(1974).
(9) (a) P. S. Engel and M. A. Schexnayder, *J. Am. Chem. Soc.*, **97**, 145 (1975); (b) M. A. Schexnayder and P. S. Engel, *Tetrahedron Lett.*, 1153 (1975); (c) R. K. Murray, D. L. Goff, and R. E. Ratych, *ibid.*, 763 (1975).
(10) Portions of these results have been presented: K. G. Hancock, P. L. Wylie, and J. T. Lau, Abstracts, First North American Chemical Congress, Mexico City, Mexico, Dec 1975, No. ORGA-133.
(11) See (a) J. C. Dalton and H.-F. Chan, *J. Am. Chem. Soc.*, **95**, 4085 (1973); (b) P. S. Engel and M. A. Schexnayder, *ibid.*, **94**, 9252 (1972), as well as the reviews cited above,[1] for excellent discussions of the role of γ-H abstraction in other β,γ-unsaturated ketones.
(12) (a) E. J. Corey and B. W. Erickson, *J. Org. Chem.*, **36**, 3553 (1971); (b) E. J. Corey and D. Crouse, *ibid.*, **33**, 298 (1968).
(13) D. Seebach, *Synthesis*, 17 (1969).
(14) Principal photoproducts have been arbitrarily defined as those with maximum uncorrected GLC yields of at least 2%; only these products have been given numerical designations.
(15) D. E. McCreer, N. W. K. Chiu, and M. G. Vinje, *Can. J. Chem.*, **43**, 1398 (1965).
(16) H. Morrison, private communication. We thank Professor Morrison for sending us infrared and NMR spectra of (*Z*)- and (*E*)-3-methylpent-3-en-2-one prior to publication.
(17) D. D. Faulk and A. Fry, *J. Org. Chem.*, **35**, 364 (1970).
(18) P. Baret, J.-L. Pierre, and R. Hielmann, *Bull. Soc. Chim. Fr.*, 4735 (1967).
(19) E. G. E. Hawkins and R. Large, *J. Chem. Soc., Perkin Trans. 1*, 280 (1974).
(20) A. Wolf, German Patent 87 237 (1953); *Chem. Abstr.*, **52**, 9226*i* (1958).
(21) K. G. Hancock and R. O. Grider, *J. Am. Chem. Soc.*, **96**, 1158 (1974).
(22) M. A. Schexnayder and P. S. Engel, *J. Am. Chem. Soc.*, **97**, 4825 (1975).
(23) (a) R. M. Silverstein, G. C. Bassler, and T. C. Morrill, "Spectrometric Identification of Organic Compounds", 3rd ed, Wiley, New York, N.Y., 1974; (b) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed, Pergamon Press, Oxford, 1969.
(24) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).
(25) P. J. Wagner, *Tetrahedron Lett.*, 5385 (1968).
(26) Lamola and Hammond[24] have tabulated values of 0.44 and 0.55, respectively, for cis–trans and trans–cis piperylene isomerizations, but these appear to be reversed, as values calculated elsewhere in their paper[24] would indicate. In addition, Wagner[25] has reported a value of 0.555 for the cis to trans isomerization. We acknowledge the help of Professor Wagner (private communication) in clarifying the situation.
(27) H. Morrison and O. Rodriquez, *J. Photochem.*, **3**, 471 (1974–1975).
(28) C. Djerassi, *Chem. Ind. (London)*, 258 (1961).
(29) W. P. Hayes and C. J. Timmons, *Spectrochim. Acta*, **21**, 529 (1965).
(30) P. J. Wagner, *Acc. Chem. Res.*, **4**, 168 (1971).
(31) P. Yates and A. G. Szabo, *Tetrahedron Lett.*, 485 (1965).
(32) R. B. LaCount and C. E. Griffin, *Tetrahedron Lett.*, 1549 (1965).
(33) F. D. Lewis and N. J. Turro, *J. Am. Chem. Soc.*, **92**, 311 (1970).
(34) (a) P. J. Wagner and A. E. Kemppainen, *J. Am. Chem. Soc.*, **94**, 7495 (1972); (b) P. J. Wagner, P. A. Kelso, A. E. Kemppainen, and R. G. Zepp, *ibid.*, **94**, 7500 (1972).
(35) D. J. Coyle, R. V. Peterson, and J. Heicklen, *J. Am. Chem. Soc.*, **86**, 3850 (1964).
(36) F. A. L. Anet and D. P. Mullis, *Tetrahedron Lett.*, 737 (1969).
(37) T. B. H. McMurry and R. R. Talekar, *J. Chem. Soc., Perkin Trans. 1*, 442 (1976).
(38) D. R. Hicks, R. C. Anderson, and B. Fraser-Reid, *Synth. Commun.*, **6**, 417 (1976).
(39) Boiling points are uncorrected. Infrared spectra were obtained on a Beckman IR-8 or a Perkin-Elmer 237 B spectrometer. Proton nuclear magnetic resonance spectra were recorded at 60 MHz on a Varian Model A-60A or EM360 spectrometer, or at 100 MHz on a Jeolco JNM-MH-100 or a Jeolco PS-100 Fourier transform spectrometer. Chemical shifts are reported in parts per million on the δ scale using tetramethylsilane, chloroform, or benzene as internal standard. Ultraviolet absorption spectra were run on Cary Model 14 and 15 spectrometers. Low-resolution mass spectral fragmentation patterns were obtained on a CEC Model 21-104 spectrometer and exact masses were obtained on a Varian Model M-66 spectrometer. Gas chromatographic analyses and preparative separations were performed on a Varian Aerograph A90-P instrument. Gas chromatographic yields were not corrected for detector response due to limited quantities of some materials available. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

General Photochemical Synthesis of 1*H*-1,2-Benzodiazepines from *N*-Iminoquinolinium Ylide Dimers[1]

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Irradiation of *N*-iminoquinolinium ylide dimers **7a–i**, prepared from *N*-aminoquinolinium mesitylenesulfonates **5a–i** by treatment with base, in methylene chloride solution containing acetic acid afforded the fully unsaturated 1*H*-1,2-benzodiazepines **8a–i** in moderate yields. The photoproducts **8a** and **8c** were reduced with lithium aluminum hydride to the 2,3-dihydrobenzodiazepines **12a** and **12c**, which were further hydrogenated over palladium/carbon to give the 2,3,4,5-tetrahydrodiazepines **13a** and **13c**, respectively. The reduced 1,2-benzodiazepines gave the corresponding mono- (**14, 15**) and diacetyl (**16, 17**) derivatives. Based on NMR studies in $CDCl_3$–acetic acid solution which demonstrate an equilibrium between the dimers **7** and the corresponding *N*-iminoquinolinium ylides **6**, a mechanism for the formation of the 1,2-benzodiazepines **8** via the diaziridine (**25**) and 2*H*-1,2-benzodiazepine (**9**) intermediates is proposed.

