16] (408 mg, 3.0 mmol) and 2.23 g (21 mmol) of dicyclopropylacetylene[14] were dissolved in 5 mL of anhydrous ether and photolyzed, with magnetic stirring, in a Pyrex tube at 5-10 °C for 5 h. The focused Osram 200-W XE mercury lamp was used. White precipitate (later yellow) was collected by filtration at the end of each hour. A total of 214 mg (33%) of $Cy_2PhC_3^+F^-$ was obtained, washed several times with dry ether, and dried under vacuum. The salt did not recrystallize well from CH_3CN/Et_2O and had to be stored over dry ice to avoid decomposition. We observed mp 79-81 °C; IR (KBr), 3375 (s), 3010 (m), 2975 (m), 1585 (m), 1490 (m), 1450 (m), 1420 (s), 900 (s), 700 (m), 740 (m), 680 (m) cm^{-1}. NMR and UV spectra are discussed under Results.

Fluoroborate Salt. To a solution of 120 mg (0.56 mmol) of $Cy_2PhC_3^+F^-$ in 10 mL of nitromethane freshly distilled from CaH_2 was added a solution of 3 mL of freshly distilled BF_3-ether in 10 mL of nitromethane. The reaction solution was protected from moisture and stirred magnetically for 1.5 h at ice-bath temperature. Solvents were removed under vacuum, and the residual white solid was dissolved in dry acetone and reprecipitated by the addition of ether. We obtained 120 mg (0.43 mmol, 77%) of $Cy_2PhC_3^+BF_4^-$ as white crystals: mp 123-125 °C; d = 1.31 g/cm^3 (flotation in $n\text{-}C_6H_{14}/CCl_4$); IR (KBr) 3400 (s), 3050 (m), 1595 (s,sh), 1470 (s), 1430 (s), 1340 (m), 1315 (m), 1060 (s,br), 900 (s), 865 (m), 775 (m), 680 (m) cm^{-1}. The NMR spectra and X-ray crystal structure (Table II, Figure 2) are discussed under Results.

Anal. Calcd for $C_{15}H_{15}BF_4$: C, 63.8; H, 5.36; F, 26.96. Found: C, 64.1; H, 5.44; F, 26.1.[38]

Acknowledgment. R.A.M., S.S., and R.C.M. thank the National Science Foundation for financial support. The Varian XL-400 NMR spectrometer and the Enraf-Nonius X-ray diffractometer were purchased with the aid of instrument grants from the National Science Foundation and the National Institutes of Health, respectively. The VAX computer was obtained with National Science Foundation support. We thank Mr. R. Beveridge for NMR spectra and Prof. A. Pardi for helpful discussions concerning their interpretation.

Registry No. 1c·F^-, 99310-18-6; **1c·BF_4^-**, 99310-20-0; **1d·Cl^-**, 75094-00-7; **1d·BF_4^-**, 75359-38-5; **1d·SbF_6^-**, 99310-21-1; **2**, 26811-00-7; **3**, 99310-17-5; dicyclopropylacetylene, 27998-49-8; cyclopropylamidine hydrochloride, 57297-29-7; 3-chloro-3-cyclopropyldiazirine, 4222-24-6; 3-fluoro-3-phenyldiazirine, 87282-19-7.

Supplementary Material Available: Listings of fractional atomic coordinates, bond distances and angles, anisotropic thermal parameters, and structure factor amplitudes for $Cy_2PhC_3^+BF_4^-$ and $Cy_3C_3^+SbF_6^-$ (20 pages). Ordering information is given on any current masthead page.

(38) The presence of boron may interfere with the fluorine analysis. The structure is secured by the X-ray analysis, however.

Selective Removal of Electron-Accepting *p*-Toluene- and Naphthalenesulfonyl Protecting Groups for Amino Function via Photoinduced Donor-Acceptor Ion Pairs with Electron-Donating Aromatics

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Contribution from the Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo 060, Japan. *Received March 11, 1985*

Abstract: When *N*-tosylamines (**3a**, **3b**, **7**, **17a**, **17b**, **21**, **23**) in aqueous ethanol were irradiated with a high-pressure mercury lamp in the presence of an electron-donating aromatic such as 1,2- (**6**) and 1,4-dimethoxybenzenes (**10**) and 1,5-dimethoxynaphthalene (**14**) and a reductant (sodium borohydride, ascorbic acid, ammonia borane, hydrazine), a photochemical detosylation proceeded quite easily to give the corresponding amines (**4a**, **4b**, **8**, **18a**, **18b**, **22**, **24**) in the high yields. On irradiation in the presence of **10** and sodium borohydride, *N*-(naphthalenesulfonyl)phenethylamine (**19**) also gave **4a**. Mechanistic studies based on fluorescence quenching, quantum yield measurement, and free energy change calculation show that this photoreaction involves an electron transfer from an electron-donating aromatic to an electron-accepting sulfonamide. A preliminary application for the synthesis of lysine peptides was also described.

Since the concept of exciplex and electron transfer was introduced into organic photochemistry a number of new reactions have been reported mainly from the mechanistic point of view.[2] However, a few reactions involving the exciplex or the electron transfer in excited donor-acceptor pairs are generally useful in synthetic organic chemistry.[3] The synthesis of various heterocycles

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(2) Gordon, W.; Ware, W. "The Exciplex"; Academic Press: New York, 1975.

