Photochemistry of Heterocyclic Compounds. 5.[1] Photochemical Reaction of 2,5-Diaryl-1,3,4-oxadiazoles with Indene

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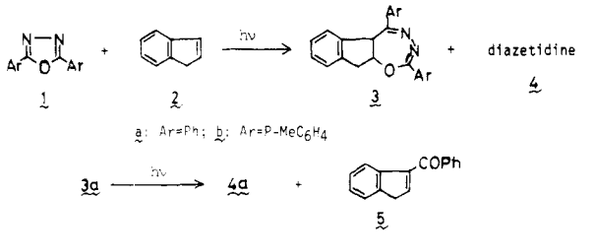
Photochemical reaction of 2,5-diaryl-1,3,4-oxadiazoles with indene has been investigated under various conditions. Irradiation of symmetrical 2,5-diaryl-1,3,4-oxadiazole with indene gives the oxadiazepine compound whose structure corresponds to a formal 1,2–1,5 cycloadduct, and/or the diazetidine compound, whose relative yields depended on the reaction conditions. In a similar photochemical reaction of 2-phenyl-5-*p*-tolyl-1,3,4-oxadiazole, a mixture of two isomeric oxadiazepines and three diazetidines is formed. Upon irradiation of 2,5-diphenyl-1,3,4-oxadiazole with indene in the presence of iodine, however, the [2 + 2] cycloadduct is obtained.

Although [2 + 2] photocycloadditions of olefins to other olefins[2] and to ketones[3] are well characterized, only a few examples of similar photocycloadditions to the carbon–nitrogen double bonds appeared in the literature.[4–7] In a preliminary communication[8] we reported some novel photoproducts from the photochemical reaction of 2,5-diphenyl-1,3,4-oxadiazole (**1a**) with indene (**2**) in the absence or presence of iodine. However, there remained some uncertainty as to the structures of products and the pathways. To resolve these problems, further investigations were undertaken. We now report here on these reactions in some detail.

Results and Discussion

In the Absence of Iodine. Irradiation of a solution of **1a** and **2** in benzene for 1 h afforded the 1:1 adduct **3a** in 31% yield, together with small quantities of the diazetidine compound **4a,** 3-benzoylindene (**5**), and benzonitrile. The yield

Scheme I



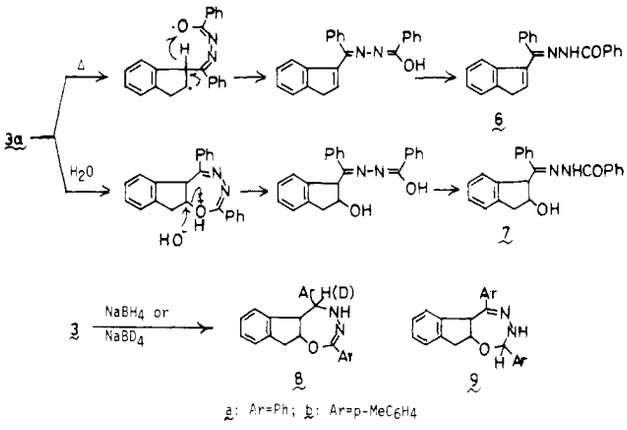
of **3a** decreased with increased irradiation time. The results under various conditions are summarized in Table I. Upon irradiation in benzene for 2 h, **3a** was converted to **4a** and **5** in 9 and 4% yields, respectively, accompanied with tarry materials. Thus, it is concluded that the primary photoproduct in this reaction is **3a.**

In the photochemical reaction of 2,5-di-*p*-tolyl-1,3,4-oxadiazole (**1b**) with **2** in diethyl ether for 1 h, the 1:1 adduct **3b** was obtained in 40% yield, along with a trace of the diazetidine compound **4b.**

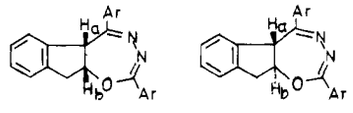
On the basis of spectral data and chemical transformations, **3a** and **3b** were assigned to be the corresponding 2,5-diaryl-5a,10a-dihydroindeno[3,2-*f*]-1,3,4-oxadiazepine whose structure corresponds to a formal 1,2–1,5 cycloadduct. The stereochemistry of **3** will be described later.

