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Studies on Diazepines. XIX.[1] Photochemical Synthesis of 2,3-Benzodiazepines from Isoquinoline *N*-Imides

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The photolysis of the isoquinoline *N*-imides (**12a—g**) under basic conditions gave the corresponding 5*H*-2,3-benzodiazepines (**13**), presumably *via* the 1*H*-2,3-benzodiazepines (**17**), together with the parent isoquinolines (**14**), whereas irradiation of these *N*-imides (**12**) under neutral conditions gave no diazepines.

Treatment of the 1-methyl-5*H*-diazepines (**13b, f**) with acetic anhydride gave the 3-acetyl-3*H*-2,3-benzodiazepines (**18**), which reverted back to the 5*H*-diazepines (**13**) on hydrolysis. However, the 1-unsubstituted 5*H*-diazepines showed no such conversion. Some reactions of the 5*H*-diazepines (**13**) thus obtained were also examined.

Keywords——photolysis; rearrangement; ring expansion; isoquinoline *N*-imides; 5*H*-2,3-benzodiazepines; 3*H*-2,3-benzodiazepines

We have previously reported the first synthesis of fully unsaturated 1*H*-1,2-benzodiazepines (**2**)[2] from the corresponding quinoline *N*-imides (**1**) by irradiation, and the conversion of the 1*H*-1,2-diazepines (**2**) to their 3*H*- (**3**)[3] and 5*H*-isomers (**4**).[4] However, an analogous route for 2,3-benzodiazepines (**6**) from isoquinoline *N*-imides (**5**) had not been successful. It is known[5] that 1-substituted isoquinoline *N*-acylimides (**5a**: X=CO_2Et, COPh, or Ac) undergo a photo-induced two-step rearrangement to form the corresponding novel 1,3-benzodiazepines (**7**), whereas both isoquinoline *N*-imides (**5b**) and 1-unsubstituted isoquinoline *N*-acylimides have been shown[6,7] upon irradiation to undergo either N–N fragmentation to the parent isoquinolines or rearrangement to 1-aminoisoquinoline derivatives, but no rearrangement with ring expansion to benzodiazepines such as **6** and **7**.

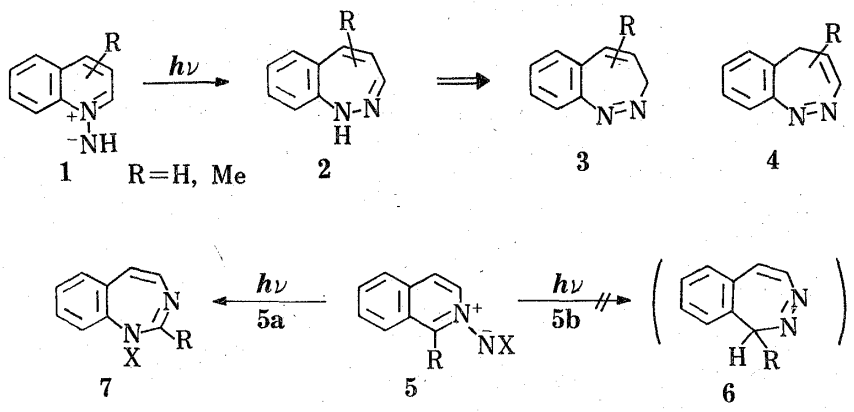
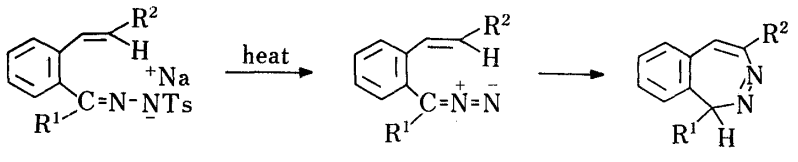


Chart 1

Therefore, we reexamined the photochemical behavior of isoquinoline *N*-imides (**5**: X=H) in more detail and now report for the first time the formation of 2,3-benzodiazepines by irradiation under basic conditions.[8] Sharp *et al.*[9] have already reported the synthesis of 1*H*-2,3-benzodiazepines (**10**) from the tosylhydrazone salts (**8**) *via* the diazo intermediates (**9**) by

thermal intramolecular cyclization. Our present result provides a new and convenient photochemical method for the preparation of 2,3-benzodiazepines from readily available isoquinolines by direct ring conversion.