Streith[2] first showed in 1968 that the photolysis of *N*-acyliminopyridinium ylides (**1**) yields the previously unknown 1*H*-1,2-diazepines (**2**) (Scheme I). Concurrent investigations by Sasaki[3] and by Snieckus,[4] and more recently by Abramovitch,[5] provided additional examples of this photoinduced ring expansion reaction. At present, this constitutes the only general route to simple, fully unsaturated 1*H*-1,2-diazepines.[6–8]

In contrast, the analogous *N*-acyliminoquinolinium (**3**)[9–11] and -isoquinolinium[10–12] ylides have been shown to rearrange upon irradiation into 2-aminoquinoline and 1-aminoisoquinoline derivatives, respectively, as well as to undergo N–N fragmentation to the respective parent heterocycles.[13] The formation of 1,2-benzodiazepines **4** from ylides **3** (Scheme I) as a result of photochemical ring expansion and solvent incorporation represents the two isolated exceptions to the above generalization.[9,10]

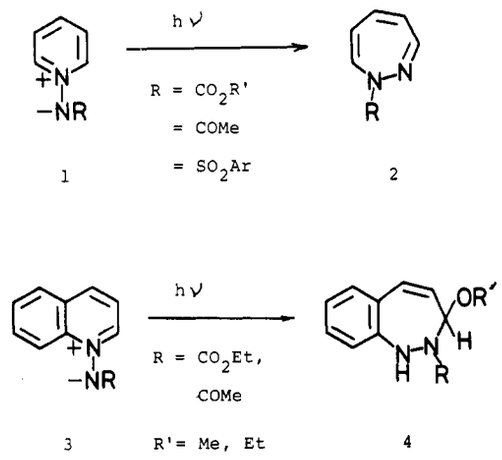
We report on the general photochemical synthesis of the hitherto unknown fully unsaturated 1*H*-1,2-benzodiazepines **8** from the *N*-iminoquinolinium ylide dimers **7**. Of the six theoretically possible benzodiazepines,[14] the 1,4-benzodiazepines have been most widely investigated owing to their useful biological activity.[15] The 1,5-benzodiazepines have also received substantial attention,[16] whereas the corresponding 1,3, 2,4, and 2,3 isomers have been neglected in comparison.[14,17] As for the 1,2 isomers, prior to the present work, only fused cyclopentano-3*H*-1,2-benzodiazepines had been reported.[18]

Table I. Preparation of 1*H*-1,2-Benzodiazepines (8)[a] by Irradiation of the *N*-Iminoquinolinium Ylide Dimers (7)

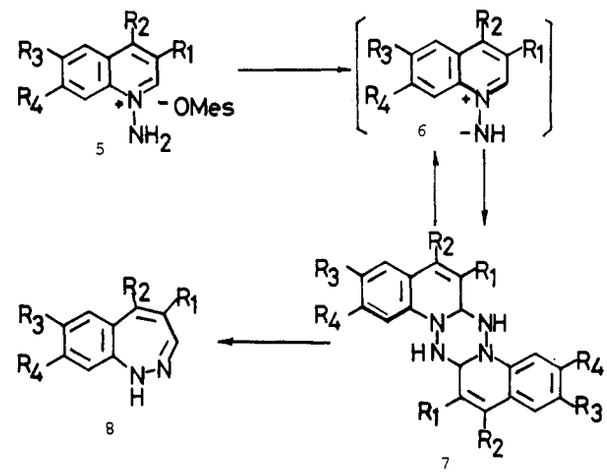
Registry no.	Compd	Reaction time, h	Yield,[b] %	Mp, °C[c]	NMR ($CDCl_3$), δ[h] 3-H	4-H	5-H	Misc[k]
264-60-8	**8a**	8	61	63–64[d]	7.07 (d)	5.97 (dd)[i]	6.86 (d)	
61702-22-5	**8b**	8	60	87–88[d]	6.97 (s)		6.65 (d)	1.92 (d, Me)[j]
54507-50-5	**8c**	10	79	63.5–64[e]	7.07 (d)	6.03 (m)		2.20 (br, Me)
59065-95-1	**8d**	9	47	94.5–95.5[f]	7.08 (d)	5.97 (dd)	6.89 (d)	2.24 (br, Me)
59065-96-2	**8e**	5	5	94.5–95.5[d]	7.08 (d)	6.02 (dd)	6.87 (d)	3.75 (s, OMe)
59065-97-3	**8f**	10	50	73–74[g]	7.05 (d)	5.94 (dd)	6.86 (d)	
61702-23-6	**8g**	15	38	114–115[d]	7.06 (d)	5.96 (dd)	6.88 (d)	3.90 (s, COOMe)
59065-99-5	**8h**	7	70	93.5–95[g]	7.05 (d)	5.92 (dd)	6.81 (d)	2.21 (br, Me)
59066-00-1	**8i**	20	62	103–104.5[g]	7.05 (d)	5.85 (dd)	6.79 (d)	3.77 (s, OMe)

[a] Satisfactory analytical data (±0.4% for C, H, and N) were obtained for all compounds listed. [b] Yields are of isolated products. [c] All compounds were recrystallized from isopropyl ether except **8g**, which was obtained from isopropyl ether–benzene. [d] Red prisms. [e] Yellow prisms. [f] Red plates. [g] Red needles. [h] See Experimental Section. Multiplicities are indicated by the usual symbols. [i] $J_{3,4}$ = 4 and $J_{4,5}$ = 11 Hz. [j] $J_{5,4\text{-Me}}$ = 1 Hz. [k] A broad signal (NH, δ 6.6–6.7) and multiplet signals (ArH, δ 6.2–8.0) appear in all spectra.

Scheme I



Scheme II



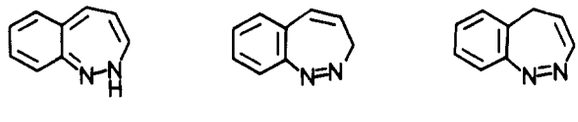
	R_1	R_2	R_3	R_4
a	H	H	H	H
b	Me	H	H	H
c	H	Me	H	H
d	H	H	Me	H
e	H	H	OMe	H
f	H	H	Cl	H
g	H	H	CO_2Me	H
h	H	H	H	Me
i	H	H	H	OMe

Results

The *N*-aminoquinolinium mesitylenesulfonates (**5**) (Scheme II) were prepared by N-amination of the corresponding quinolines with *O*-mesitylenesulfonylhydroxylamine according to the method of Tamura and co-workers.[10] Treatment of the salts **5** with potassium carbonate in dimethylformamide according to the method of Okamoto and co-workers[19] afforded in good yield the *N*-iminoquinolinium ylide dimers **7** presumably via the *N*-iminoquinolinium ylides **6**.

Irradiation of the dimers **7** in methylene chloride solution containing acetic acid resulted in the formation of the corresponding 1*H*-1,2-benzodiazepines **8** in the yields shown in Table I. In addition, small amounts of 2-aminoquinoline derivatives and parent quinolines were also isolated.

The reaction times, yields, and physical data of the new 1,2-benzodiazepines **8** are collected in Table I. The ^1H NMR spectral data, summarized in Table I, are consistent with the proposed structures and eliminate from further consideration the tautomeric 2*H*- (**9**), 3*H*- (**10**),[20] and 5*H*- (**11**) benzodi-

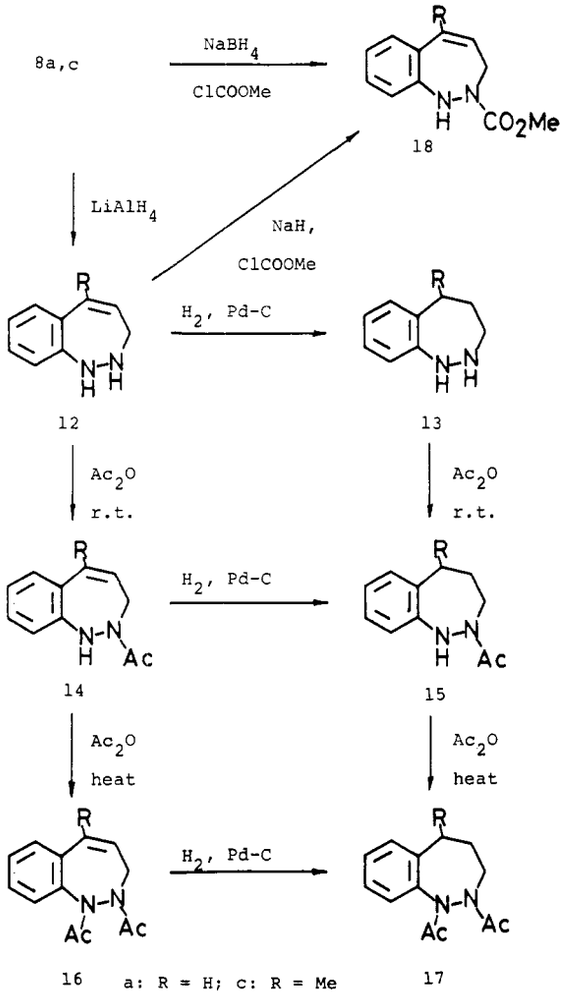


azepine structures as well as the diaziridine structure **25** (Scheme V). Complete characterization by IR, UV, and mass spectrometry was carried out for compounds **9a–c** (see Experimental Section). Further confirmation of structure was achieved by the following chemical studies.