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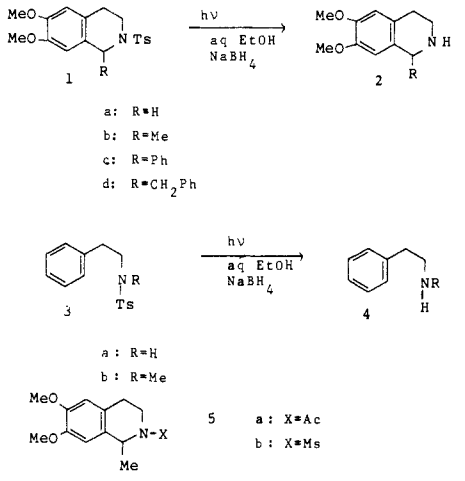
Scheme I



by the intramolecular photo-Friedel–Crafts reaction between electron-donating aromatic rings and electron-accepting chloracetamide groups developed in this laboratory also provides a useful example in electron-transfer photochemistry.[4] As another example, we report here a photochemical hydrolysis of *p*-toluenesulfonamides in the presence of electron-donating aromatic compounds. This reaction is of mechanistical interest as a typical photosensitized electron-transfer reaction and also may be useful in organic synthesis, especially in peptide chemistry.[5]

The *N*-tosyl group is one of the most stable protecting groups for amino function, and only the reduction with sodium in liquid ammonia is practically the useful deprotection method.[6] However, many serious side reactions have been reported,[7] and the selective photocleavage of the *N*-tosyl protecting group in this report can be expected to avoid such side reactions.[5]

Umezawa and Hoshino reported previously that, on irradiation with a high-pressure mercury lamp in the presence of sodium borohydride, 6,7-dimethoxytetrahydroisoquinoline *N*-tosylates (**1a–d**) were readily cleaved to the corresponding tetrahydroisoqunolines (**2a–d**) in over 80% yields,[8] whereas under the same conditions *N*-tosylphenethylmines (**3a**, **3b**) gave detosylated phenethylamines (**4a**, **4b**) only in less than 40% yields.[9,10] Sulfonamides are known to give the corresponding amines by radical cleavage on irradiation though sometimes in very poor yields.[11] The photocleavage of **3** via the direct photoexcitation must be an additional example of the radical cleavage, but the high yields of **2** from **1** suggest that an alternative mechanism acts in the photocleavage of **1**.

Since **1** has both the electron-donating dimethoxybenzene and electron-accepting tosylamide groups, an intramolecular electron transfer must have occurred in the initial step of the photolysis of **1**. Actually, **1b** is almost completely missing the strong fluorescence of 1,2-dimethoxybenzene, which was, however, observed without quenching in the *N*-acetyl (**5a**) and the *N*-mesyl derivatives (**5b**).[10] Both **5a** and **5b** were completely stable under the above irradiation conditions and recovered unchanged. The fluorescence quenching in **1b** can be explained in terms of the exciplex formation or the electron transfer between the dimethoxybenzene and the tosyl (aromatic sulfonyl) groups, though no new emission was observed. The *N*-acetyl and the *N*-mesyl (aliphatic sulfonyl) groups must be too weak as electron acceptors to form excited donor–acceptor pairs with the dimethoxybenzene ring.

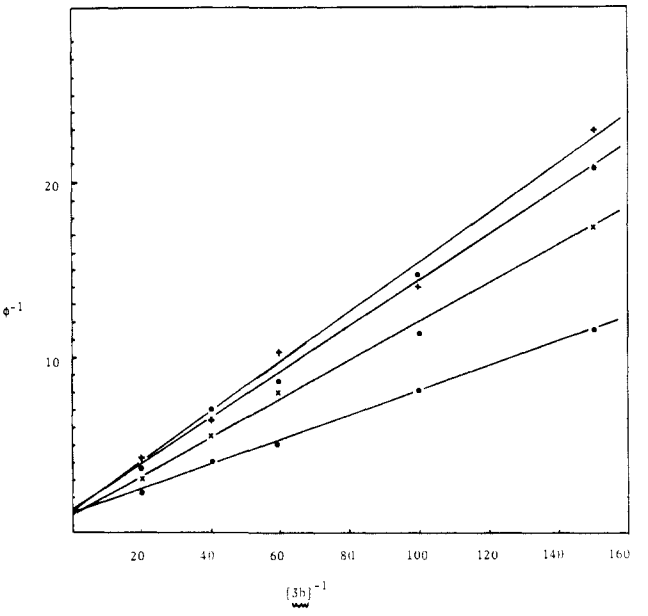
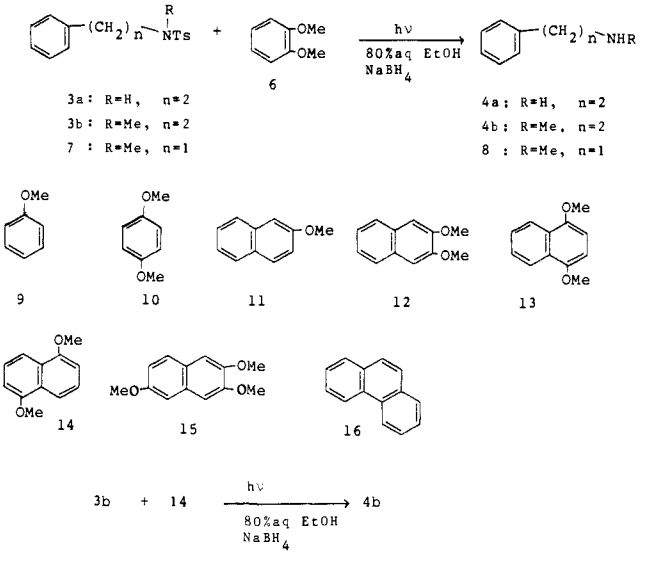


Figure 1. Dilution plot for disappearance of **3b** in the presence of **6** (×), **10** (○), **13** (+), and **14** (●).

Scheme II



Results and Discussion

Photolysis of Aromatic Sulfonamides in the Presence of Methoxy Derivatives of Benzene and Naphthalene. When a 95% ethanol solution of **3b** (10 mM) and veratrol (**6**; 30 mM) was irradiated with a 100-W high-pressure mercury lamp, the reaction mixture gradually turned orange and **4b** was isolated in 66% yield. In the presence of sodium borohydride the yield of **4b** was improved to 86%. Similarly, **3a** and **7** readily gave **4a** and **8**, respectively, in high yields. Anisole (**9**) and 1,4-dimethoxybenzene (**10**) also acted as electron donors in this photoreaction (Table I).