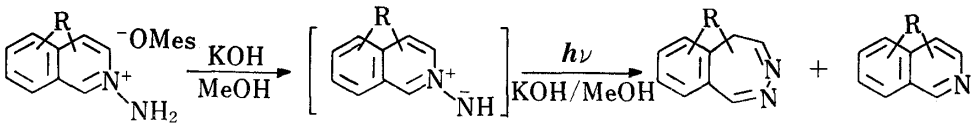


8 9 10

R^1, R^2=Me, Ph

Chart 2

The *N*-aminoisoquinolinium mesitylenesulfonates (**11a**—**g**) were prepared by amination of the corresponding isoquinolines (**14**) with *O*-mesitylenesulfonylhydroxylamine (H_2NOMes) according to the method of Tamura *et al.*[6] It is known that the salts (**11a**, **b**), upon treatment with bases, give the unstable *N*-imides (**12a**, **b**).[6,7] Irradiation of the *N*-imides (**12a**, **b**) in a neutral solution, *e.g.*, in benzene, methanol, or methylene chloride solution, gave no benzodiazepines as already reported.[6,7] However, treatment of these salts (**11a**—**g**) with excess potassium hydroxide in methanol followed by irradiation of the alkaline solution containing the *N*-imides (**12**) resulted in the formation of the desired 2,3-benzodiazepines (**13**), together with the parent isoquinolines (**14**). The isolated yields of these products are shown in Chart 3.



11 12 13 14

11a:	R = H	25—30%	15—20%
11b:	R = 1-Me	35—40%	15—20%
11c:	R = 3-Me	45—50%	20—25%
11d:	R = 6-Me	50—55%	10—15%
11e:	R = 8-Me	55—60%	10—15%
11f:	R = 1,3-diMe	30—35%	30—35%
11g:	R = 7-OMe	45—50%	35—40%

Chart 3

The 5*H*-2,3-benzodiazepines (**13**) obtained are susceptible to decomposition by silica gel or alumina, and thus can be isolated only by Sephadex chromatography. The diazepines (**13a**, **b**) were identified by comparison with authentic samples prepared by the method of Sharp *et al.*,[9] who described the synthesis of **13a**, **b**, but gave no spectral data. The other new diazepines (**13c**—**g**) were characterized by elemental analysis and by ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectral comparison with **13a**, **b**. These data are collected in Table I.

The formation of the 5*H*-2,3-benzodiazepines (**13**) from the *N*-imides (**12**) may proceed by photo-induced rearrangement to the diaziridines (**15**) followed by ring expansion to the *o*-quinonoid intermediates (**16**), which would tautomerize to the more stable 1*H*-diazepines (**17**). The 1*H*-diazepines (**17**) may then isomerize to the products (**13**) under the basic reaction condition. 1*H*-2,3-Benzodiazepines are known to be converted readily to 5*H*-isomers by treatment with bases[9] and are also known to be very sensitive to light, giving various decomposition products.[10] The latter fact may explain our finding that the irradiation of the *N*-imides (**12**) under neutral conditions gave no diazepines. In contrast, the 5*H*-diazepines (**13**) are relatively

Table I. 5*H*-2,3-Benzodiazepines (**13**)