Lithium aluminum hydride reduction of **8a,c** afforded in quantitative yields the 2,3-dihydrodiazepines **12a** and **12c**, respectively, which upon further catalytic hydrogenation gave the corresponding tetrahydrobenzodiazepines **13a** and **13c** (Scheme III). Treatment of **12a,c** and **13a,c** with acetic anhydride at room temperature provided the expected[21] 2-acetyl derivatives **14a,c** and **15a,c**, respectively, which upon reflux with the same reagent gave the corresponding 1,2-diacetyl-1,2-benzodiazepines **16a,c** and **17a,c**.[22] Compounds **16a,c** and **17a,c** could also be directly prepared from **12a,c** and **13a,c**, respectively, using the latter conditions. Catalytic hydrogenation of **14a,c** and **16a,c** yielded the tetrahydro derivatives **15a,c** and **17a,c**, respectively. Finally, acylation of **12a,c** with methyl chloroformate in the presence of sodium hydride af-

forded respectively the 2-methoxycarbonyl-2,3-dihydrobenzodiazepines **18a,c** which were also directly obtained from the photoproducts **8a,c** by reductive carbomethoxylation as shown in Scheme III.

Scheme III



Whereas the above metal hydride reduction proceeded without rupture of the heterocyclic ring, catalytic hydrogenation of **8a,c** resulted in the formation of the parent quinolines **21a,c** in 90% yields (Scheme IV). Since the formation of ammonia was detected, these reactions may proceed by initial reductive N–N bond fission to give **19a,c** which upon cyclization (**20a,c**) and elimination of ammonia leads to the quinoline derivatives **21a,c.**

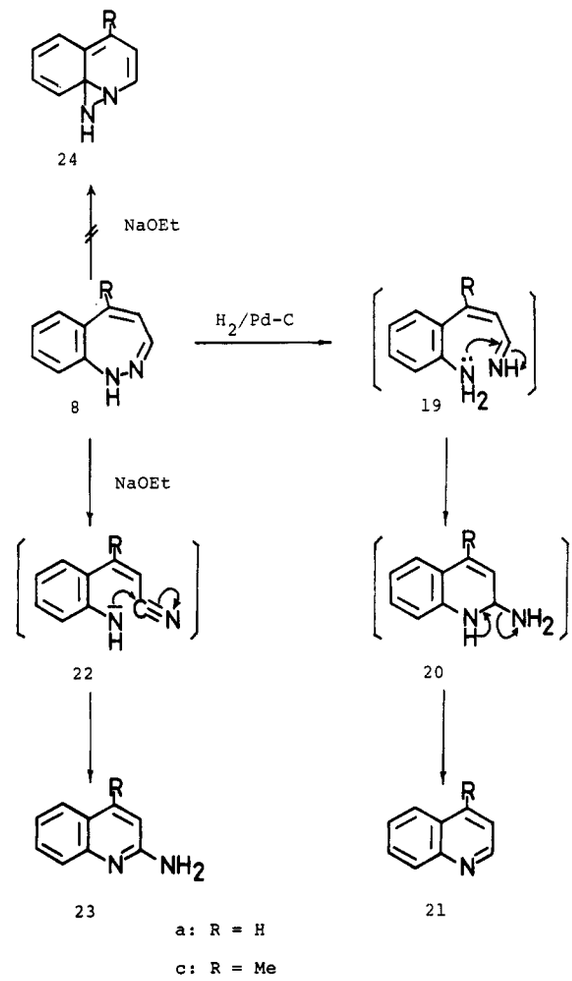
Ring contraction without expulsion of one nitrogen atom was observed when compounds **8a** and **8c** were subjected to treatment with excess sodium ethoxide in ethanol to give in high yield 2-aminoquinoline (**23a**) and 2-aminolepidine (**23c**), respectively. These results have excellent analogy to observations made with 1-acyl-1*H*-1,2-diazepines (**2**)[23] and may be similarly explained by invoking C-3 proton abstraction concomitant with N–N bond cleavage to give intermediate **22** which upon cyclization and tautomerization leads to the observed products **23a** and **23c.** The absence of quinoline products (**21a,c**) speaks against equilibration of **8a,c** with the energy-demanding, dearomatized diaziridine valence isomers **24a,c** under these reaction conditions. On the basis of previous observation,[24] the species **24a,c** would have been expected to lose nitrene fragments to give compounds **21a,c.**

The irradiation of *N*-iminoquinolinium ylide dimers **8a** and **8c** was studied in methylene chloride and in methylene chloride with added acetic acid and diethylamine, respectively.

Table II. Effect of Solvent on Product Yields in the Photolysis of Dimers 7a and 7c

		Yields, %		
Compd	Product	CH_2Cl_2 AcOH	Solvent CH_2Cl_2	CH_2Cl_2 Et_2NH
	Diazepine **8a**	61	32	22
7a	Quinoline	7.5	18	28
	2-Aminoquinoline	0.1	1.5	3
	Diazepine **8c**	79	52	17
7c	Lepidine	4	13	17
	2-Aminolepidine		0.2	1.2

Scheme IV



The results of product distribution, summarized in Table II, show that the effect of diethylamine is to increase the amount of quinoline derivatives at the expense of the corresponding benzodiazepines. On the other hand, the formation of the benzodiazepines is increased and that of the quinolines is diminished in the presence of acetic acid.[25] Consequently, acetic acid has a favorable effect on the overall transformation **7** → **8.** Okamoto has previously shown that the *N*-iminoquinolinium ylides **6** formed by base treatment of the corresponding salts **5** are unstable and can only be isolated as the dimers **7.**[19] We now provide evidence that in $CDCl_3$–acetic acid solution these dimers exist in equilibrium with the ylides **6.**

The NMR spectrum of **7a** in $CDCl_3$ (Figure 1a) shows, aside from an unassigned multiplet at δ 6.4–7.5 (4 H), two doublets and one quartet in the region δ 5.4–5.8 (3 H) which are assigned to H_a, H_b, and H_c. Assignments were confirmed by