When heated in xylene under reflux, **3a** readily isomerized to 3-benzoylindene benzoylhydrazone (**6**). On treatment with water in boiling carbon tetrachloride **3a** was converted into *cis*-1-benzoyl-2-hydroxyindan benzoylhydrazone (**7**). Reduction of **3a** with sodium borohydride afforded the dihydro compound whose structure was assigned to 2,5-diphenyl-4,5,5a,10a-tetrahydroindeno[3,2-*f*]-1,3,4-oxadiazepine (**8a**), but not the 2,3,5a,10a-tetrahydro compound **9** on the basis of its spectral data. The NMR spectrum of **8a** exhibits three methine proton signals at δ 4.07 (dd), 5.23 (m), and 5.84 (d, J = 7.2 Hz), besides methylene, aromatic, and NH proton signals. When the doublet at δ 5.84 or the multiplet at δ 5.23 is irradiated, the double doublet at δ 4.07 changes to a doublet with J = 7.5 or 7.2 Hz, respectively. In addition, the doublet at δ 5.84 does not appear in the spectrum of **8a**-d_1 which was prepared by reduction of **3a** with sodium borohydride-d_4. Similarly, reduction of **3b** gave the corresponding tetrahydro compound **8b** (Scheme II).

Scheme II



Two configurations, cis-fused and trans-fused adducts, are possible for the structure of **3.** However, the spectral data do not permit a clear assignment as to which configurations would be more reasonable for **3.** Here we assumed that the



3 (cis) **3** (trans)

moiety ArC=NN=COAr in the seven-membered cyclic ring of **3** is coplanar. An inspection of the Dreiding models indicates that the dihedral angle θ between H_a and H_b is ca. 40–45° in the cis-fused adduct, whereas it is ca. 150–155° in the trans-fused adduct. The calculated J_{ab} values are 4–4.7 and 6.8–7.5 Hz when θ is 40–45 and 150–155°, respectively. The observed J_{ab} value (3.8 Hz) in **3b** is compatible with the calculated value (4 Hz) when θ is 45°.[9] Thus the cis-fused adduct appears to be a more reasonable structure than the trans-fused adduct.

Structural elucidation of the diazetidine compound **4** was accomplished on the basis of spectral data and chemical transformation. The NMR spectrum of **4a** exhibits signals at δ 3.2–4.1 (m, 5 H, 2 CH_2 and >CH), 4.57 (m, 1 H, >CH), 5.82 and 6.41 (each d, 1 H, >CH), besides aromatic protons (18 H).

Table I. Photochemical Reaction of 1a and 2 under Various Conditions[a]

Solvent	Irradn time, h	Products, % 3a	4a	5	C_6H_5CN
Benzene	1	31	1	5	3
Benzene	4	21	2	3	2
Benzene	8	Trace	4	3	2
Benzene[b]	12		5		
Et_2O	1	46	1	4	2
Et_2O	4	27	2	2	1
Et_2O	8	16	2	2	1
n-Hexane	1	31	1	5	3
Dioxane	1	30	1	2	1
Tetrahydrofuran	1	40	1	4	2
CH_3CN	1	54	1	1	2

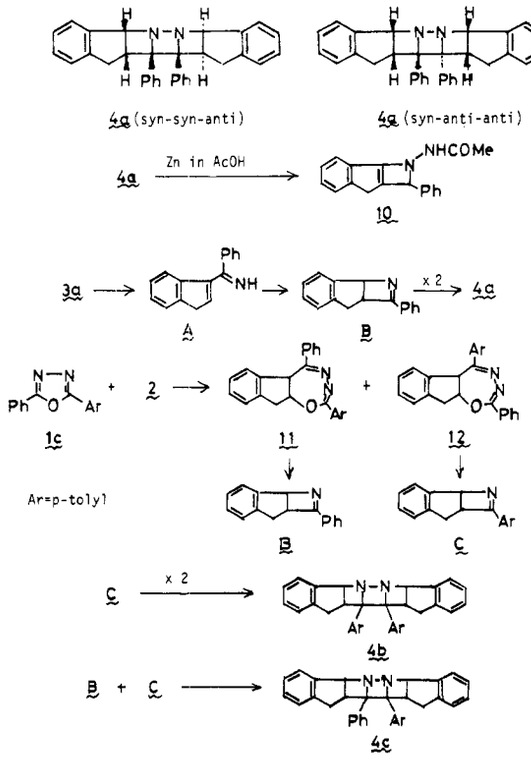
[a] A solution of **1a** and **2** (molar ratio 1:4) in the solvent was irradiated below 20 °C, in a nitrogen atmosphere. **1a** was recovered in 10–30% yield in each run. [b] Irradiated at room temperature.