Because of its lower oxidation potential **10** was expected to be a better electron donor. Actually, both the $k_q\tau$ value calculated from the linear Stern–Volmer plot of fluorescence quenching of

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Table I. Photolysis of Sulfonamides in the Presence of Electron Donors and Reductants[a]

sulfonamide (mM)	donor (mM)	reductant (mM)	solvent	filter	amine (yield, %)[b]
3b (10)	**6** (30)		EtOH		**4b** (66)
3b (10)	**6** (30)	$NaBH_4$ (100)	80% EtOH		**4b** (87)
3a (10)	**6** (30)	$NaBH_4$ (100)	80% EtOH		**4a** (87)
7 (10)	**6** (30)	$NaBH_4$ (100)	80% EtOH		**8** (87)
3b (10)	**10** (30)	$NaBH_4$ (100)	80% EtOH		**4b** (81)
3a (10)	**10** (30)	$NaBH_4$ (100)	80% EtOH		**4a** (89)
3b (10)	**9** (40)	$NaBH_4$ (100)	80% EtOH		**4b** (91)
3b (4.2)	**14** (7.6)	$NaBH_4$ (40)	80% MeCN	Pyrex	**4b** (70)
3b (4.2)	**14** (7.6)	$NaBH_4$ (40)	80% THF	Pyrex	**4b** (78)
3b (4.2)	**14** (7.6)	$NaBH_4$ (40)	90% EtOH	Pyrex	**4b** (84)
3b (8.3)	**14** (4.4)	$NaBH_4$ (43)	EtOH	Pyrex	**4b** (88)
17b (3)	**14** (3)	$NaBH_4$ (15)	90% EtOH	Pyrex	**18b** (75)
19 (6.4)		$NaBH_4$ (64)	90% EtOH	Pyrex	**4a** (64)
19 (6.4)	**10** (64)	$NaBH_4$ (64)	90% EtOH	Pyrex	**4a** (88)
3b (10)	**14** (5)	AA[c] (30)	80% EtOH	Pyrex	**4b** (85)
17b (1)	**14** (0.5)	NH_2NH_2 (20)	90% EtOH	Pyrex	**18b** (80)
17a (2)	**14** (0.5)	NH_3BH_3 (10)	70% EtOH	Pyrex	**18a** (72)
21 (9.1)	**14** (4.5)	AA[c] (45)	90% EtOH	Pyrex	**22** (81)
23 (9.1)	**14** (4.5)	AA[c] (45)	90% EtOH	Pyrex	**24** (77)
25 (4.2)	**14** (4.2)	NH_3BH_3 (42)	83% EtOH	Pyrex	**26** (82)[d]
27 (5.4)	**35** (2.5)	AA[c] (25)	70% EtOH	Pyrex	**28** (79)[e]
29 (4.2)	**14** (4.2)	NH_3BH_3 (42)	83% EtOH	Pyrex	**30** (86)[f]
31 (3.6)	**35** (2.7)	AA[c] (11)	45% EtOH	Pyrex	**32** (81)[g]
33 (4.2)	**14** (4.2)	NH_3BH_3 (42)	83% EtOH	Pyrex	**34** (80)[h]

[a] Irradiation with a 100-, 200-, or 300-W high-pressure mercury lamp for 1–3 h. [b] Isolated yield as HCl salts. [c] AA: ascorbic acid. [d] Isolated as Boc-L-Lys(N^{ϵ}-Cbz)OMe for structural confirmation. [e] Isolated as L-LysOMe–2HCl.[26] [f] Isolated as Boc-Gly-L-Lys(N^{ϵ}-Cbz)OMe. [g] Isolated as Cbz-Gly-L-Lys(N^{ϵ}-Cbz)OH.[27] [h] Isolated as Boc-Gly-L-Pro-L-Lys(N^{ϵ}-Cbz)OMe.[28]

Table II. Fluorescence Quenching ($k_q\tau$), Limiting Quantum Yields (ϕ_{lim}), and Stern–Volmer Constants (K_{SV}) for Disappearance of **3b**, Oxidation Potentials [$E_{1/2}$(ox)], Excited Singlet Energies (E_{0-0}), and Calculated Free Energy Changes (ΔG)

fluorophor (donor)	$k_q\tau$,[a] M^{-1}	k_q, 10^9 M^{-1} s^{-1}	ϕ_{lim}[b]	K_{SV}[c]	$E_{1/2}$(ox), V	E_{0-0}, kcal/mol	ΔG,[d] kcal/mol
6	9.9		1.01[e]	9.0	1.45[f]	101.7[g]	−15.7
10	16.5[h]	8.25	0.92[i]	15.8	1.35[f]	95.0[g]	−11.4
					1.15[j]		−17.1
9					1.78[f]	103[k]	−8.46
11	0				1.52[l]	86.8[g]	+0.74
12	0				1.39[l]	88.5[g]	−3.95
13	8.1[m]	1.04	0.93[n]	7.7	1.10[l]	83.9[g]	−6.04
14	9.6[m]	0.72	0.83[n]	9.3	1.28[l]	87.8[g]	−5.79
15	0.8						
16	0				1.50[o]	82.9[k]	+4.18

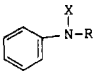
[a] For an EtOH solution (10^{-3}–10^{-5} M), quenched by *N*-tosylmethylamine (**20**). [b] Quantum yields for disappearance of **3b** extrapolated to infinite **3b** concentration in the presence of a donor (1 mM) and ammonia borane (50 mM) (from the intercepts in Figure 1). [c] Stern–Volmer constants (intercept/slope ratios) from Figure 1.[12] [d] Reference 18. [e] 90% EtOH solution, 276-nm light. [f] Reference 29. [g] Obtained from the 0–0 bands of excitation spectra when the fluorescence spectra of donors were measured at 77 K. [h] Reference 30. [i] 90% EtOH, 290-nm light. [j] Reference 31. [k] Reference 32. [l] Reference 33. [m] Reference 34. [n] 90% EtOH solution, 310-nm light. [o] Reference 35.

10 by *N*-tosylmethylamine (**20**), and the Stern–Volmer constant (K_{SV})[12] calculated from quantum yields for disappearance of **3b** in the presence of **10** were apparently larger than those of **6**, and the fluorescence quenching rate constant (k_q = 8.25 × 10^9 M^{-1} s^{-1}) is very close to the diffusion-controlled rate constant (Table II, Figure 1).