Compd. No.	R	Formula (MS *m/e*: M^+)	Analysis (%) Calcd (Found) C	H	N	NMR ($CDCl_3$) δ J=Hz
13a[a]	H	$C_9H_8N_2$ (144)	74.97 (75.21	5.59 5.57	19.43 19.45)	3.1 (2H, d, J=5, 5-H_2), 7.0—7.6 (5H, m, 4- and Ar-H), 8.56 (1H, d, J=1, 1-H)
13b[a]	1-Me	$C_{10}H_{10}N_2$ (158)	75.92 (75.89	6.37 6.47	17.71 17.57)	2.53 (3H, s, 1-Me, 2.88 and 3.22 (each 1H, dd, J=12 and 6, 5-H_2), 7.1—7.6 (5H, m, 4- and Ar-H)
13c[b]	4-Me	$C_{10}H_{10}N_2$ (158)	75.92 (75.80	6.37 6.31	17.71 17.75)	2.14 (3H, s, 4-Me), 3.14 (2H, br, 5-H_2), 7.0—7.5 (4H, m, Ar-H, 8.56 (1H, s, 1-H)
13d[a]	7-Me	$C_{10}H_{10}N_2$ (158)	75.92 (75.69	6.37 6.32	17.71 17.70)	2.30 (3H, s, 7-Me), 2.99 (2H, br d, J=5, 5-H_2, 6.8—7.2 (4H, m, 4- and Ar-H), 8.32 (1H, d, J=1, 1-H)
13e[a]	9-Me	$C_{10}H_{10}N_2$ (158)	75.92 (75.88	6.37 6.25	17.71 17.64)	2.45 (3H, s, 9-Me), 2.81 and 3.36 (each 1H, dd, J=13 and 6, 5-H_2), 7.0—7.4 (4H, m, 4- and Ar-H), 8.65 (1H, d, J=1, 1-H)
13f[a]	1,4-diMe	$C_{11}H_{12}N_2$ (172)	76.71 (76.71	7.02 6.91	16.27 16.22)	2.06 (3H, s, 4-Me), 2.47 (3H, s, 1-Me), 3.17 and 2.91 (each 1H, d, J=13, 5-H_2)
13g[a]	8-OMe	$C_{10}H_{10}N_2O$ (174)	68.95 (69.16	5.79 5.71	16.08 16.05)	3.04 (2H, br, 5-H_2), 3.74 (3H, s, 8-OMe, 6.9—7.3 (4H, m, 4- and Ar-H), 8.45 (1H, d, J=1, 1-H)

a) Yellow viscous oil. *b*) mp 106—108°C, yellow needles (from benzene–*n*-hexane).

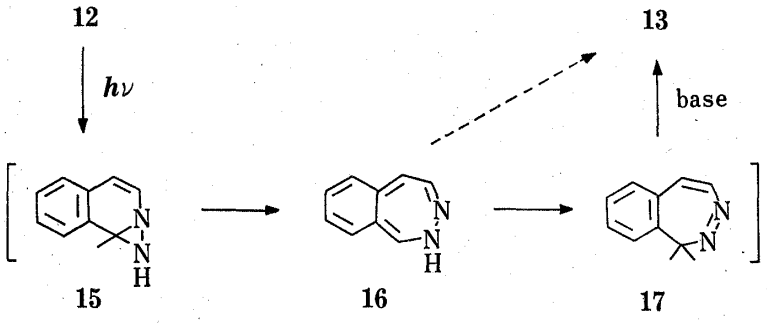


Chart 4

stable to light, undergoing no change upon irradiation for 2 h, which is longer than the present reaction time (0.5—1 h). Therefore, another possible route, direct formation of **13** from the *o*-quinonoid intermediates (**16**) by a 1,5-hydrogen shift, seems unlikely.

The chemical reactivity of 5*H*-2,3-benzodiazepines has not been much studied.[9,10] Therefore, we examined some reactions of the diazepines (**13**) thus obtained. Treatment of the 1-methyl-5*H*-diazepines (**13b**, **f**) with acetic anhydride gave the 3-acetyl-3*H*-2,3-benzodiazepines (**18**) in 50—60% yields, and these readily reverted back to the 5*H*-diazepines (**13**) on being hydrolyzed with either hydrochloric acid or sodium hydroxide. These compounds (**18**) are the first reported examples of fully unsaturated 3*H*-2,3-benzodiazepines. However, 1-unsubstituted 5*H*-diazepines (**13a**, **c**—**e**), upon treatment with acetic anhydride, gave complex mixtures of products and no 3*H*-benzodiazepines, as in the case of the acetylation of 4-phenyl-5*H*-2,3-benzodiazepine.[11] These results indicate that the presence of a substituent in the 1-position is required for this conversion of 5*H*-2,3-diazepines to 3*H*-2,3-diazepines. A similar conversion has been observed for the acetylation of monocyclic 3,5,7-triphenyl-4*H*-1,2-diazepine, which gives 3,5,7-triphenyl-1-acetyl-1*H*-1,2-diazepine.[12]