The mass spectrum shows the parent ion (M^+) at *m/e* 438 and fragment ions at *m/e* 436 ($M^+ - H_2$), 408 ($436^+ - N_2$), and 219 ($M^+/2$). Reduction of **4a** with zinc dust in boiling acetic acid afforded the indenoazetine derivative **10.**

Six configurations, syn-syn-syn, anti-syn-anti, syn-anti-syn, syn-syn-anti, syn-anti-anti, and anti-anti-anti forms, are conceivable for the structure of **4a.** On the basis of NMR spectral data and of inspection of the Dreiding models, the structure of **4a** is assumed to be either syn-syn-anti or syn-anti-anti form.[10]

As mentioned above, photolysis of **3a** afforded **4a** and 3-benzoylindene (**5**). Although the exact pathway for the formation of **4a** from **3a** is not clear, it might be viewed as proceeding via initial formation of imine A from **3a** with loss of benzonitrile oxide or phenyl isocyanate.[11] This is followed by cyclization with the concurrent rearrangement to form azetine B, and subsequent dimerization of B gives **4a** (Scheme III).

Scheme III

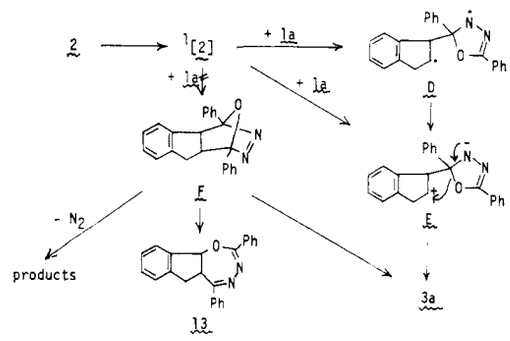


The process of the formation of B from **3a** seems to be somewhat analogous to that of photoisomerization of indoxazene to benzoxazole via a benzoisonitrile intermediate.[12] The formation of **4a** via dimerization of azetine B seems to be supported by the following result. The photochemical reaction of 2-phenyl-5-*p*-tolyl-1,3,4-oxadiazole (**1c**) with **2** afforded a mixture of two isomeric oxadiazepines, **11** and **12,** and three diazetidines, **4a, 4b,** and **4c.** As shown in Scheme III, diazetidines, **4a–c,** may be interpreted as arising via dimerization or coupling of azetines B and C which formed from **11** and **12,** respectively. Irradiation of **2** with benzonitrile did not give **4a.** In the photochemical reaction of **1a** and **2** in the presence of *p*-tolunitrile, no diazetidines, **4b** and **4c,** were formed. Thus, interaction between **2** and benzonitrile can be excluded from the pathway for the formation of **4a.**

The electronic absorption spectrum of **1a** shows strong absorption bands in the region of about 300–320 nm, while that of **2** displays no appreciable absorption above 310 nm.[13] In contrast to irradiations with light from a high-pressure mercury lamp under various conditions (Table I), irradiation of an ether solution of **1a** and **2** with monochromatic light (313 nm) for 20 h did not give **3a.** Even if irradiation of a solution of **1a** and **2** in diethyl ether with light from a high-pressure mercury lamp was performed under air for 1 h, **3a** was obtained in 27% yield; a lowering of the yield would be attributable to polymerization of **2** by oxygen.

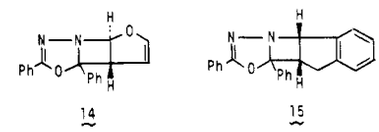
Although mechanistic considerations are still speculative, a possible pathway for the formation of **3a** is outlined in Scheme IV on the basis of above observations. The reaction

Scheme IV



starts with a singlet excited state of **2,** and the subsequent interaction with **1a** forms either diradical D or betaine E. Ring opening of E with concurrent ring closure gives **3a.** Another pathway through [2 + 4] cycloadduct F would be excluded from the possible one, since compounds such as isomeric oxadiazepine **13** and products derived from F with loss of nitrogen were not detected in the reaction mixture. In view of the exclusive cis addition, an exciplex might be involved in the reaction. However, no charge-transfer band was observed on mixing **1a** and **2.**