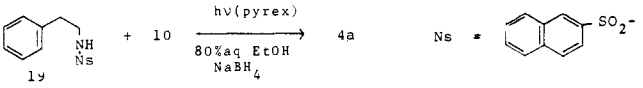
As electron donors which absorb light of longer wavelengths methoxynaphthalenes (**11**–**15**) and phenanthrene (**16**) were also examined for $k_q\tau$ and disappearance quantum yields of **3b** (Table II, Figure 1). Because of their high oxidation potentials, **11**, **12**, **15**, and **16** were not or hardly effective, whereas **13** and **14** were, however, more useful practically than **10** because their strong absorption above 300 nm avoids the side reactions due to the direct photolysis of sulfonamides.

In fact, **3b** was recovered unchanged when irradiated with light of wavelength longer than 300 nm in the presence and absence of sodium borohydride in aqueous ethanol. Addition of **14** resulted in the smooth cleavage of **3b** to give **4b**. In this case the incident light was absorbed only by **14**. In aqueous acetonitrile and tetrahydrofuran, this photoreaction also proceeded smoothly though

Scheme III



17a: R=H, X=Ts
17b: R=Me, X=Ts
18a: R=X=H
18b: R=Me, X=H



the yields were somewhat inferior.

The direct photolysis of *N*-tosylaniline (**17a**) is known to give sulfones formed via the photo-Fries-type rearrangement[13] as well

(12) The Stern–Volmer constants (K_{SV}) in Table II were calcualted from intercept/slope ratios in Figure 1, plotted according to the equation $\phi^{-1} = \phi_{lim}^{-1}(1 + K_{SV}^{-1}[\mathbf{3b}]^{-1})$, and are in good agreement with the $k_q\tau$ values (fluorescence quenching) in Table II.

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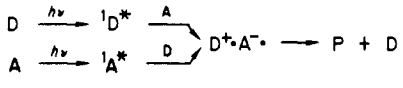
Scheme IV

as the expected aniline (**18a**) only in 21% yield,[13e] though an arylquinolinylmethanesulfonylamide gave aniline (**18a**) in 58% yield by the direct photolysis in 2-propanol.[14] On irradiation in the presence of **14** and sodium borohydride, however, **17b** gave only **18b** in 75% yield without any detectable formation of the rearranged sulfones. In the presence of ammonia borane as a reductant (see below), **17a** itself gave aniline (**18a**) in 72% yield (Table I), though **17a** was recovered unchanged in the presence of sodium borohydride because of the formation of the sodium salt of **17a**.

When irradiated in the presence of sodium borohydride with light of wavelength longer than 300 nm, the 2-naphthalenesulfonamide (**19**) gave **4a** via the direct photolysis in 64% yield, and interestingly addition of **10**, though unable to absorb the light, improved the yield to 88%.

These results described hitherto indicate that the present photolysis of sulfonamides was initiated by the formation of radical ion pairs or the electron transfer between electron-donating methoxyaromatics and electron-accepting sulfonamides through excitation either by donors or by acceptors as shown in the following scheme.



D: donor (dimethoxybenzenes, dimethoxynaphthalenes)
A: acceptor (tosylamides, naphthalenesulfonamides)
$D^{+}\cdot A^{-}\cdot$: radical ion pair
P: product

Effect of Reducing Agents. As described above when irradiated without sodium borohydride, a colorless aqueous ethanol solution of **3b** and **14** gradually produced a yellow to deep orange color, which was probably responsible for the inhibition of the photoreaction. However, the solution was maintained completely colorless by the addition of sodium borohydride, and hence the photoreaction proceeded more rapidly and efficiently.

Ascorbic acid was also effective as a reducing agent. In the presence of it instead of sodium borohydride, the solution was again colorless all through the photoreaction, and **4b** was isolated in 86% yield. *N*-Tosyl derivatives of a tetrahydropyridine carboxylic ester (**21**)[15] and an aminocyclohexanol (**23**)[16] in the presence of **14** and ascorbic acid also gave the corresponding amines, **22** and **24**, respectively, in reasonable yields (Table I).

In order to obtain reducing agents preferably close to neutral, other than sodium borohydride (basic) and ascorbic acid (acidic), amine boranes were next examined. A 95% ethanol solution of **17b** (10 mM) and **14** (5 mM) in the presence of an amine borane (50 mM) was irradiated with light of wavelength longer than 300 nm, and the disappearance of **17b** was followed high performance liquid chromatographically. Pyridine borane completely inhibited this photoreaction, and **17b** was recovered unchanged. In fact, pyridine borane quenched the fluorescence of **14** much more efficiently than the tosylamides and the k_q was calculated to be 9.7×10^9 M^{-1} s^{-1}. Other amine boranes were effective in the order of ammonia borane > *tert*-butylamine borane > dimethylamine borane, reflecting the relative order of reactivity for the reduction of aldehydes.[17] Ammonia borane is undoubtedly promising as a neutral reducing agent. However, hydrazine was found to be the most effective though somewhat basic. On irradiation in the presence of **14** and excess hydrazine, **17b** gave **18b** in 80% yield (Table I).

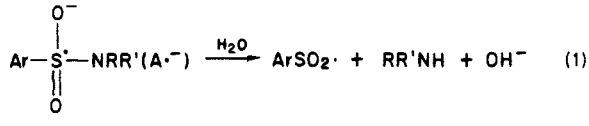
Relative effectiveness of the above reducing agents expressed as relative quantum yields for disappearance of **17b** in the presence of them was calculated as follows: pyridine borane, 0; none, 1.0; dimethylamine borane, 2.6; *tert*-butylamine borane, 3.6; ascorbic acid, 3.7; sodium borohydride, 4.2; ammonia borane, 4.9; hydrazine, 7.2.