Reduction of the 5*H*-diazepine (**13b**) with sodium borohydride in ethanol at room temperature gave the 3,4-dihydro compound (**19**) in 57% yield, and this was further treated with

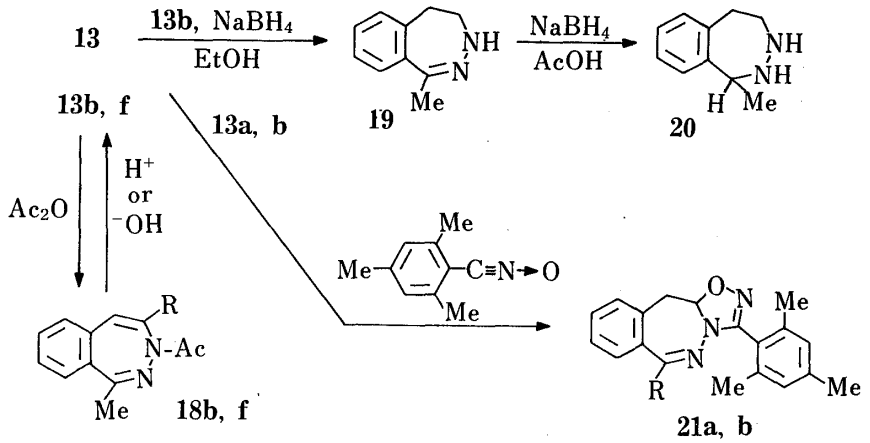


Chart 5

the same reagent in acetic acid to give the tetrahydro compound (**20**) in 30% yield. Nitrile oxides are known to readily undergo 1,3-dipolar cycloaddition with imine double bonds.[13] Treatment of the 5*H*-diazepines (**13a, b**) with a large excess of mesitylnitrile oxide[14] in anhydrous ether gave the mono-adducts (**21**) as the sole products in 60—65% yields. No other possible products such as mono-adducts with the C_1=N function and bis-adducts were obtained. These results show that the N_3=C_4 imine double bond in the diazepines (**13**) is more reactive with the above reagent than the C_1=N_2 double bond.

The ^{1}H-NMR spectra of the 5*H*-diazepines (**13**) showed a temperature dependence similar to those of 1-phenyl-5*H*-2,3-benzodiazepine,[9] 4*H*-1,2-diazepines,[15] and 3*H*-1,2-benzodiazepines[3] consistent with the predictable temperature-dependent inversion of the diazepine ring. For example, the C-5 methylene protons of **13b** show a doublet at δ 2.96 at 140°C, which broadens with decreasing temperature and splits into ABX type quartets centered on δ 2.76 and 3.16 below 90°C, the change being complete at 29°C. The energy of activation for the ring inversion was estimated by spectral analysis using the literature method.[3,15] The $\Delta G^{\neq}$ value (17.5±0.3 kcal mol^{-1}) for **13b** at the coalescence temperature (90°C) is slightly lower than those for the phenyl-substituted 2,3-benzodiazepines,[9] and is similar to that for 3,5,7-triphenyl-4*H*-1,2-diazepine.[15]

Experimental

The general experimental procedures were the same as in Part XVIII.[1]

Starting Materials——1-Methyl-,[16] 3-methyl-,[17] 6-methyl-,[18] 8-methyl-,[18] 1,3-dimethyl-,[17] and 7-methoxyisoquinoline[19] were prepared by the cited procedures.

