

accompanied oligomer formation was barely affected by penta-1,3-diene (73mm). In contrast, the yields of (**3c** and **d**) were not reduced by the addition of the diene up to 50mm. Similarly, the yield of (**2b**) was reduced by 91% in the presence of the diene (39mm), whereas that of (**3b**) was virtually invariant. In the case of the photoreaction of (**1e**), the diene (30mm) quenched the reduction of the nitro group leading to (**4**) and intermediate products but hardly decreased the yield of (**3e**). These quenching data are consistent with the mechanism⁴ that the photomethanolysis reaction occurs from the excited singlet states¹ (π, π^*) of the *p*-substituted-benzoyl moieties of aziridines, while the homolysis products result from their lowest triplet states³ (π, π^*). In addition, the photoreduction of (**1e**) to (**4**) must be a triplet reaction as is commonly the case for aromatic nitro compounds. It is evident from the Table that the quenching of these triplet reactions accounts for decreased conversions of (**1a**, **b**, and **e**) in the presence of penta-1,3-diene. This in turn implies that the triplet state of (**1e**) can be reduced at the nitro group while preserving the aziridine ring. In association with the above mechanism, the quantitative conversion of (**1d**) into (**3d**) is also noteworthy. Thus, it is suggested that the excited singlet state of (**1d**) undergoes methanolysis more rapidly than if pronounced intersystem crossing takes place, as a result of the internal heavy-atom effect⁶ of the bromo substituent, to the triplet state. The origin of the dual reactivity of (**1b**) to produce both (**2b**) and (**3b**) is now being explored.

For comparison, Ar-purged solutions of (**1c** and **d**) (24mm) in propan-2-ol were also irradiated for 5 h. In contrast to the heterolytic ring-opening reaction in methanol, the formation of *N*-ethyl derivatives (**2c**) (61%) and (**2d**) (100%) under these conditions was observed by ¹H n.m.r. This indicates that propan-2-ol can be a less reactive nucleophile compared with methanol, but a better hydrogen donor for the aziridine rings of (**1c** and **d**) in their excited states.

In summary we have shown that the photochemical ring-opening mode of 1-(*p*-substituted-benzoyl)aziridines depends significantly on the *para*-substituents as well as the alcohol solvents employed.

Experimental

Materials—Methanol and propan-2-ol were of spectroscopic grade and used without further purification. Penta-1,3-diene (*cis-trans* mixture) was distilled before use.

Preparation of (1a–e)—The 1-(*p*-bromobenzoyl)aziridine (**1d**) was prepared by the reaction of aziridine (1.6 g, 37 mmol) with *p*-bromobenzoyl chloride (7.8 g, 36 mmol) in the presence of triethylamine (3.6 g, 35 mmol) in acetone (320 ml), in a manner analogous to the preparation of 1-(2-naphthoyl)aziridine.³ The crude reaction mixture was chromatographed on a silica gel column and (**1d**) (3.3 g, 41%) was eluted with CH₂Cl₂, $\delta_{\text{H}}(\text{CDCl}_3)$ 2.38 (4 H, s), 7.58 (2 H, d, *J* 8.0 Hz), and 7.95 (2 H, d, *J* 8.0 Hz) (Found: C, 47.9; H, 3.5; N, 6.3; O, 6.8; Br, 35.4. C₉H₈BrNO requires C, 47.8; H, 3.6; N, 6.2; O, 7.1; Br, 35.3%). The aziridines (**1a–c**) were prepared following the reported procedures⁷ and purified by vacuum distillation, column chromatography on silica gel with CH₂Cl₂, and repeated recrystallization from diethyl ether. 1-(*p*-Nitrobenzoyl)aziridine (**1e**) was prepared by the method reported⁸ and purified by repeated recrystallization from light petroleum. All compounds (**1a–e**) gave satisfactory spectroscopic and elemental analysis data.

Spectroscopic Measurements—I.r. spectra were measured with a JASCO A-302 spectrophotometer. ¹H n.m.r. spectra

were recorded on a JEOL PMX-60 spectrometer with tetramethylsilane as internal standard.

Photolyses and Analyses—Solutions of (**1a–e**) (25–33mm) in methanol or propan-2-ol (20 ml) were placed in a Pyrex glass tube (17 mm in diameter), purged for 30 min with Ar under cooling, and then sealed off before irradiation. Irradiation was performed at room temperature using a merry-go-round apparatus equipped with a 400 W high-pressure mercury arc (Eiko-sha 400). After removal of the solvent, the residual mixture was subjected to spectroscopic measurements and h.p.l.c. analysis with a TOYO SODA HLC-802UR high-performance liquid chromatograph under the conditions reported.³ Conversions of the aziridines and the product yields were determined by the simultaneous use of ¹H n.m.r. (CDCl₃) and h.p.l.c. (eluted with tetrahydrofuran). Benzene was used as internal standard for h.p.l.c. In the ¹H n.m.r. analysis, the decrement in the aziridinyl protons of (**1a–e**) and the increment in the methyl protons of (**2a** and **b**) or the methoxy protons of (**3b–e**) were measured by reference to the total amount of the benzoyl protons of all components. The relative errors were estimated as $< \pm 7\%$ except for the yield of (**3c**) which is $\pm 18\%$.

In the quenching experiments, Ar-purged solutions of (**1a–e**) (21–30mm) in methanol containing penta-1,3-diene (30–73mm) were irradiated under the same conditions as above.

Identifications—The photoproducts obtained by the preparative irradiations of the aziridines (**1a**, **b**, **d**, and **e**) (> ca. 80% conversions) in Ar-purged methanol were identical with authentic specimens prepared as follows.