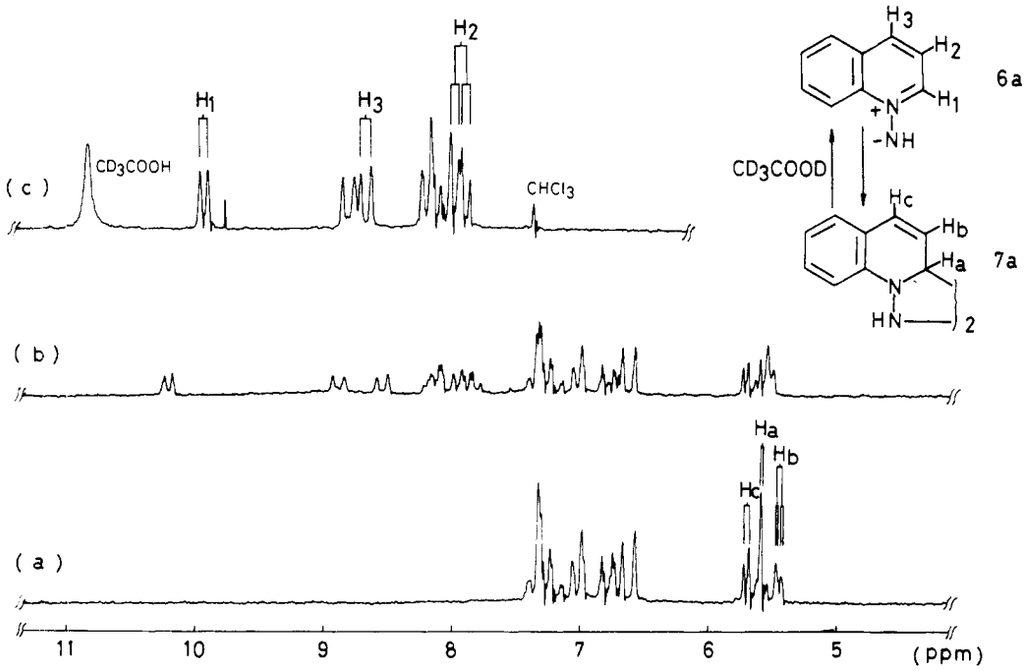


Figure 1. NMR spectra of **7a** in (a) $CDCl_3$ solution, (b) $CDCl_3$ solution containing 1 equiv of CD_3COOD, and (c) $CDCl_3$ solution containing 5 equiv of CD_3COOD.

spin-decoupling experiments. These spectral features are consistent with the presence of dimer **7a** in $CDCl_3$ solution. However, in $CDCl_3$ containing 1 molar equiv of acetic acid (Figure 1b), the spectrum is significantly different in that a number of new signals appear at low field. A limiting spectrum was observed upon addition of 5 molar equiv of acetic acid (Figure 1c) which no longer showed evidence for the presence of the dimer **7a** and instead exhibited a distinct set of signals consistent with the presence of the monomeric structure **6a:** δ 9.85 (d, H_1), 7.86 (dd, H_2), 8.58 (d, H_3), 8.90 (d, H_8), and 7.9–8.25 (m, H_4, H_5, and H_6), $J_{1,2}$ = 6 and $J_{2,3}$ = 8 Hz. Strong support for these proton assignments and thus for structure **6a** was obtained by spectral comparison with *N*-ethoxycarbonyliminoquinolinium ylide,[19] which shows δ 9.35 (d, H_1), 7.63 (dd, H_2), 8.34 (d, H_3), 8.92 (d, H_8), and 7.7–8.1 (m, H_4, H_5, and H_6), $J_{1,2}$ = 6 and $J_{2,3}$ = 8 Hz.

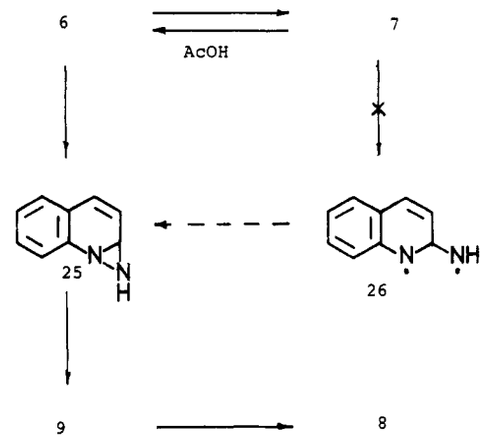
Discussion

On the basis of the above results, we suggest that methylene chloride–acetic acid solutions of dimer **7** contain equilibrium concentrations of *N*-iminoquinolinium ylide **6** and that it is this species which, by analogy with previous mechanistic proposals for the photochemical rearrangement of *N*-acyliminopyridinium ylides,[6a] undergoes internal 1,3-photocycloaddition to give the diaziridines **25** and then valence tautomerization to yield the *o*-quinonoid 2*H*-1,2-benzodiazepine **9**.[26] Aromatic stability considerations would dictate that the latter would rapidly undergo a photochemically allowed [1,7] sigmatropic hydrogen shift to give the observed product (**8**) (Scheme V).

Schmitz and Ohme[27] have reported that the pyrolysis of 3,4-dihydro-*N*-iminoisoquinolinium ylide dimer gives 4,5-dihydro-3*H*-2,3-benzodiazepine. This reaction may be reasonably envisaged to proceed via a diradical intermediate resulting initially from homolytic N–N bond fission. In the present photochemical reaction, the thermal formation of diaziridine **25** from dimer **7** via the intermediate diradical **26** is unlikely in view of the fact that separate pyrolysis of **7** gave the parent quinoline as the sole product without detectable amounts of ring expansion or rearrangement products.

Examination of Table I does not reveal a qualitative trend

Scheme V



in the effect of substituents on the photochemical rearrangement. Thus electron-donating substituents at C_4 and C_7 provide good yields of benzodiazepines (**8c, 8h, 8i**), whereas both electron-donating and -withdrawing groups at C_6 give lower or poor yields of products (**8d–g**). In view of the small number of cases studied and the potential variation in the photochemical instability of the products as a function of substituent, no conclusions regarding these effects can be drawn at this time.

Finally, a number of other 2- and 4-substituted *N*-aminoquinolinium salts (2-Me, 2-Cl, 2-Ph, 4-Cl, 4-NO_2, 4-OMe) were also prepared. However, upon treatment with base, these did not yield the corresponding dimers. Attempts to obtain benzodiazepines by treatment of the salts with aqueous potassium carbonate–methylene chloride followed by irradiation of the organic phase (presumably containing the *N*-iminoquinolinium ylides) were not successful.

In conclusion, we have described a photochemical synthetic entry into the previously unknown 1*H*-1,2-benzodiazepines (**8**) class of heterocycles. These compounds are now available for further physicochemical studies. An analogous preparative route for 2,3-benzodiazepines from *N*-aminoisoquinolinium salts has not been successful to date.

Table III. *N*-Aminoquinolinium Mesitylenesulfonates (5) and *N*-Iminoquinoline Dimers (7)[a]

Compd	5			7		
	Mp, °C	Yield, %	Registry no.	Mp, °C	Yield, %	Registry no.
a	131–133[b]	94	39996-55-9	154–156[c]	62	7184-52-3
b	136–137	92	61702-25-8	187–188	84	61702-36-1
c	151–152	96	57489-82-4	186–187	56	54507-49-2
d	142–143	94	61702-27-0	155–157	77	59066-14-7
e	163–165	95	61740-70-3	142–145	55	59066-15-8
f	229–231	93	61702-29-2	184–186	86	59066-16-9
g	192–194	89	61702-31-6	200–202	93	61702-37-2
h	217–219	94	61702-33-8	149–150	52	59066-18-1
i	170–172	95	61702-35-0	154–156	59	59066-19-2

[a] Satisfactory analytical data (±0.4% for C, H, and N) were obtained for all new compounds listed in the table. [b] Lit.[10] mp 132–133 °C. [c] Lit.[19] mp 155–156 °C.

Experimental Section

Melting points were measured on a Yamato Model MP-21 apparatus and are uncorrected. Infrared spectra were determined in KBr pellets with a JASCO IRA-2 spectrophotometer. Mass spectra were obtained on a JEOL-D100 instrument. NMR spectra were recorded on Hitachi R-20, R-22, and JEOL JNM-MH-100 spectrometers in deuteriochloroform solution using tetramethylsilane as internal standard unless otherwise stated. Spectral assignments were confirmed by spin-decoupling experiments and, in the case of NH protons, by exchange with D_2O. Ultraviolet spectra were recorded on a Hitachi Model 323 spectrophotometer in ethanol solution. Microanalyses were performed by the Microanalytical laboratory, Showa University, Tokyo, Japan. Column and thin layer chromatography were carried out with alumina and silica gel obtained from Merck Co. Ltd.