***N*-Aminoisoquinolinium Mesitylenesulfonates (11a—g)**——General Procedure: The reported procedures for the preparation of **11a**, **11b**,[6] and **11f**[5] were employed. A solution of *O*-mesitylenesulfonylhydroxylamine (1.1 mol eq) in CH_2Cl_2 (100—200 ml) was added dropwise to a solution of an isoquinoline derivative (**14**: 0.02—0.07 mol) in CH_2Cl_2 (20—50 ml) with constant stirring in an ice bath. The reaction mixture was stirred for an additional 1 h and then ether (*ca.* 500 ml) was added to the mixture. The resulting crystalline precipitate was collected by filtration and recrystallized from EtOH or EtOH–AcOEt to give the corresponding salt (**11**).

11a: 75% yield, mp 135—136°C (lit.,[6] mp 134—135°C).

11b: 84% yield, mp 177—178°C (lit.,[6] mp 175—176°C).

11c: 97% yield, mp 170—171°C. IR (KBr) cm^{-1}: 3250 (NH). NMR (CD_3OD) δ: 2.86 (3H, s, 3-Me), 7.8—8.3 (5H, m, 4- and Ar–H), 9.59 (1H, s, 1-H), $^-$OMes [2.22 (3H, s), 2.58 (6H, s), 6.80 (2H, s)]. *Anal.* Calcd for $C_{19}H_{22}N_2O_3S$: C, 63.67; H, 6.19; N, 7.81. Found: C, 63.62; H, 6.20; N, 7.81.

11d: 83% yield, mp 192—194°C. IR (KBr) cm^{-1}: 3250 (NH). NMR (CD_3OD) δ: 2.67 (3H, s, 6-Me), 7.8—8.4 (5H, m, 3-, 4-, and Ar–H), 9.47 (1H, s, 1-H), $^-$OMes [2.20 (3H, s), 2.59 (6H, s), 6.80 (2H, s)]. *Anal.* Calcd for $C_{19}H_{22}N_2O_3S$: C, 63.67; H, 6.19; N, 7.81. Found: C, 63.96; H, 6.20; N, 7.80.

11e: 75% yield, mp 178—179.5°C. IR (KBr) cm^{-1}: 3225 (NH). NMR (CD_3OD) δ: 2.82 (3H, s, 8-Me), 7.7—8.2 (5H, m, 3-, 4-, and Ar-H), 9.64 (1H, s, 1-H), $^-$OMes [2.20 (3H, s), 2.58 (6H, s), 6.79 (2H, s)]. *Anal.* Calcd for $C_{19}H_{22}N_2O_3S$: C, 63.67; H, 6.19; N, 7.81. Found: C, 63.70; H, 6.36; N, 7.80.

11f: 84% yield, mp 207—208°C (lit.,[5] mp 207—208.8°C).

11g: 91% yield, mp 190—192°C. IR (KBr) cm^{-1}: 3275 (NH). NMR (CD_3OD) δ: 3.90 (3H, s, 7-OMe), 7.4—8.3 (5H, m, 3-, 4-, and Ar–H), 9.28 (1H, s, 1-H), $^-$OMes [2.11 (3H, s), 2.54 (6H, s), 6.64 (2H, s)]. *Anal.* Calcd for $C_{19}H_{22}N_2O_4S$: C, 60.94; H, 5.92; N, 7.48. Found: C, 60.98; H, 5.85; N, 7.42.

Photolysis of the Salts (11): Formation of the 5*H*-2,3-Benzodiazepines (13a—g)——General Procedure: A solution of KOH (*ca.* 3 mol eq, 400—450 mg) in MeOH (10 ml) was added dropwise to a stirred solution of a salt (**11**: *ca.* 1 g) in MeOH (250 ml) during 10 min under irradiation. The reaction mixture was further irradiated. The photolysis was followed in terms of the disappearance of the ultraviolet (UV) absorption at 252—255 nm due to the imide (**12**) and was complete in 20—50 min. After removal of the solvent *in vacuo* below 25°C, the residue was extracted with CH_2Cl_2. The extract was washed with satd. NaCl, dried over $MgSO_4$, and concentrated *in vacuo*. The resulting residue was chromatographed on Sephadex (LH-20) using $CHCl_3$–*n*-hexane (9: 2) as an eluent to give the corresponding diazepine (**13**) and parent isoquinoline (**14**) successively. The yields of these products are shown in Chart 3. Analytical and some spectral data for the 2,3-benzodiazepines (**13**) are summarized in Table I.