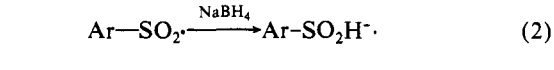
Reaction Mechanism. When a solution of **3b** and **14** was irradiated in an aprotic solvent such as benzene and acetonitrile under argon, no reaction occurred and both the starting materials were completely recovered, though the fluorescence of **14** was quenched rather efficiently by *N*-tosylmethylamine (**20**) in benzene and acetonitrile with $k_q = 6.3 \times 10^8$ and 7.4×10^8 M^{-1} s^{-1}, respectively. This fluorescence quenching can be explained in terms of the exciplex formation between electron-donating **14** and electron-accepting **20**, though no exciplex emission was observed.

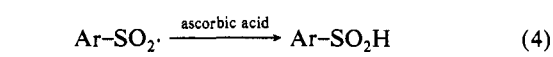
In a more polar aqueous solution the initial step of the photolysis of sulfonamides must be the electron transfer to form a radical cation ($D^{+}\cdot$) and a radical anion ($A^{-}\cdot$) as shown in the above scheme. This electron-transfer mechanism is further supported by the negative values of free energy changes (ΔG) involved in the electron-transfer processes calculated by the Weller equation (Table II).[18] Compound **10** must be the most effective though it is necessary to use light of wavelength less than 300 nm.

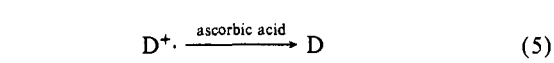
In the naphthalene series the ΔG value of **13** is more negative than that of **14**, but **14** was actually more effective in the photolysis of tosylamides, probably because the lifetime of the excited singlet state of **14** (12.6 ± 0.2 ns) is longer than that of **13** (7.8 ± 0.2 ns) as reflected in the $k_q\tau$ and K_{SV}[12] values (Table II). Compounds **11**, **12**, and **16** having more positive ΔG values were actually ineffective in this photolysis.

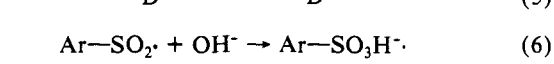
Principal processes in this photolysis after the electron transfer can be described as shown in eq 1–7. Equation 8 shows the electron back-donation from the radical anion to the radical cation recovering the starting materials.

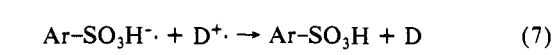


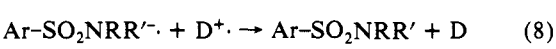


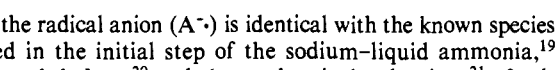












Since the radical anion ($A^{-}\cdot$) is identical with the known species generated in the initial step of the sodium–liquid ammonia,[19] sodium–naphthalene,[20] and electrochemical reductions[21] of sulfonamides, the first step of its decomposition in an aqueous solvent must be the hydrolysis as shown in eq 1.

Equations 2–7 presumably show further principal processes in the presence of sodium borohydride (eq 2, 3), ascorbic acid (eq

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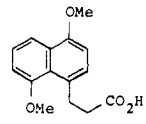
Scheme V

Boc-L-Lys(N^{ϵ}-X)OR
25: R=Me, X=Ts
26: R=Me, X=H
27: R=H, X=Ts
28: R=X=H

Boc-Gly-L-Lys(N^{ϵ}-X)OR
29: R=Me, X=Ts
30: R=Me, X=H
31: R=H, X=Ts
32: R=X=H

Boc-Gly-L-Pro-L-Lys(N^{ϵ}-X)OMe
33: X=Ts
34: X=H



35

4, 5), and no reducing agent (eq 6, 7) on the basis of the following evidence.

(1) Since the donors acted as catalysts in the photoreactions, most of them were recovered unchanged especially in the presence of reducing agents. (2) When an ethanol solution of **3b** and **14** in the presence of excess sodium borohydride was irradiated with light of wavelength longer than 300 nm, toluenesulfinic acid (71%), as its methyl ester, as well as the phenethylamine (**4b**; 88%) and the recovered donor (**14**; 91%) were readily isolated. No toluenesulfonic acid was detected. Therefore, sodium borohydride undoubtedly acted as a reducing agent to the sulfonyl radical (eq 2, 3). (3) In the presence of ascorbic acid instead of sodium borohyride, methyl toluenesulfinate (73%), **4b** (85%), and **14** (91%) were similarly isolated (eq 4, 5). (4) Even in the absence of a reducing agent, the donor (**14**) was also recovered in good yield. On irradiation in the presence of sodium ethoxide (6 mM) instead of the reducing agents, an anhydrous ethanol solution of **3b** (7 mM) and **14** (5 mM) gave **4b** (62%), **14** (77%), and ethyl toluenesulfonate (45%), which was probably formed by the reaction of the sulfonyl radical with the ethoxy anion. Equation 6 shows the quenching of the sulfonyl radical with the hydroxy anion in an aqueous solution without a reducing agent, though this process must be slower than those in eq 2 and 4, because slow and inefficient quenching of radical species is usually responsible for side-reactions. Although the electron back-donation in eq 8 usually cannot be neglected, it was calculated to be negligibly small in the case of the photolysis of **3b** in the presence of **14** and sodium borohydride.[22]

Preliminary Application to Peptide Synthesis. Selection of protecting groups for amino and other functional groups is very important in peptide synthesis. For the protection of α-amino groups in amino acids and peptides *tert*-butoxycarbonyl (Boc) groups have been most commonly used and ϵ-amino groups of lysine residues are usually protected with benzyloxycarbonyl (Cbz) groups in order to distinguish from the α-amino protection. However, there is a serious problem that th Cbz groups are sometimes cleaved under deprotective conditions for the Boc groups.[23]

The tosyl group is the most stable protecting group of side chains of lysine residues and removable by reduction with sodium in liquid ammonia. However, the tosyl protection is not practically useful in the peptide synthesis, because many side reactions such as the reductive fission of proline peptides have been reported.[7]

Since only the *N*-tosyl group among the usual protecting and functional groups as well as peptide bonds can form a donor-acceptor ion pair with an excited electron-donating aromatic, the photochemical hydrolysis of tosylamides presented in this report may be a selective method for the detosylation of lysine peptides. As preliminary experiments some model N^{ϵ}-tosyllysine peptides, Boc-L-Lys(N^{ϵ}-Ts)OMe (**25**), Boc-L-Lys(N^{ϵ}-Ts)OH (**27**), Boc-Gly-L-Lys(N^{ϵ}-Ts)OMe (**29**), Boc-Gly-L-Lys(N^{ϵ}-Ts)OH (**31**), Boc-Gly-L-Pro-L-Lys(N^{ϵ}-Ts)OMe (**33**), in aqueous ethanol were irradiated with a high pressure mercury lamp (Pyrex filter) in the presence of an electron donor [**14**, or a water-soluble donor (**35**)] and excess reductant (ascorbic acid or ammonia borane). Only the selective cleavage of the *N*-tosyl protection occurred to give the corresponding detosylated peptides in good yields. No cleavage of peptide bonds was observed. Results are shown in Table I. Further applications will be reported elsewhere.