In the Presence of Iodine. With or without benzophenone as a sensitizer, irradiation of **1a** with furan in benzene gives the trans [2 + 2] cycloadduct **14,** whereas in the presence of



iodine 3-benzoylfuran benzoylhydrazone is formed.[4] In order to compare with the above reaction, the photochemical reaction of **1a** with **2** in the presence of iodine was investigated. The results are shown in Table II. As shown in Table II, irradiation in the presence of iodine (5 mol % to **1a**) afforded **4a** and the cis [2 + 2] cycloadduct **15,** whereas in the presence of

Table II. Photochemical Reaction of 1a with 2 in the Presence of Iodine[a]

Solvent	I_2, mol % to 1a	Irradn time, h	Product, % 4a	15
Benzene	5	12	9	4
Benzene	20	12	0	10
Et_2O	20	10	0	9

[a] A solution of **1a** and **2** (molar ratio 1:4) in the solvent was irradiated under nitrogen.

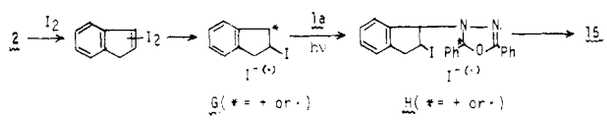
20 mol % iodine **15** was only obtained. The structure of **15** was confirmed on the basis of spectral data.

The electronic spectrum of a mixture of **1a** and iodine does not show any other absorption bands than those of **1a** and iodine. Upon irradiation of **1a** in the presence of iodine, however, a complex with iodine was obtained, which on treatment with $Na_2S_2O_3$ gave **1a** quantitatively.

Although the electronic spectrum of a mixture of **2** and iodine shows no other absorption bands than individual absorption bands of **2** and iodine, the NMR spectrum in $CDCl_3$ or C_6D_6 changes with time. After 12 h olefinic proton signals of **2** (δ 6.25 and 6.7) disappear, and new broad signals show up at δ 2–4; **2** on treatment with $Na_2S_2O_3$ afforded a white, polymeric powder of **2.** This fact indicates that iodine interacts with the olefinic bond of **2** to form a σ complex via a π complex in a similar manner as the iodine-induced isomerization of olefins.[14] After a solution of **2** and iodine (5 mol % to 2) in benzene was allowed to stand for 12 h (that is, the formation of σ complex), **1a** was added to the solution. Then the resulting solution was irradiated to give **15** in 2% yield.

The exact pathway for the formation of **15** is not clear, but we tentatively propose the pathway depicted in Scheme V.

Scheme V



Photochemical reaction of **1a** with the complex G forms the intermediate H, which undergoes ring closure with loss of iodine to yield the [2 + 2] cycloadduct **15.**

Experimental Section

Melting points are uncorrected. The IR spectra were taken with a Jasco Model IRA-1 grating infrared spectrophotometer. The NMR spectra were recorded at 60 MHz on a Hitachi R-20 spectrometer with tetramethylsilane as an internal standard and the chemical shifts are expressed in δ values. The UV spectra were taken with a Hitachi 124 spectrometer. The mass spectra were obtained on a Hitachi RMS-4 mass spectrometer with a direct inlet and an ionization energy of 70 eV. Unless otherwise stated, irradiations were performed with Pyrex-filtered light from a 300-W high-pressure mercury lamp (Taika HLV-B) below 20 °C, in a nitrogen atmosphere. Irradiation with monochromatic light (313 nm) was performed with a 100-W high-pressure mercury lamp (Riko UVL-100P) utilizing the potassium biphthalate aqueous solution[15] as a filter.