Treatment of the Diazepines (13b, f) with Acetic Anhydride——A solution of a diazepine (**13b, f**: 60 mg) in Ac_2O (5 ml) was heated at 140°C for 5 h. After removal of the excess reagent *in vacuo*, the residue was dissolved in CH_2Cl_2 (50 ml). The solution was successively washed with satd. $NaHCO_3$ and satd. NaCl, and then dried and concentrated *in vacuo*. The residue was chromatographed on silica gel using ether–*n*-hexane (1: 3) as an eluent to give the corresponding 3-acetyl-3*H*-2,3-benzodiazepine (**18**).

18b: 45 mg, 59% yield, mp 110—111°C, yellow prisms (from isopropyl ether–*n*-hexane). IR (KBr) cm^{-1}: 1660 (C=O). MS *m/e*: 200 (M^+). NMR δ: 2.20 (3H, s, Ac–Me), 2.40 (3H, s, 1-Me), 6.07 (1H, d, 5-H), 6.67 (1H, d, 4-H), 7.0—7.4 (4H, m, Ar–H), $J_{4,5}=8$ Hz. *Anal.* Calcd for $C_{12}H_{12}N_2O$: C, 71.98; H, 6.04; N, 13.99. Found: C, 71.76; H, 5.92; N, 14.06.

18f: 37 mg, 50% yield, orange oil. IR ($CHCl_3$) cm^{-1}: 1645 (C=O). MS *m/e*: 214 (M^+). NMR δ: 2.07 (3H, s, Ac–Me), 2.24 (3H, br d, 4-Me), 2.42 (3H, s, 1-Me), 6.22 (1H, br q, 5-H), 7.0—7.5 (4H, m, Ar–H). *Anal.* Calcd for $C_{13}H_{14}N_2O$: C, 72.87; H, 6.59; N, 13.08. Found: C, 72.81; H, 6.49; N, 12.88.

Hydrolysis of the 3-Acetyl-3*H*-2,3-diazepines (18)——i) By Acid: A mixture of **18** (30 mg), MeOH (5 ml), and 10% HCl (0.6 ml) was stirred for 20 h at room temperature and then diluted with CH_2Cl_2 (50 ml). The mixture was successively washed with satd. $NaHCO_3$ and satd. NaCl, dried, and then concentrated *in vacuo*. The residue was chromatographed on Sephadex (LH-20) using $CHCl_3$–*n*-hexane (9: 2) as an eluent to give the corresponding 5*H*-diazepine (**13b, f**) in *ca.* 50% yield.

ii) By Base: A mixture of **18** (50 mg), EtOH (5 ml), and 10% NaOH (0.2 ml) was refluxed for 12 h. After removal of EtOH *in vacuo*, the residue was extracted with benzene. The extract was washed with satd. NaCl, dried, and then concentrated *in vacuo*. The residue was chromatographed as described for i) to give the corresponding 5*H*-diazepine (**13b, f**) in 85—90% yield.