Experimental Section

General Photolysis Procedure of Tosylamides. A stirred solution of an *N*-tosylamide (**3a**, **3b**, **7**, **17b**; 0.3–1.0 mmol), a donor (**6**, **9**, **10**, **14**; 0.3–4.0 mmol), and sodium borohydride (1.5–10 mmol) in an aqueous solvent (100 mL) was irradiated with a 100- or 200-W high-pressure mercury lamp (Eikosha, Osaka) under nitrogen for 1–2 h. When 1,5-dimethoxynaphthalene (**14**) was used as a donor, a Pyrex filter was applied to cut off the light below 300 nm. The reaction mixture was acidified with 2 N hydrochloric acid and then concentrated in vacuo. After the residue was taken up in water (50 mL) and washed with dichloromethane, the aqueous layer was neutralized and saturated with potassium carbonate and extracted with dichloromethane. The extract was dried (Na_2SO_4), acidified with hydrogen chloride in methanol, and then concentrated in vacuo to leave an amine hydrochloride (**4a**, **4b**, **8**, **18b**), which was identified by comparing its melting point and IR and NMR spectra with those of an authentic sample.

Ascorbic acid, ammonia borane, or hydrazine was similarly used as a reductant in place of sodium borohydride.

The results are summarized in Table I.

Photolysis of *N*-2-Naphthalenesulfonylphenethylamine (19). A 90% aqueous ethanol solution (100 mL) of **19** (200 mg, 0.64 mmol) and sodium borohydride (243 mg, 6.4 mmol) with or without 1,4-dimethoxybenzene (**10**; 887 mg, 6.4 mmol) was irradiated with the 200-W lamp through a Pyrex filter. Workup was the same as described above for **4a** hydrochloride, and the results are shown in Table I.

Fluorescence Quenching. A. Quenching by *N*-Tosylmethylamine (20). Fluorescence measurements were taken by using a Hitachi MPF-1A spectrofluorometer. Spectrograde ethanol was used as a solvent. The concentration (c) of a fluorophore (donor) and the wavelengths of excitation (λ_{ex}) and emission maximum (λ_{em}) are as follows (compound, c, λ_{ex}, λ_{em}): (**6**, 4.3×10^{-5} M, 287 nm, 305 nm; **10**, 1.08×10^{-4} M, 294 nm, 306 nm; **12**, 6.37×10^{-5} M, 322 nm, 340 nm; **13**, 6.38×10^{-5} M, 330 nm, 351 nm; **14**, 6.18×10^{-5} M, 324 nm, 342 nm; **15**, 6.02×10^{-5} M, 331 nm, 350 nm. The concentration of *N*-tosylmethylamine (**20**) as a quencher was normally in the 10^{-2}–10^{-1} M range. The $k_q\tau$ values were obtained from linear Stern–Volmer plots of the fluorescence intensities at maximum wavelengths vs. various amounts of quencher (**20**). The correlation coefficients from the least-squares analyses of the plots were 0.99 or better. The results are shown in Table II.

B. Quenching by Pyridine Borane. Fluorescence spectra of **14** (6.18×10^{-5} M) with various amounts of pyridine borane (10^{-3}–10^{-1} M) were measured (λ_{ex} 324 nm, λ_{em} 342 nm), and the values of $k_q\tau$ and k_q were obtained to be 122 M^{-1} and 9.7×10^9 M^{-1} s^{-1}, respectively.

Quantum Yields of Disappearance of 3b in the Presence of Dimethoxybenzenes (6, 10) and Dimethoxynaphthalenes (13, 14). Ninety percent aqueous ethanol solutions (2.5 mL) of various amounts of **3b** (6.66–50 mM), ammonia borane (50 mM), and a donor (**6**, **10**, **13**, **14**; 1 mM) were irradiated with 276-nm light (for **6**), 290-nm light (for **10**), or 310-nm light (for **13**, **14**) from a monochromatic irradiator (JASCO CRM-FA Spectro Irradiator). Aliquots (0.5 mL) were diluted with an internal standard solution (0.5 mL) of *N*-tosylbenzylamine (8–50 mM) and dried over 3A molecular sieves. A gas chromatograph (Shimazu GC-4APFE) was used for quantitative analyses of the recovered **3b** (3% OV 17, 250 °C, internal standard *N*-tosylbenzylamine). Quantum yields for disappearance of **3b** were determined relative to the potassium ferrioxalate actinometer[24] and the mean values of three measurements. In every case, the conversion of **3b** was less than 10%. Linear (least-squares) double-reciprocal plots (ϕ^{-1} vs. $[\mathbf{3b}]^{-1}$) according to the equation $\phi^{-1} = \phi_{lim}^{-1}(1 + K_{SV}^{-1}[\mathbf{3b}]^{-1})$ gave quantum yields for disappearance of **3b** extrapolated to infinite **3b** concentration (ϕ_{lim} in Table II) and Stern–Volmer constants (K_{SV} in Table II). The following values were also obtained. Correlation coefficient: **6**, 0.999; **10**, 0.999; **13**, 0.994; **14**, 0.999. Intercept: **6**, 0.99; **10**, 1.09; **13**, 1.08; **14**, 1.21. Slope: **6**, 0.11; **10**, 0.069; **13**, 0.14; **14**, 0.13.