Photolyses were carried out under a nitrogen atmosphere using an immersion apparatus equipped with a 400-W high-pressure mercury lamp (Nikko Sekiei Co., Japan) and a Pyrex filter, which was cooled internally with running water.

Materials. Quinoline, 4-, 6-, and 7-methylquinoline, 6-chloroquinoline, 2-aminoquinoline, and 2-aminolepidine were obtained from Tokyo Kasei Kogyo Co., Japan. 3-Methyl-,[28] 6-methoxy-,[29] 6-methoxycarbonyl-,[30] and 7-methoxyquinoline[31] were prepared by literature procedures.

Preparation of *N*-Aminoquinolinium Mesitylenesulfonates (5a–i). General Procedure. The procedure of Tamura and coworkers[10] for the preparation of **5a** was employed. A solution of *O*-mesitylenesulfonylhydroxylamine (0.11 mol) in methylene chloride (150 mL) was added dropwise to a solution of quinoline derivative (0.1 mol) in methylene chloride (100 mL) with constant stirring in an ice bath. The reaction mixture was stirred further for 30 min at room temperature and then cooled in an ice bath. After addition of ether (200–500 mL) to the mixture, the resulting crystalline precipitate was collected and recrystallized from ethanol or ethanol–ethyl acetate to give the salt (**5**).

The results are presented in Table III.

Preparation of *N*-Iminoquinoline Dimers (7a–i). General Procedure. The procedure was adapted from that of Okamoto and co-workers.[19]

To a solution of the *N*-aminoquinolinium salt (**5**, 70 mmol) in dimethylformamide (200–300 mL) was added solid potassium carbonate (10.6 g, 77 mmol) in small portions with stirring at room temperature. After stirring for an additional 2 h, 300–600 mL of ice-cooled water was added slowly to the reaction mixture. The resulting crystalline precipitate was collected by filtration and washed with cold water and then with several portions of methanol to give the dimer (**7**), which was used in the following photolysis without further purification. Further reprecipitation with 5% aqueous potassium hydroxide solution from an aqueous 5% hydrogen chloride solution of the dimer furnished an analytical sample. The results are presented in Table III.

Preparation of 1*H*-1,2-Benzodiazepines (8a–i). General Photolysis Procedure. A solution of the dimer **7** (5 mmol) and acetic acid (3 g, 50 mmol) in methylene chloride (300 mL) was irradiated under a nitrogen atmosphere. The photolysis was followed by the disappearance of the absorption at 230–250 nm due to **7** in the UV spectrum and was complete in 5–20 h. After acetic acid was removed by extraction with saturated aqueous sodium bicarbonate, the reaction solution was washed with water, dried over $MgSO_4$, and evaporated to dryness. The resulting residue was chromatographed over alumina using *n*-hexane–methylene chloride (1:1) as eluent. Recrystallization from isopropyl ether–benzene gave the diazepines (**8**).

Reaction times of the photolysis, yields, and physical data of **8** are collected in Table I. NMR spectral data are also collected in Table I while salient IR and mass spectral data of **8a–c** are described below. **8a:** 3270 cm^{-1} (NH); mass spectrum *m/e* (rel intensity) 144 (M^+, 100), 117 (68), and 116 (11); λ_{max} (ϵ) 250 nm (17 000). **8b:** 3270 cm^{-1} (NH); mass spectrum *m/e* (rel intensity) 158 (M^+, 100), 131 (64), and 130 (80); λ_{max} (ϵ) 245 nm (16 000). **8c:** 3290 cm^{-1} (NH); mass spectrum *m/e* (rel intensity) 158 (M^+, 100), 131 (27), and 130 (73); λ_{max} (ϵ) 246 nm (16 000).

2,3-Dihydro-1*H*-1,2-benzodiazepine (12a). To a suspension of $LiAlH_4$ (0.5 g) in anhydrous ether (100 mL) cooled in an ice bath was added dropwise a solution of the diazepine **8a** (1.0 g) in ether (50 mL) with stirring. The mixture was allowed to warm to room temperature and was stirred for an additional 15 min. The reaction mixture was cooled in an ice bath and the excess reagent was decomposed with water. After removal of the resulting inorganic salts by filtration, the ether solution was dried ($MgSO_4$) and evaporated to dryness to give **12a:** colorless needles (isopropyl ether); 970 mg (96%); mp 56–58 °C; ν 3240 cm^{-1} (NH); mass spectrum *m/e* 146 (M^+); δ 3.5 (1 H, br, NH), 3.75 (2 H, m, 3-H), 5.7 (1 H, br, NH), 5.95 (1 H, m, 4-H), 6.40 (1 H, m, 5-H), and 6.6–7.5 (4 H, m, Ar-H), $J_{3,4}$ = 3, $J_{3,5}$ = 1, and $J_{4,5}$ = 13 Hz.

Anal. Calcd for $C_9H_{10}N_2$: C, 73.94; H, 6.90; N, 19.16. Found: C, 74.03; H, 6.81; N, 19.36.

5-Methyl-2,3-dihydro-1*H*-1,2-benzodiazepine (12c). The reaction of 5-methyl-1,2-benzodiazepine (**8c,** 1.0 g) with $LiAlH_4$ (0.5 g) was carried out and worked up in the same manner as described for **12a** to give **12c:** colorless needles (isopropyl ether); 954 mg (94%); mp 75–76 °C; ν 3230 cm^{-1} (NH); mass spectrum *m/e* 160 (M^+); δ 2.13 (3 H, m, 5-Me), 3.72 (2 H, m, 3-H), 4.1 (2 H, br, NH), 5.98 (1 H, m, 4-H), and 6.5–7.6 (4 H, m, Ar-H), $J_{3,4}$ = 3 and $J_{3,5\text{-Me}} = J_{4,5\text{-Me}}$ = 1 Hz.

Anal. Calcd for $C_{10}H_{12}N_2$: C, 74.96; H, 7.55; N, 17.49. Found: C, 75.05; H, 7.41; N, 17.63.

2,3,4,5-Tetrahydro-1*H*-1,2-benzodiazepine (13a). A solution of **12a** (276 mg) in methanol (10 mL) was hydrogenated with 5% Pd/C (300 mg) with stirring under atmospheric pressure at room temperature. The reaction mixture was subjected to filtration and the filtrate was evaporated to dryness in vacuo. After treating with active charcoal in benzene, the residue was recrystallized from isopropyl ether–*n*-hexane to give **13a:** colorless needles; 252 mg (90%); mp 56–57 °C; ν 3320 cm^{-1} (NH); mass spectrum *m/e* 148 (M^+); δ 1.5–2.6 (2 H, m, 4-H), 2.7–3.3 (2 H, m, 5-H), 2.8–4.0 (2 H, m, 3-H), 4.1 (2 H, br, NH), and 6.6–7.5 (4 H, m, ArH).

Anal. Calcd for $C_9H_{12}N_2$: C, 72.94; H, 8.16; N, 18.90. Found: C, 73.16; H, 8.08; N, 19.07.

5-Methyl-2,3,4,5-tetrahydro-1*H*-1,2-benzodiazepine (13c). A solution of **12c** (240 mg) was hydrogenated with 5% Pd/C (300 mg) and worked up in a similar manner as that described for the preparation of **13a** to give **13c:** colorless needles (isopropyl ether–*n*-hexane); 209 mg (86%); mp 45–46 °C; ν 3270 cm^{-1} (NH); mass spectrum *m/e* 162 (M^+); δ 1.33 (3 H, d, J = 7 Hz, 5-Me), 1.0–2.0 (2 H, m, 4-H), 2.9–3.3 (3 H, m, 3-H and 5-H), 3.3 (1 H, br, NH), and 6.5–7.4 (4 H, m, ArH).