Photochemical Reaction of 2,5-Diphenyl-1,3,4-oxadiazole (1a) with Indene (2). A solution of 1.11 g (5×10^{-3} mol) of **1a** and 2.32 g (2×10^{-2} mol) of **2** in 250 mL of benzene was irradiated below 20 °C for 1 h. The solvent from the mixture was removed in vacuo to afford a residue, which was triturated with 20 mL of diethyl ether giving crystals. Filtration gave 0.53 g (31%) of oxadiazepine **3a,** which was subjected to microanalysis without further purification. The ether filtrate was evaporated in vacuo, and the residue was chromatographed on alumina using benzene and then benzene–chloroform (1:1) as eluents. From the benzene elution 1.41 g (61%) of **2,** 30 mg (3%) of benzonitrile, 9 mg (1%) of diazetidine **4a,** and 55 mg (5%) of 3-benzoylindene (**5**) were obtained, and the benzene–chloroform elution gave 0.22 g (20%) of **1a.**

3a: pale yellow needles, mp 181 °C dec; IR (KBr) 1605, 1570 cm^{-1}; mass spectrum *m/e* 338 (M^+, rel intensity 4), 233 (M^+ − PhCO, 41), 115 ([2 − H]$^+$, 100), 105 ($PhCO^+$, 43), 77 (31). Anal. Calcd for $C_{23}H_{18}N_2O$: C, 81.63; H, 5.36; N, 8.28. Found: C, 81.88; H, 5.05; N, 8.10.

4a: yellow needles, mp 284–285 °C; NMR (CF_3COOH) δ 3.2–4.1 (m, 5 H), 4.57 (m, 1 H), 5.82, 6.41 (each d, 1 H, J = 7.5 Hz), 7–8 (m, 18 H); UV max (EtOH) 246 nm (log ϵ 3.68 sh), 435 (3.73); mass spectrum *m/e* 438 (M^+, rel intensity 28), 436 ($M^+ - H_2$, 11), 408 ($436^+ - N_2$, 2), 331 (408^+ − Ph, 56), 230 (20), 219 ($M^+/2$, 25), 202 (19), 115 (57), 103 ($PhCN^+$, 100), 77 (56). Anal. Calcd for $C_{32}H_{26}N_2$: C, 87.64; H, 5.98; N, 6.39. Found: C, 87.62; H, 5.67; N, 6.41.

5: yellow oil; IR (neat) 1630 cm^{-1} (C=O); NMR ($CDCl_3$) δ 3.86 (d, 2 H, CH_2, J = 2.5 Hz), 6.7–8.2 (m, 10 H, =CH and aromatic protons); mass spectrum *m/e* 220 (M^+, rel intensity 12), 115 (55), 105 (89), 77 (100).

Similar photochemical reactions were carried out under various conditions, and the results are given in Table I.

Photochemical Reaction of 2,5-Di-*p*-tolyl-1,3,4-oxadiazole (1b) with 2. A solution of 1.25 g (5×10^{-3} mol) of **1b** and 2.32 g (2×10^{-2} mol) of **2** in 250 mL of diethyl ether was irradiated below 20 °C for 1 h, during which time there was precipitation of oxadiazepine **3b.** Filtration and recrystallization from benzene afforded 0.73 g (40%) of **3b,** mp 135–137 °C dec, as pale yellow needles. The ether filtrate was evaporated in vacuo, and the residue was chromatographed on alumina in a similar manner as above, giving 10 mg (1%) of diazetidine **4b,** mp 267–268 °C dec, as yellow needles, together with 0.42 g (33%) of **1b** and 1.12 g (48%) of **2.**

3b: IR (KBr) 1605, 1595, 1560 cm^{-1}; NMR (benzene-d_6) δ 2.0, 2.16 (each s, 3 H), 2.8–3.9 (pair of dd, 2 H, CH_2, J = 18, 8, and 2.5 Hz, changed to a double doublet when irradiated at δ 6.36), 4.12 (d, 1 H, >CH, J = 3.8 Hz, changed to a singlet when irradiated at δ 6.36), 6.36 (m, 1 H, >CH), 6.7–8.8 (m, 12 H, aromatic protons); mass spectrum *m/e* 366 (M^+, rel intensity 14), 247 ($M^+ - MeC_6H_4CO$, 8), 119 ($MeC_6H_4CO^+$, 100), 115 (8), 91 ($MeC_6H_4^+$, 53). Anal. Calcd for $C_{25}H_{22}N_2O$: C, 81.94; H, 6.05; N, 7.65. Found: C, 81.65; H, 6.24; N, 7.56.