Effect of Reductants. A 95% aqueous ethanol solution of *N*-tosyl-*N*-methylaniline (**17b**; 10 mM), **14** (5 mM), and a reductant (50 mM) in a quartz test tube was irradiated with a 300-W high-pressure mercury lamp (Pyrex filter) on the merry-go-round apparatus. At regular time intervals, 0.2-mL aliquots were withdrawn, and the recovered **17b** was analyzed quantitatively by a high-performance liquid chomatograph

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(Hitachi Liquid Chromatograph 635A; 4 × 25 cm column packed with Merk LiChrosorb 5160; elutant, hexane:EtOAc = 4:1; pressure, 70 kg/cm^2; internal standard, *N*-tosylaniline). The relative disappearance rates of **17b** in the presence of the reductants to that in the absence of a reductant were obtained as follows: pyridine borane, 0; none, 1.0; dimethylamine borane, 2.6; *tert*-butylamine borane, 3.6; ascorbic acid, 3.7; sodium borohydride, 4.2; ammonia borane, 4.9; hydrazine, 7.2.

Excited Singlet Energy. The excited singlet energy (kcal/mol) of a donor (**6**, **19**, **11**, **12**, **13**, **14**) was obtained from the 0–0 band of the excitation spectrum when the fluorescence spectrum of the donor was measured in anhydrous ethanol at 77 K.

Photolysis of 3b in Anhydrous Ethanol in the Presence of Sodium Borohydride. An anhydrous ethanol solution (120 mL) of **3b** (289 mg, 1 mmol), **14** (100 mg, 0.53 mmol), and sodium borohydride (200 mg, 5.2 mmol) was irradiated under nitrogen with the 200-W lamp (Pyrex filter) for 3.5 h. After the addition of acetone to decompose excess sodium borohydride, the solvent was evaporated in vacuo, and the residue was extracted with dichloromethane and water. The aqueous layer was acidified with hydrochloric acid (pH 1) and extracted with ether, and the ether extract was evaporated in vacuo. The residue was treated with diazomethane in ether to give a colorless oil of methyl toluenesulfinate (121 mg, 71%): IR (Nujol) 1135, 965 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.44 (3 H, s), 3.47 (3 H, s), 7.34 (2 H, d, J = 8 Hz), 7.60 (2 H, d, J = 8 Hz); MS, m/z (relative intensity) 170 (M^+, 65), 139 (100).

The dichloromethane layer was extracted with 10% hydrochloric acid, and the extract was washed with dichloromethane and concentrated in vacuo to give **4b** hydrochloride (80 mg, 88%). The remaining dichloromethane layer was washed with saturated sodium bicarbonate and sodium chloride solutions, dried (Na_2SO_4), and evaporated in vacuo to give the recovered **14** (91 mg, 91%).

Photolysis of 3b in the Presence of Ascorbic Acid. An 80% ethanol solution (120 ml) of **3b** (396 mg, 1.2 mmol), **14** (113 mg, 0.6 mmol), and ascorbic acid (634 mg, 3.6 mmol) was irradiated under argon with the 300-W lamp for 3 h. The solvent was evaporated in vacuo and to the residue was added to water. After neutralization with sodium carbonate, the mixture was extracted with ether. The aqueous layer was acidified (pH 1) with hydrochloric acid and extracted again with ether. This ether extract was treated with an ether solution of diazomethane to give methyl toluenesulfinate (150 mg, 73%). The former ether layer was washed with 10% hydrochloric acid, dried, and evaporated to give **14** (130 mg, 91%). The acidic washing was neutralized with potassium carbonate and extracted with dichloromethane. The extract was dried (K_2CO_3) and treated with hydrogen chloride in methanol to give **4b** hydrochloride (175 mg, 85%).

Photolysis of 3b in the Presence of Sodium Ethoxide. An anhydrous ethanol solution (110 mL) of **3b** (223 mg, 0.77 mmol), **14** (100 mg, 0.53 mmol), and sodium ethoxide prepared from 50% sodium dispersion (32 mg, 0.66 mmol) in ethanol was irradiated under argon with the 200-W lamp (Pyrex filter) for 4.5 h. After evaporation of the solvent in vacuo, to the residue was added water (20 mL), and the mixture was extracted with dichloromethane. The extract was dried and evaporated, and the residue was separated on a silica gel preparative TLC (hexane:EtOAc = 10:1) to give the recovered **14** (77 mg, 77%) and ethyl toluenesulfonate (69 mg, 45%), mp 31–33 °C. The aqueous layer was saturated with potassium carbonate and extracted with dichloromethane. The extract was treated with hydrogen chloride in methanol to give **4b** hydrochloride (82 mg, 62%).

***N*$^\alpha$-*tert*-Butoxycarbonyl-*N*$^\epsilon$-tosyl-L-lysine (27).** *N*$^\epsilon$-Tosyl-L-lysine (6.0 g, 20 mmol) was treated with di-*tert*-butyl dicarbonate (4.37 g, 20 mmol) in the presence of 1 N sodium hydroxide in the usual manner[25] to give **27** (8.0 g) as a colorless oil: $[\alpha]^{18}_D$ + 11.0° (*c* 1.0, EtOH); IR ($CHCl_3$) 1700, 1155 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.43 (9 H, s), 1.00–1.80 (6 H, m), 2.41 (3 H, s), 2.91 (2 H, q, J = 7 Hz), 4.00–4.20 (1 H, m), 5.16 (1 H, d, J = 8 Hz), 6.80 (1 H, br s), 7.24 (2 H, d, J = 8 Hz), 7.68 (2 H, d, J = 8 Hz).

27 Methyl Ester (25). **27** (1.0 g) was esterified with diazomethane to give **25** (1.03 g; 99%) as a colorless oil: IR ($CHCl_3$) 1735, 1700, 1155 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.10–1.90 (6 H, m), 1.44 (9 H, s), 2.44 (3 H, s), 2.92 (2 H, q, J = 7 Hz), 3.70 (3 H, s), 4.00–4.40 (1 H, m), 4.68 (1 H, t, J = 7 Hz), 5.02 (1 H, d, J = 8 Hz), 7.28 (2 H, d, J = 8 Hz), 7.70 (2 H, d, J = 8 Hz).