Anal. Calcd for $C_{10}H_{14}N_2$: C, 74.03; H, 8.70; N, 17.27. Found: C, 73.91; H, 8.63; N, 17.22.

2-Acetyl-2,3-dihydro-1*H*-1,2-benzodiazepine (14a). A mixture

of **12a** (276 mg) and acetic anhydride (6 mL) was stirred at room temperature overnight. The reaction mixture was evaporated to dryness in vacuo below 60 °C and the residue was dissolved in methylene chloride (150 ml). The solution was washed with saturated aqueous sodium bicarbonate and then with water, dried over $MgSO_4$, and evaporated. The resulting residue was chromatographed over alumina using methylene chloride–*n*-hexane (1:1) as eluent to give **14a:** colorless prisms (isopropyl ether); 315 mg (89%); mp 108–109 °C; ν 3260 (NH) and 1640 cm^{-1} (C=O); mass spectrum *m/e* 188 (M^+); δ 2.01 and 2.14 (3 H, s, Ac-Me), 4.3–4.6 (2 H, m, 3-H), 5.5–6.0 (1 H, m, 4-H), 6.2–6.6 (1 H, m, 5-H), 6.6 (1 H, br, NH), and 6.7–7.3 (4 H, m, Ar-H), $J_{3,4}$ = 4, $J_{3,5}$ = 1, and $J_{4,5}$ = 12 Hz.

Anal. Calcd for $C_{11}H_{12}N_2O$: C, 70.18; H, 6.43; N, 14.88. Found: C, 70.06; H, 6.15; N, 14.62.

2-Acetyl-5-methyl-2,3-dihydro-1*H*-1,2-benzodiazepine (14c). The diazepine **12c** (316 mg) was acetylated with acetic anhydride (6 mL) at room temperature by a procedure similar to that described for the preparation of **14a** to give **14c:** colorless prisms (benzene–isopropyl ether); 370 mg (93%); mp 89–90 °C; ν 3270 (NH) and 1645 cm^{-1} (C=O); mass spectrum *m/e* 202 (M^+); δ 2.06 and 2.15 (3 H, s, Ac-Me), 2.20 (3 H, m, 5-Me), 4.1–4.5 (2 H, m, 3-H), 5.6–6.1 (1 H, m, 4-H), 5.9 (1 H, br, NH), and 6.9–7.5 (4 H, m, ArH).

Anal. Calcd for $C_{12}H_{14}N_2O$: C, 71.26; H, 6.98; N, 13.85. Found: C, 70.97; 6.85; N, 13.99.

2-Acetyl-2,3,4,5-tetrahydro-1*H*-1,2-benzodiazepine (15a). From 13a. A mixture of **13a** (128 mg) and acetic anhydride (6 mL) was allowed to react and worked up in the same manner as described for **14a** to give **15a:** colorless prisms (isopropyl ether); 125 mg (76%); mp 100–102 °C; ν 3280 (NH) and 1630 cm^{-1} (C=O); mass spectrum *m/e* 190 (M^+); δ 2.05 and 2.12 (3 H, s, Ac-Me), 1.7–2.2 (2 H, m, 4-H), 2.6–3.1 (2 H, m, 5-H), 3.6–4.0 (2 H, m 3-H), 6.7–7.3 (4 H, m, ArH), and 7.1 (1 H, br, NH).

Anal. Calcd for $C_{11}H_{14}N_2O$: C, 69.44; H, 7.42; N, 14.73. Found: C, 69.26; H, 7.24; N, 14.61.

From 14a. A solution of **14a** (100 mg) in methanol (10 mL) was hydrogenated in the presence of 5% Pd/C (100 mg) and worked up in a manner similar to that described for the preparation of **13a** to give 98 mg (97%) of **15a.**

2-Acetyl-5-methyl-2,3,4,5-tetrahydro-1*H*-1,2-benzodiazepine (15c). From 13c. A mixture of **13c** (67 mg) and acetic anhydride (3 mL) was allowed to react and worked up in a manner similar to that described for **14a** to give **15c:** colorless prisms (isopropyl ether–benzene); 72 mg (89%); mp 113.5–115 °C; ν 3300 (NH) and 1640 cm^{-1} (C=O); mass spectrum *m/e* 204 (M^+); δ 1.25 and 1.38 (3 H, d, 5-Me), 1.6–2.2 (2 H, m, 4-H), 2.05 and 2.10 (3 H, s, Ac-Me), 2.9–3.6 (1 H, m, 5-H), 3.7–4.0 (2 H, m, 3-H), 6.8–7.3 (4 H, m, ArH), and 7.0 (1 H, br, NH), $J_{5,5\text{-Me}}$ = 7 Hz.

Anal. Calcd for $C_{12}H_{16}N_2O$: C, 70.56; H, 7.90; N, 13.72. Found: C, 70.49; H, 7.76; N, 13.98.

From 14c. A solution of **14c** (100 mg) in methanol (10 mL) was hydrogenated in the presence of 5% Pd/C (100 mg) and worked up as described for **13a** to give 97 mg (96%) of **15c.**

1,2-Diacetyl-2,3-dihydro-1*H*-1,2-benzodiazepine (16a). A mixture of **14a** (200 mg) and acetic anhydride (8 mL) was refluxed for 4 h and evaporated to dryness in vacuo. The residue was dissolved in methylene chloride (100 mL) and the resulting solution was successively washed with sodium bicarbonate solution and water and evaporated to dryness. The resulting residue was chromatographed over alumina using *n*-hexane–methylene chloride (1:1) as eluent to give **16a:** colorless prisms (isopropyl ether–benzene); 224 mg (91%); mp 78–80 °C; ν 1660 (C=O) and 1695 cm^{-1} (C=O); mass spectrum *m/e* 230 (M^+); δ 2.04, 2.08, and 2.23 (6 H, s, Ac-Me), 4.0–5.6 (2 H, m, 3-H), 5.7–6.1 (1 H, m, 4-H), 6.3–6.7 (1 H, m, 5-H), and 7.2–7.5 (4 H, m, ArH).

Anal. Calcd for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.17. Found: C, 67.71; H, 6.02; N, 12.49.

1,2-Diacetyl-5-methyl-2,3-dihydro-1*H*-1,2-benzodiazepine (16c). Compound **14c** (300 mg) was acetylated under conditions similar to those described for the preparation of **16a** to give **16c:** colorless prisms (isopropyl ether–benzene); 336 mg (94%); mp 104.5–105.5 °C; ν 1665 (C=O) and 1700 cm^{-1} (C=O); mass spectrum *m/e* 244 (M^+); δ 1.88, 1.95, 2.08, and 2.30 (6 H, s, Ac-Me), 2.1 (3 H, m, 5-Me), 4.0–5.1 (2 H, m, 3-H), 5.5–5.9 (1 H, m, 4-H), and 6.8–7.5 (4 H, m, ArH).

Anal. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 68.95; H, 6.47; N, 11.61.

1,2-Diacetyl-2,3,4,5-tetrahydro-1*H*-1,2-benzodiazepine (17a). From 15a. A mixture of **15a** (80 mg) and acetic anhydride (8 mL) was allowed to react and worked up in the same manner as described for the preparation of **16a** to give **17a:** colorless prisms (isopropyl ether–benzene); 88 mg (90%); mp 91–93 °C; ν 1670 cm^{-1} (C=O); mass spectrum *m/e* 232 (M^+); δ 2.03, 2.13, 2.16, and 2.29 (6 H, s, Ac-Me), 1.6–2.3 (2 H, m, 4-H), 2.8–3.5 (3 H, m, 3-H and 5-H), 4.6–5.1 (1 H, m, 3-H), and 7.2–7.5 (4 H, m, ArH).