(a) *N*-Ethylbenzamide (**2a**) and *N*-Ethyl-*p*-methylbenzamide (**2b**).—Benzoyl chloride (1.8 g, 13 mmol) was added dropwise to a mixture of aqueous (70%) ethylamine (8.3 ml, 13 mmol) and NaOH (0.6 g, 15 mmol) in water (300 ml) maintained at below 0 °C. The reaction mixture was extracted with CH₂Cl₂ and the organic layer was washed with water. Evaporation of CH₂Cl₂ *in vacuo* followed by recrystallization from hexane gave (**2a**) (1.8 g, 90%), $\delta_{\text{H}}(\text{CDCl}_3)$ 1.22 (3 H, t, *J* 7.1 Hz), 3.49 (2 H, qd, *J* 6.6, 1.8 Hz), 6.29 (1 H, br), and 7.53 (5 H, m) (Found: C, 72.6; H, 7.6; N, 9.3; O, 10.4. C₉H₁₁NO requires C, 72.5; H, 7.4; N, 9.4; O, 10.7%). Similarly, the reaction of *p*-methylbenzoyl chloride with aqueous ethylamine in the presence of NaOH gave 77% (**2b**), $\delta_{\text{H}}(\text{CDCl}_3)$ 1.23 (3 H, t, *J* 7.1 Hz), 2.40 (3 H, s), 3.55 (2 H, qd, *J* 6.7, 1.8 Hz), 6.25 (1 H, br), 7.22 (2 H, d, *J* 8.0 Hz), and 7.70 (2 H, d, *J* 8.0 Hz) (Found: C, 73.6; H, 8.0; N, 8.3; O, 9.6. C₁₀H₁₃NO requires C, 73.6; H, 8.0; N, 8.6; O, 9.8%).

(b) *N*-(2-Methoxyethyl)-*p*-methylbenzamide (**3b**), *N*-(2-Methoxyethyl)-*p*-bromobenzamide (**3d**), and *N*-(2-Methoxyethyl)-*p*-nitrobenzamide (**3e**).—Typically, to a solution of the aziridine (**1b**, **d**, or **e**) (ca. 250 mg) in methanol (150 ml), a catalytic amount of BF₃·OEt₂ was added under Ar and left for 30 min under stirring. After the addition of water (ca. 30 ml), the resulting mixture was extracted with 30% v/v benzene-CHCl₃ to give > 90% of the title product. Compound (**3b**) showed $\delta_{\text{H}}(\text{CDCl}_3)$ 2.38 (3 H, s), 3.38 (3 H, s), 3.63 (4 H, m), 6.47 (1 H, br), 7.22 (2 H, d, *J* 8.2 Hz), and 7.72 (2 H, d, *J* 8.2 Hz) (Found: C, 68.6; H, 7.9; N, 7.3; O, 16.2. C₁₁H₁₅NO₂ requires C, 68.4; H, 7.8; N, 7.25; O, 16.6%). Compound (**3d**) showed $\delta_{\text{H}}(\text{CDCl}_3)$ 3.38 (3 H, s), 3.58 (4 H, m), 6.56 (1 H, br), and 7.60 (4 H, s) (Found: C, 46.6; H, 4.9; N, 5.4; O, 12.4; Br, 30.7. C₁₀H₁₂BrNO₂ requires C, 46.5; H, 4.65; N, 5.4; O, 12.4; Br, 31.0%). Compound (**3e**) showed $\delta_{\text{H}}(\text{CDCl}_3)$ 3.40 (3 H, s), 3.60 (4 H, m), 6.98 (1 H, br), 7.85 (2 H, d, *J* 8.4 Hz), and 8.21 (2 H, d, *J* 8.4 Hz) (Found: C, 54.0; H, 5.4; N, 12.65; O, 27.95. C₁₀H₁₂N₂O₄ requires C, 53.6; H, 5.4; N, 12.5; O, 28.6%).

(c) N-(2-Methoxyethyl)-p-aminobenzamide (4).—Compound (3e) (110 mg, 0.49 mmol) dissolved in 78% v/v ethanol-water (80 ml) was refluxed for 5 h over a mixture of zinc dust (1.0 g, 15 mg-atom) and calcium chloride (33 mg, 0.3 mmol) under stirring. The mixture after filtration was concentrated and poured into excess of CHCl_3 to obtain the precipitate. The recrystallization of the resulting solid from methanol gave 52% of hygroscopic (4), ν_{max} (KBr) 3 450 and 3 325 (NH_2), 3 220 (NH), 1 627 (C=O), 1 553 (NH), 1 307 (C-N), and 1 110 (C-O-C) cm^{-1} ; δ_{H} (CD_3OD) 3.30 (3 H, s), 3.48 (4 H, s), 6.58 (2 H, d, J 8.4 Hz), and 7.52 (2 H, d, J 8.4 Hz) (Found: C, 62.2; H, 7.5; N, 14.05). $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_2$ requires C, 61.9; H, 7.2; N, 14.4%.

After irradiation of (1c) (4.5mm) in Ar-purged methanol for 33 h, the reaction mixture was concentrated and chromatographed on a silica gel column. Compound (3c) was eluted with CH_2Cl_2 , δ_{H} (CDCl_3) 3.43 (3 H, s), 3.70 (4 H, s), 3.83 (3 H, s), 6.17 (1 H, br), 6.84 (2 H, d, J 8.4 Hz), and 7.71 (2 H, d, J 8.4 Hz) (Found: C, 63.0; H, 7.4; N, 6.7; O, 22.6). $\text{C}_{11}\text{H}_{15}\text{NO}_3$ requires C, 63.15; H, 7.2; N, 6.7; O, 23.0%.

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