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***N*$^\alpha$-*tert*-Butoxycarbonylglycyl-*N*$^\epsilon$-tosyl-L-lysine Methyl Ester (29).** *N*$^\alpha$-*tert*-Butoxycarbonylglycine (526 mg, 3 mmol), *N*$^\epsilon$-tosyl-L-lysine methyl ester hydrochloride (1.052 g, 3 mmol), and triethylamine (304 mg, 3 mmol) in dichloromethane (12 mL) were treated with DCC (618 mg, 3 mmol) in the usual manner to give **29** (1.40 g, 99%) as a colorless oil: IR ($CHCl_3$) 1740, 1710, 1690, 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.00–2.00 (6 H, m), 1.44 (9 H, s), 2.42 (3 H, s), 2.74–3.04 (2 H, m), 3.76 (3 H, s), 3.94 (2 H, d, J = 6 Hz), 4.58 (1 H, dt, J = 5, 8 Hz), 5.12 (1 H, t, J = 5 Hz), 5.40 (1 H, t, J = 6 Hz), 6.82 (1 H, d, J = 8 Hz), 7.28 (2 H, d, J = 8 Hz), 7.72 (2 H, d, J = 8 Hz).

***N*$^\alpha$-*tert*-Butoxycarbonylglycyl-*N*$^\epsilon$-tosyl-L-lysine (31).** **29** (1.40 g) was treated with potassium carbonate in aqueous methanol to give **31** (1.37 g, 97%) as a colorless oil: $[\alpha]^{17}_D$ +8.6° (*c* 1.0, EtOH); IR (Nujol) 3250, 1710, 1660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.00–2.00 (6 H, m), 1.40 (9 H, s), 2.83 (2 H, br s), 3.87 (2 H, d, J = 6 Hz), 4.56 (1 H, q, J = 7 Hz), 5.70 (2 H, br s), 7.27 (2 H, d, J = 8 Hz), 7.70 (2 H, d, J = 8 Hz).

***N*$^\alpha$-*tert*-Butoxycarbonylglycyl-L-prolyl-*N*$^\epsilon$-tosyl-L-lysine Methyl Ester (33).** A colorless oil of **33** (2.17 g, 95%) was synthesized from *tert*-butoxycarbonylglycyl-L-proline (1.32 g, 5 mmol), *N*$^\epsilon$-tosyl-L-lysine methyl ester hydrochloride (1.75 g, 5 mmol), triethylamine (0.5 g, 5 mmol), and DCC (1.03 g, 5 mmol) in dichloromethane (50 mL) in the usual way.

Photolysis of Peptide Derivatives. A. Photolysis of Amino Acid and Peptide Esters in the Presence of Ammonia Borane. A substrate (0.5 mmol), **14** (94 mg, 0.5 mmol), and ammonia borane (155 mg, 5 mmol) in 83% aqueous ethanol (120 mL) were irradiated with the 300-W mercury lamp (Pyrex filter) for 2 h. After evaporation of the solvent, the residue was chromatographed on a silica gel column. Elution with MeOH–H_2O–AcOH (40:20:1) gave a detosylated amine, which was converted to a benzyloxycarbonyl derivative in the usual way for the structural confirmation.

***N*$^\alpha$-*tert*-Butoxycarbonyl-*N*$^\epsilon$-benzyloxycarbonyl-L-lysine Methyl Ester (26):** yield, 162 mg (82%); colorless oil; IR ($CHCl_3$) 1730, 1710, 1500 cm^{-1}; ^{1}H NMR δ 1.10–1.90 (6 H, m), 1.22 (9 H, s), 3.16 (2 H, q, J = 7 Hz), 4.00–4.40 (1 H, m), 4.60–5.00 (1 H, t, J = 7 Hz), 5.04 (1 H, d, J = 7 Hz), 5.08 (2 H, s),7.30 (5 H, s).

***N*$^\alpha$-*tert*-Butoxycarbonylglycyl-*N*$^\epsilon$-benzyloxycarbonyl-L-lysine Methyl Ester (30):** yield, 188 mg (86%); colorless oil; IR ($CHCl_3$) 1740, 1710, 1680 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.0–2.0 (6 H, m), 1.40 (9 H, s), 2.42 (3 H, s), 2.92 (2 H, q, J = 7 Hz), 3.70 (3 H, s), 3.85 (2 H, d, J = 6 Hz), 4.50 (1 H, dt, J = 5, 8 Hz), 5.00 (1 H, t, J = 7 Hz), 5.22 (1 H, d, J = 5 Hz), 5.60 (1 H, t, J = 6 Hz), 7.28 (5 H, s).

***N*$^\alpha$-*tert*-Butoxycarbonylglycyl-L-propyl-*N*$^\epsilon$-benzyloxycarbonyl-L-lysine Methyl Ester (34):** yield, 219 mg (80%); colorless oil; IR ($CHCl_3$) 1740, 1705, 1690, 1640 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.00–2.20 (10 H, m), 1.42 (9 H, s), 3.17 (2 H, q, J = 8 Hz), 3.40–3.90 (2 H, m), 3.68 (3 H, s), 3.90–4.20 (2 H, m), 4.30–4.70 (2 H, m), 5.06 (2 H, s), 5.12 (1 H, t, J = 8 Hz), 5.70 (1 H, d, J = 7 Hz), 6.32 (1 H, t, J = 7 Hz), 7.30 (5 H, s).

B. Photolysis of Amino Acid and Peptide Derivatives in the Presence of Ascorbic Acid. A substrate (0.5 mmol), 4,8-dimethoxypropionic acid (0.3 mmol), and ascorbic acid (3 mmol) in 70% aqueous ethanol (120 mL) were irradiated as described above. After addition of Dowex 50 (H^+ form, 35 mL) the mixture was allowed to stand overnight. The Dowex 50 was then collected by filtration and eluted with 1 M pyridine–acetic acid buffer to give a peptide, which was converted to a methyl ester hydrochloride or a benzyloxycarbonyl derivative. Results are shown in Table I.

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