4b: IR (KBr) 1570 cm^{-1}; NMR ($CDCl_3$) δ 2.49, 2.56 (each s, 3 H, CH_3), 2.85–4.0 (m, 5 H, 2 CH_2 and >CH), 5.35 (m, 2 H, 2 >CH), 6.13 (d, 1 H, >CH, J = 7 Hz), 6.7–8.1 (m, 16 H, aromatic protons); mass spectrum *m/e* 466 (M^+, rel intensity 9), 465 (38), 464 ($M^+ - H_2$, 100), 438 ($M^+ - N_2$, trace), 436 ($464^+ - N_2$, trace), 373 ($464^+ - MeC_6H_4$, 2), 233 ($M^+/2$, 10), 232 (23), 231 (23), 202 (14), 117 ($MeC_6H_4CN^+$, 3), 115 (39), 91 ($MeC_6H_4^+$, 7). Anal. Calcd for $C_{34}H_{30}N_2$: C, 87.51; H, 6.48; N, 6.00. Found: C, 87.48; H, 6.29; N, 6.16.

Photolysis of Oxadiazepine 3a. A suspension of 0.75 g of **3a** in 250 mL of benzene was irradiated below 20 °C for 2 h, during which time the reaction mixture changed to a solution. The solvent from the mixture was removed in vacuo, and the residue was chromatographed on alumina using benzene as an eluent to give 45 mg (9%) of **4a** and 20 mg (4%) of **5,** along with tarry materials.

Isomerization of Oxadiazepine 3a. A solution of 0.1 g of **3a** in 20 mL of xylene was refluxed for 30 min. The solvent from the mixture was removed in vacuo, and the residue was triturated with small amounts of diethyl ether to give pink crystals. Recrystallization from ethanol afforded 95 mg (95%) of 3-benzoylindene benzoylhydrazone (**6**), mp 184–185 °C dec, as pink needles: IR (KBr) 3360 (NH), 1690 cm^{-1} (C=O); NMR ($CDCl_3$) δ 3.43 (d, 2 H, CH_2, J = 2.5 Hz), 6.32 (t, 1 H, =CH, J = 2.5 Hz), 7.2–8.0 (m, 14 H, aromatic protons), 8.1 (br, 1 H, NH); mass spectrum *m/e* 338 (M^+, rel intensity 28), 233 (M^+ − PhCO, 33), 223 ($M^+ - C_9H_7$, 9), 217 (M^+ − $PhCONH_2$, 20), 203 (13), 115 (13), 105 (100), 77 (90). Anal. Calcd for $C_{23}H_{18}N_2O$: C, 81.63; H, 5.36; N, 8.28. Found: C, 81.52; H, 5.34; N, 8.32.

***cis*-1-Benzoyl-2-hydroxyindan Benzoylhydrazone (7).** A solution of 0.2 g of **3a** in 20 mL of carbon tetrachloride was refluxed with 0.1 mL of water for 20 min. The reaction mixture was evaporated in vacuo to leave a residue, which was triturated with small amounts of diethyl ether to give crystals. Recrystallization from ethanol afforded 165 mg (78%) of **7,** mp 127–128 °C, as colorless prisms: IR (KBr) 3310 (NH), 3260 (OH), 1670 cm^{-1} (C=O); NMR (CCl_4) δ 2.9–3.5 (m, 2 H, CH_2), 4.25 (m, 1 H, >CH), 5.09 (d, 1 H, >CH, J = 8.4 Hz), 5.2 (br, 1 H, OH), 7.0–8.0 (m, 14 H, aromatic protons), 8.2 (br, 1 H, NH); mass spectrum *m/e* 356 (M^+, rel intensity trace), 338 ($M^+ - H_2O$, trace), 236 (M^+ − PhCONH, trace), 220 (M^+ − $PhCONHNH_2$, 19), 191 (220^+ − CHO, 3), 136 ($PhCONHNH_2^+$, 10), 115 (45), 105 (100), 77 (97). Anal. Calcd for $C_{23}H_{20}N_2O_2$: C, 77.50; H, 5.66; N, 7.86. Found: C, 77.66; H, 5.74; N, 7.88.