Anal. Calcd for $C_{13}H_{16}N_2O_2$: C, 67.22; H, 6.94; N, 12.06. Found: C, 66.98; H, 6.86; N, 11.93.

From 16a. A solution of **16a** (45 mg) in methanol (8 mL) was hydrogenated over 5% Pd/C (45 mg) and worked up as described for the preparation of **13a** to give 44 mg (97%) of **17a.**

1,2-Diacetyl-5-methyl-2,3,4,5-tetrahydro-1*H*-1,2-benzodiazepine (17c). From 15c. A mixture of **15c** (57 mg) and acetic anhydride (5 mL) was allowed to react and worked up in the same manner as described for the preparation of **16a** to give **17c:** colorless prisms (isopropyl ether–benzene); 65 mg (94%); mp 115–117 °C; ν 1680 cm^{-1} (C=O); mass spectrum *m/e* 246 (M^+); δ 1.13, 1.32, 1.37, and 1.43 (3 H, d, 5-Me), 1.80, 2.02, 2.04, 2.11, 2.13, 2.16, 2.32, and 2.35 (6 H, s, Ac-Me), 1.6–2.3 (2 H, m, 4-H), 3.0–3.6 (3 H, m, 3-H and 5-H), 4.4–4.9 (1 H, m, 3-H), and 7.2–7.3 (4 H, m, ArH).

Anal. Calcd for $C_{14}H_{18}N_2O_2$: C, 68.27; H, 7.37; N, 11.37. Found: C, 68.18; H, 7.20; N, 11.00.

From 16c. A solution of **16c** (50 mg) in methanol (8 mL) was hydrogenated over 5% Pd/C (50 mg) and worked up in the manner described for the preparation of **13a** to give 49 mg (97%) of **17c.**

2-Methoxycarbonyl-2,3-dihydro-1*H*-1,2-benzodiazepine (18a). From 12a. To a mixture of **12a** (280 mg), sodium hydride (50% in paraffin oil, 213 mg), and tetrahydrofuran (15 mL) cooled in an ice bath was added dropwise with stirring a solution of methyl chloroformate (420 mg) in tetrahydrofuran (5 mL). The reaction mixture was stirred for 2 h and evaporated to dryness in vacuo below 40 °C. The residue was dissolved in cold water (20 mL) and the resulting solution was extracted with methylene chloride. The organic extract was washed with water, dried ($MgSO_4$), and evaporated to dryness. The residue was chromatographed over alumina using benzene as eluent to give **18a:** colorless plates (isopropyl ether); 260 mg (67%); mp 109–110 °C; ν 3280 (NH) and 1680 cm^{-1} (C=O); mass spectrum *m/e* 204 (M^+); δ 3.06 (3 H, s, CO_2Me), 4.45 (2 H, m, 3-H), 5.75 (1 H, m, 4-H), 6.35 (1 H, m, 5-H), 6.2 (1 H, br, NH), and 6.6–7.25 (4 H, m, ArH), $J_{3,4}$ = 3, $J_{3,5}$ = 1.5, and $J_{4,5}$ = 12 Hz.

Anal. Calcd for $C_{11}H_{12}N_2O_2$: C, 64.69; H, 5.92; N, 13.72. Found: C, 64.86; H, 5.75; N, 13.79.

From 8a. To a solution of **8a** (144 mg) and $NaBH_4$ (190 mg) in tetrahydrofuran (15 mL) cooled in an ice bath was added dropwise with stirring a solution of methyl chloroformate (120 mg) in tetrahydrofuran (5 mL). After further stirring for 1 h at room temperature, the reaction mixture was evaporated to dryness in vacuo. The residue was dissolved in water (20 mL) and the resulting solution was extracted with methylene chloride. The organic extract was washed with water, dried ($MgSO_4$), and evaporated to dryness. The residue was chromatographed over silica gel using methylene chloride as eluent to give 89 mg (44%) of **18a.**

2-Methoxycarbonyl-5-methyl-2,3-dihydro-1*H*-1,2-benzodiazepine (18c). From 12c. A mixture of **12c** (291 mg), sodium hydride (213 mg), and tetrahydrofuran (15 mL) was treated with a solution of methyl chloroformate (420 mg) under conditions similar to those described for the preparation of **18a.** Similar workup gave **18c:** colorless plates (isopropyl ether); 310 mg (79%); mp 100–101 °C; ν 3280 and 3310 (NH) and 1700 cm^{-1} (C=O); mass spectrum *m/e* 218 (M^+); δ 2.15 (3 H, m, 5-Me), 3.60 (3 H, s, CO_2Me), 4.40 (2 H, m, 3-H), 5.78 (1 H, m, 4-H), 6.3 (1 H, br, NH), and 6.9–7.5 (4 H, m, ArH), $J_{3,4}$ = 4 and $J_{3,5\text{-Me}}$ = 1.5 Hz.

Anal. Calcd for $C_{12}H_{14}N_2O_2$: C, 66.03; H, 6.47; N, 12.84. Found: C, 66.13; H, 6.29; N, 12.66.

From 8c. A solution of **8c** (158 mg) and $NaBH_4$ (190 mg) in tetrahydrofuran was treated with methyl chloroformate (120 mg) according to the conditions used for the preparation of **18a.** Similar workup gave 103 mg (48%) of **18c.**

Reaction of 1*H*-1,2-Benzodiazepines (8a,c) with Sodium Ethoxide. To a solution of **8** (150 mg) in ethanol (15 mL) was added excess sodium ethoxide (70 mg) and the mixture was refluxed for 20 h. After removal of the solvent in vacuo, water (20 mL) was added to the residue and the mixture was extracted with methylene chloride. The extract was dried ($MgSO_4$) and evaporated to dryness. The resulting residue was recrystallized from benzene to give 2-aminoquinoline derivative (**23**) which was shown to be identical with an authentic sample by melting point and mixture melting point comparison.

From **8a:** 2-aminoquinoline (**23a**), 138 mg (92%), mp 134–135 °C.

From **8c:** 2-aminolepidine (**23c**), 131 mg (87%), mp 131–133 °C.

Catalytic Reduction of 1*H*-1,2-Benzodiazepines (8a,c). The diazepine **8** (1.0 mmol) was hydrogenated over 5% Pd/C (150 mg) in

methanol (10 mL) with stirring at room temperature under atmospheric pressure. After uptake of ca. 1 mmol of hydrogen, the reaction was stopped. The reaction mixture, exhibiting a strong odor of ammonia, was evaporated to dryness in vacuo and the residue was purified by short-path distillation under reduced pressure to give the parent quinoline which was characterized as its picrate.

From **8a** (144 mg): quinoline, 121 mg (94%).

From **8c** (158 mg): lepidine, 127 mg (89%).

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Registry No.—**6a,** 59046-19-4; **12a,** 55379-60-7; **12c,** 54507-51-6; **13a,** 59066-24-9; **13c,** 59066-25-0; **14a,** 59066-20-5; **14c,** 59066-21-6; **15a,** 59066-22-7; **15c,** 59066-23-8; **16a,** 59066-26-1; **16c,** 59066-27-2; **17a,** 59066-28-3; **17c,** 59066-29-4; **18a,** 61702-38-3; **18c,** 54507-52-7; **23a,** 580-22-3; **23c,** 27063-27-0; methyl chloroformate, 79-22-1.