Reduction of the Diazepine (13b) with $NaBH_4$ in Ethanol——Solid $NaBH_4$ (500 mg) was added in small portions to a solution of **13b** (240 mg) in EtOH (10 ml) with stirring in an ice bath. The reaction solution was stirred for an additional 20 h at room temperature and was then concentrated *in vacuo* below 25°C. The residue was extracted with CH_2Cl_2 and the extract was washed with satd. NaCl, dried, and concentrated *in vacuo*. The residue was chromatographed on silica gel using ether as an eluent to give the 3,4-dihydrodiazepine (**19**): 135 mg, 57% yield, yellow oil. IR ($CHCl_3$) cm^{-1}: 3325 (NH). MS *m/e*: 160 (M^+). NMR δ: 2.29 (3H, s, 1-Me), 2.80 (2H, t, $J=6$ Hz, 5-H_2), 3.55 (2H, t, $J=6$ Hz, 4-H_2), 5.1 (1H, br, NH), 7.0—7.3 (4H, m, Ar–H). *Anal.* Calcd for $C_{10}H_{12}N_2$: C, 74.96; H, 7.55; N, 17.49. Found: C, 74.80; H, 7.71; N, 17.54.

Reduction of the Dihydrodiazepine (19) with $NaBH_4$ in Acetic Acid——Solid $NaBH_4$ (200 mg) was added in small portions to a solution of **19** (100 mg) in AcOH (5 ml) with stirring in an ice bath. The reaction solution was stirred for an additional 10 min and was then diluted with CH_2Cl_2 (100 ml). After removal of AcOH by extraction with satd. $NaHCO_3$, the solution was washed with satd. NaCl, dried, and concentrated *in vacuo*. The resulting residue was chromatographed on silica gel using CH_2Cl_2–MeOH (100: 1) as an eluent to give the tetrahydrodiazepine (**20**): 30 mg, 30% yield, pale yellow oil. IR ($CHCl_3$) cm^{-1}: 3320 (NH). MS *m/e*: 162 (M^+). NMR δ: 1.51 (3H, d, $J=7$ Hz, 1-Me), 3.0—3.2 (4H, m, 4- and 5-H_2), 3.75 (2H, br, NH) 4.26 (1H, q, 1-H), 7.0—7.4 (4H, m, Ar–H). *Anal.* Calcd for $C_{10}H_{14}N_2$: C, 74.03; H, 8.72; N, 17.27. Found: C, 73.79; H, 8.73; N, 17.03.

Cycloaddition of the 5*H*-Diazepines (13a, b) with Mesitylnitrile Oxide——A mixture of a diazepine (**13a, b**: 50—60 mg), mesitylnitrile oxide[14] (250 mg, *ca.* 5 mol eq), and anhydrous ether (10 ml) was stirred for 3 d at room temperature in the dark. After removal of the solvent *in vacuo*, the residue was chromatographed on silica gel using ether–*n*-hexane (1: 8) as an eluent to give the corresponding adduct (**21a, b**) in 60—65% yield, and this was recrystallized from benzene–*n*-hexane.

21a: mp 115—116.5°C. MS *m/e*: 305 (M^+). NMR δ: 2.30 (9H, br s, Mes–Me_3), 3.23 (1H, dd, $J=15$ and 8 Hz, one of 5-H_2), 3.70 (1H, dd, $J=15$ and 2 Hz, one of 5-H_2), 5.73 (1H, dd, $J=8$ and 2 Hz, 4-H), 6.93 (2H, br s, Mes–H_2), 7.19 (1H, s, 1-H), 7.2—7.4 (4H, m, Ar–H). *Anal.* Calcd for $C_{19}H_{19}N_3O$: C, 74.73; H, 6.27; N, 13.76. Found: C, 74.74; H, 6.27; N, 13.76.

21b: mp 162—164°C. MS *m/e*: 319 (M^+). NMR δ: 2.19 (3H, s, 1-Me), 2.24 (6H, s, Mes–Me_2), 2.26 (3H, s, Mes–Me), 3.00 (1H, dd, $J=14$ and 9 Hz, one of 5-H_2), 3.41 (1H, dd, $J=14$ and 2 Hz, one of 5-H_2),

5.56 (1H, dd, $J=9$ and 2 Hz, 4-H), 6.77 (2H, br s, Mes–H_2), 7.0—7.4 (4H, m, Ar–H). *Anal.* Calcd for $C_{20}H_{21}N_3O$: C, 75.21; H, 6.63; N, 13.15. Found: C, 75.31; H, 6.62; N, 13.22.

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