Reduction of Oxadiazepine 3a with Sodium Borohydride. A suspension of 0.2 g of **3a** in 50 mL of methanol was stirred with 0.1 g of sodium borohydride at room temperature for 2 h. The reaction

mixture was poured into 100 mL of water giving 0.2 g (ca. 100%) of crystals. Recrystallization from methanol afforded dihydro compound **8a,** mp 184–185 °C, as colorless needles: IR (KBr) 3240 (NH), 1640 cm^{-1} (C=N); NMR ($CDCl_3$) δ 2.85–3.4 (m, 2 H, CH_2), 4.07 (dd, 1 H, >CH), 5.23 (m, 1 H, >CH), 5.84 (d, 1 H, >CH, J = 7.2 Hz), 6.5–7.7 (m, 14 H, aromatic protons), 7.95 (br, 1 H, NH); mass spectrum m/e 340 (M^+, rel intensity 5), 249 ($M^+ - PhCH_2$, 10), 235 ($M^+ - PhCO$, 4), 225 ($M^+ - C_9H_7$, 36), 220 ($M^+ - PhCON$, 6), 205 ($220^+ - NH$), 147 ($PhCONHN^+{\equiv}CH$, 36), 128 ($205^+ - Ph$, 6), 121 ($PhCONH_2^+$, 44), 116 ($C_9H_8^+$, 81), 115 (27), 105 (100), 91 (32), 77 (52). Anal. Calcd for $C_{23}H_{20}N_2O$: C, 81.15; H, 5.92; N, 8.23. Found: C, 81.00; H, 5.86; N, 8.17.

Similarly, reduction of **3a** with sodium borohydride-d_4 in methanol-d_1 and recrystallization of the product from methanol afforded dihydro compound **8a**-d_1, mp 186–187 °C, as colorless needles in quantitative yield. Anal. Calcd for $C_{23}H_{19}DN_2O$: C, 80.91; H, 6.20; N, 8.21. Found: C, 80.79; H, 5.85; N, 8.22.

In a similar reduction of oxadiazepine **3b** with sodium borohydride as above, dihydro compound **8b,** mp 203–204 °C, as colorless needles was obtained quantitatively: IR (KBr) 3250 (NH), 1640 cm^{-1} (C=N); NMR ($CDCl_3$) δ 2.25, 2.35 (each s, 3 H, CH_3), 2.7–3.4 (m, 2 H, CH_2), 4.10 (dd, 1 H, >CH, J = 6.8 and 7.5 Hz), 5.30 (m, 1 H, >CH), 5.87 (d, 1 H, >CH, J = 7.5 Hz), 6.3–7.7 (m, 13 H, NH and aromatic protons). Anal. Calcd for $C_{25}H_{24}N_2O$: C, 81.49; H, 6.57; N, 7.60. Found: C, 81.44; H, 6.54; N, 7.61.

2*H*-1-Acetamido-2-phenylazeto[3,4-*b*]indene (10). A solution of 0.2 g of diazetidine **4a** in 15 mL of acetic acid was refluxed with 2.0 g of zinc dust for 10 h. The reaction mixture was filtered, and the filtrate was poured into 200 mL of water, which was extracted with 250 mL of diethyl ether. The ether extract was evaporated in vacuo to leave crystals which on recrystallization from methanol afforded the azetine **10,** mp 216–217 °C, as colorless needles: IR (KBr) 3280 (NH), 1655 cm^{-1} (C=O); NMR ($CDCl_3$) δ 2.35 (s, 3 H, $COCH_3$), 4.57 (m, 2 H, CH_2), 5.17 (m, 1 H, >CH), 7.0–8.0 (m, 10 H, NH and aromatic protons); UV max (EtOH) 260 nm (log ϵ 3.44), 267 (3.61), 274 (3.74), 288 (3.84); mass spectrum m/e 276 (M^+, rel intensity 99), 234 ($M^+ - CH_2{=}C{=}O$, 100), 233 ($M^+ - COMe$, 53), 219 ($M^+ - MeCON$, 31), 161 ($PhC{\equiv}N^+NHCOMe$, 5), 130 (35), 118 ($161^+ - COMe$, 22), 116 (19), 115 (20), 203 (10), 77 (23).

Photochemical Reaction of 2-Phenyl-5-*p*-tolyl-1,3,4-oxadiazole (1c) with 2. A solution of 1.18 g (5×10^{-3} mol) of **1c** and 2.32 g (2×10^{-2} mol) of **2** in 250 mL of diethyl ether was irradiated below 20 °C for 1 h. Filtration gave 0.47 g (27%) of a mixture of oxadiazepines, **11** and **12,** as pale yellow needles: IR (KBr) 1605, 1570 cm^{-1}. The ether filtrate was evaporated in vacuo, and chromatographic separation afforded 5 mg of a mixture of diazetidines, together with 0.35 g (30%) of **1c** and 1.0 g (45%) of **2.** The IR spectrum of the mixture of diazetidines was very similar to those of diazetidines **4a** and **4b,** and its mass spectrum showed parent ions at m/e 466 (**4b**$^+$), 452 (**4c**$^+$), and 448 (**4a**$^+$).