References and Notes

(1) Preliminary communication: T. Tsuchiya, J. Kurita, H. Igeta, and V. Snieckus, *J. Chem. Soc., Chem. Commun.*, 640 (1974).
(2) J. Streith and J. M. Cassal, *Angew. Chem., Int. Ed. Engl.*, **7**, 129 (1968).
(3) T. Sasaki, K. Kanematsu, A. Kakehi, I. Ichikawa, and K. Hayakawa, *J. Org. Chem.*, **35**, 426 (1970); T. Sasaki, K. Kanematsu, and A. Kakehi, *Chem. Commun.*, 432 (1969).
(4) A. Balasubramanian, J. M. McIntosh, and V. Snieckus, *J. Org. Chem.*, **35**, 433 (1970); V. Snieckus, *Chem. Commun.*, 831 (1969).
(5) R. A. Abramovitch and T. Takaya, *J. Org. Chem.*, **38**, 3311 (1973).
(6) Reviews: (a) J. M. Cassal, A. Frankowski, J. P. Luttringer, J. Streith, G. Taurand, and B. Willing, *J. Heterocycl. Chem., Suppl.*, **2**, 12 (1974); (b) H.-J. Timpe, *Adv. Heterocycl. Chem.*, **17**, 213 (1974).
(7) For a nonphotochemical route to highly substituted 1*H*-1,2-diazepines, see D. J. Harris, G. Y.-P. Kan, V. Snieckus, and O. Buchardt, *Synthesis*, 603 (1975).
(8) For an organometallic route to simple but diversely N-substituted 1*H*-1,2-diazepines, see D. J. Harris and V. Snieckus, *J. Chem. Soc., Chem. Commun.*, 844 (1976).
(9) T. Shiba, K. Yamane, and H. Kato, *Chem. Commun.*, 1592 (1970).
(10) Y. Tamura, S. Matsugashita, H. Ishibashi, and M. Ikeda, *Tetrahedron*, **29**, 2359 (1973).
(11) T. Tsuchiya, unpublished results, University of Waterloo, 1974.
(12) J. Becher and C. Lohse, *Acta Chem. Scand.*, **26**, 4041 (1972).
(13) Unfortunately, N–N fragmentation is also the exclusive reaction observed in the photolysis of other diverse heterocyclic *N*-ylides; see ref 6b.
(14) F. D. Popp and A. C. Noble, *Adv. Heterocycl. Chem.*, **8**, 21 (1967); J. A. Moore and E. Mitchell, "Heterocyclic Compounds", Vol. 9, R. C. Elderfield, Ed., Wiley, New York, N.Y., 1967, p 224; G. A. Archer and L. H. Sternbach, *Chem. Rev.*, **69**, 747 (1969).
(15) L. H. Sternbach, "The Benzodiazepines", Ravan Press, New York, N.Y., 1973, p 1; L. H. Sternbach, *Angew. Chem., Int. Ed. Engl.*, **10**, 34 (1971); A. V. Bogatskii and S. A. Andronati, *Russ. Chem. Rev. (Engl. Transl.)*, **39**, 1064 (1970).
(16) D. Lloyd, H. McNab, and D. R. Marshall, *Adv. Heterocycl. Chem.*, **17**, 1 (1974).
(17) For a new general route to 2,3-benzodiazepines, see A. A. Reid, J. T. Sharp, H. R. Sood, and P. B. Thorogood, *J. Chem. Soc., Perkin Trans. 1*, 2543 (1973).
(18) R. H. Findlay, J. T. Sharp, and P. B. Thorogood, *Chem. Commun.*, 909 (1970). Recently, 3-substituted 1,2-benzodiazepines have been prepared by cyclization of *o*-vinylphenylhydrazoyl chlorides [L. Garanti, A. Scandroglio, and G. Zecchi, *Tetrahedron Lett.*, 3349 (1975)] and by base or acid treatment of 3*H*-1,2-benzodiazepine *N*-oxides [T. Tsuchiya and J. Kurita, *J. Chem. Soc., Chem. Commun.*, 419 (1976)].
(19) T. Okamoto, M. Hirobe, and T. Yamazaki, *Chem. Pharm. Bull.*, **14**, 512 (1966).
(20) 3*H*-1,2-Benzodiazepines have been prepared from **8**; see J. Kurita and T. Tsuchiya, *J. Chem. Soc., Chem. Commun.*, 936 (1974).
(21) Houben-Weyl, "Methoden der Organischen Chemie", Vol. X/2, H. Muller, Ed., Georg Thieme Verlag, Stuttgart, 1967, p 355.
(22) The NMR spectra of the dihydro- and tetrahydrodiazepines, especially the acetyl derivatives **14–17**, show temperature dependence suggesting conformational isomerism owing to ring inversion phenomena. Further studies are in progress.
(23) M. Nastasi and J. Streith, *Bull. Soc. Chim. Fr.*, 635 (1973); see also ref 6b.
(24) D. J. Harris, M. T. Thomas, V. Snieckus, and E. Klingsberg, *Can. J. Chem.*, **52**, 2805 (1974), and references cited therein.
(25) Further irradiation of the isolated benzodiazepines **8** in neutral or basic solution resulted in recovery of starting materials. Irradiation in acidic solution resulted in gradual decomposition but did not produce quinoline derivatives.
(26) The possibility of the intermediacy of the diaziridine valence isomer **24** instead of **25** is unlikely in light of the photoisomerization of quinoline *N*-oxides [C. Kaneko, *J. Synth. Org. Chem., Jpn.*, **26**, 767 (1968); G. G. Spence, E. C. Taylor, and O. Buchardt, *Chem. Rev.*, **70**, 231 (1970)].
(27) E. Schmitz and R. Ohme, *Chem. Ber.*, **95**, 2012 (1962).
(28) W. P. Utermohlen, Jr., *J. Org. Chem.*, **8**, 544 (1943).
(29) C. E. Kaslow and S. Raymond, *J. Am. Chem. Soc.*, **68**, 1102 (1946).
(30) R. G. Jones, Q. F. Soper, O. K. Behrens, and J. W. Corse, *J. Am. Chem. Soc.*, **70**, 2843 (1948).
(31) L. Bradford, T. J. Elliatt, and F. M. Rowe, *J. Chem. Soc.*, 437 (1947).

Amidrazones. 4.[1] Ylide Syntheses

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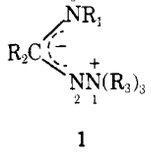
Aminimides derived from imidic acids (**3**) are conveniently prepared by the reaction of molar equivalents of a nitrile, 1,1,1-trimethylhydrazinium chloride (or tosylate), and KO-*t*-Bu in refluxing *t*-BuOH. Alkylation of 1,1,1-trimethyl-2-acetimidoylhydrazinium hydroxide inner salt (**3a**) with MeI and EtI gave N^3-alkylated salts which afforded N^3-substituted ylides (**6**) on neutralization. Reaction of 1,1,1-trimethyl-2-α-methoxybenzylidenehydrazinium tosylate (**11**) with either aniline or benzylamine gave 1,1-dimethyl-2-α-methoxybenzylidenehydrazine (**12**).

This paper summarizes the results of our study of preparative procedures for amidrazone ylides. These compounds, which may also be classified as aminimides[2] derived from imidic acids, are represented by the general structure **1**. The recommended[3] method for numbering the nitrogen atoms in amidrazones is also designated in structure **1** and is used throughout this paper.



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The preparation of ylides of type **1** has received scant attention. Appel and co-workers[4] have reported the preparation of 1,1,1-trimethyl-2-acetimidoylhydrazinium hydroxide inner salt (**3a**) by the addition of the *tert*-butyl alcohol complex of 1,1,1-trimethylhydrazinium hydroxide inner salt (**2**) to acetonitrile. We have previously reported[1] the preparation of ylide **4** by the reaction of **2** (generated in situ) with *N*-phenylbenzimidoyl chloride. Recently, Abramovitch and coworkers[5] obtained pyridinium ylides (**5**) by neutralization of the salts obtained by the reaction of 1-aminopyridinium fluoroborates with aryldiazonium fluoroborates in acetonitrile.

Subsequent to our communication describing the prepa-