Reduction of 0.2 g of the mixture of **11** and **12** with 0.1 g of sodium borohydride in 50 mL of methanol afforded 0.2 g of colorless crystals: mp 176–183 °C; IR (KBr) 3240 (NH), 1640 cm^{-1} (C=N); NMR ($CDCl_3$) δ 2.24, 2.30 (each s, 1.5 H, CH_3), 2.7–3.4 (m, 2 H, CH_2), 4.06 (dd, 1 H, >CH), 5.25 (m, 1 H, >CH), 5.84 (d, 1 H, >CH), 6.3–8.0 (m, 14 H, NH and aromatic protons). Thus it is clear that the initial mixture consists of equimolar amounts of **11** and **12.**

Photochemical Reaction of 1a with 2 in the Presence of Iodine. A solution of 1.7 g (7.7×10^{-3} mol) of **1a,** 3.6 g (3.1×10^{-2} mol) of **2,** and 0.1 g (3.9×10^{-4} mol) of iodine in 500 mL of benzene was irradiated for 12 h. The solvent from the mixture was removed in vacuo, and chromatographic separation of the residue on alumina using benzene as an eluent afforded 180 mg (9%) of diazetidine **4a** and 90 mg (4%) of [2 + 2] cycloadduct **15.**

15: colorless prisms, mp 196.5–197 °C; IR (KBr) 1630 cm^{-1} (C=N); UV max ($CHCl_3$) 260 nm (log ϵ 3.36), 268 (3.45), 274 (3.53), 306 (3.83); NMR ($CDCl_3$) δ 3.45 (m, 2 H, CH_2), 4.45 (m, 1 H, >CH), 6.45 (d, 1 H, >CH, J = 10.8 Hz), 7.0–8.1 (m, 14 H, aromatic protons); mass spectrum m/e 338 (M^+, rel intensity 100), 235 ($M^+ - PhCN$, 30), 222 ($M^+ - C_9H_8$, 6), 205 ($235^+ - NO$, 8), 194 ($222^+ - N_2$, 2), 128 ($205^+ - Ph$, 13), 119 ($222^+ - PhCN$, 2), 115 (12), 105 (97), 77 (100). Anal. Calcd for $C_{23}H_{18}N_2O$: C, 81.63; H, 5.36; N, 8.28. Found: C, 81.81; H, 5.11; N, 8.11.

The results under other reaction conditions are given in Table II.

Registry No.—**1a,** 725-12-2; **1b,** 2491-91-0; **1c,** 1874-47-1; **2,** 95-13-6; **3a,** 61528-63-0; **3b,** 61528-64-1; **4a,** 19921-15-4; **4b,** 61528-65-2; **5,** 61528-66-3; **6,** 59106-02-4; **7,** 61528-67-4; **8a,** 61528-68-5; **8a**-d_1, 61528-69-6; **8b,** 61528-70-9; **10,** 61528-71-0; **11,** 61528-72-1; **12,** 61528-73-2; **15,** 19921-16-5; B, 61528-74-3; C, 61528-75-4.

References and Notes

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(10) The Dreiding model for syn-syn-syn form cannot be framed owing to significant steric hindrance. On the basis of inspection of the Dreiding models for anti-syn-anti, syn-anti-syn, and anti-anti-anti forms, the hydrogens at 5a and 5d positions, and the hydrogens at 11a and 13a positions might be anticipated to display the same NMR chemical shifts, respectively.
(11) Neither benzonitrile oxide nor phenyl isocyanate could be detected in the reaction mixture.
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(13) The UV spectra of **1a** and **2** are as follows. **1a:** UV max (Et_2O) 285 nm (log ϵ 4.41), 302 (4.32), 315 (3.99); max (C_6H_6) ca. 290 nm (4.36), 304 (4.28), 320 (3.84). **2:** UV max (Et_2O) 256 nm (log ϵ 3.94), 288 (2.76), 296 (2.44); max (C_6H_6) ca. 290 nm (2.84), 298 (2.34).
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