potassium, which is in line with the increase in reactivity. Further substantiation of this point can be made by the fact that even with a sodium catalyst, the addition of these two alkylpyridines to ethylene was found to occur at the same rate when the reaction was run at elevated temperatures in an autoclave.[10]

Experimental Section

Synthesis of 4-Alkyl- and Alkenylpyridines.—The 4-substituted pyridines were prepared in liquid ammonia from 4-alkylpyridines, alkyl- or alkenylbromides, and sodium amide according to the general procedure described by Brown and Murphey.[18] Table I lists the products synthesized by this method along with their yields and physical constants.

Competitive Reactions.—The competitive reactions were carried out using the 4-substituted pyridines that had been dried over Linde 5-A Molecular Sieves and immediately redistilled before use. All materials were of >99.5% purity as determined by vpc. The following describes a typical competitive reaction: In a dry box, 0.025 mol of two 4-alkylpyridines were weighed and the alkylpyridines were then transferred to a three-necked flask of 20-ml capacity that had previously been flushed with nitrogen. The flask was equipped with a specially designed drum-shaped high-speed stirrer and a Dry Ice condenser to which a calcium chloride drying tube was attached. *Ca.* 2.5×10^{-3} g-atom of alkali metal was freshly cut and allowed to disperse in the combined alkylpyridines. After the metal was completely dispersed (2–3 hr), 5×10^{-3} mol of freshly distilled isoprene was added. Samples were withdrawn at 0.5-hr intervals for a total of 4 hr and decomposed with methanol. The products were then analyzed by vpc and the ratio of products was determined to calculate the relative rates of reaction. All products were synthesized individually and their physical constants and thermal conductivities were determined. All new products were identified by their nmr, ir, refractive indices, and elemental analyses. The new products are reported in Table III.

Homogeneous Catalyzed Reactions.—All of the needed reactants and solvents were distilled immediately before use. In a dry box, 0.025 mol of two 4-alkylpyridines were weighed and injected into a 30-dram vial containing 15 ml of a 0.5 *M* potassium *t*-butoxide in dimethyl sulfoxide or N-methyl-2-pyrrolidone solution. A rubber septum was inserted and the catalyst solutions were removed to the laboratory, where the reactions were carried out at room temperature following a procedure similar to that of Schriesheim and coworkers for the isomerization of olefins.[19] The samples from these reactions were quenched with methanol and the product ratios were determined by gas chromatography.

Analyses.—The infrared spectra of the pyridines were taken with a Baird Model 4-55 infrared spectrophotometer. Nmr analyses were performed on a Varian Model A-60 spectrophotometer using TMS as an internal standard. Refractive indices were measured on a Zeiss Opton refractometer thermostated at 20 ± 0.1°. Vpc separations and identifications were made using an F & M Model 720 dual-column gas chromatograph equipped with a thermal-conductivity detector using helium as a carrier gas. Separations, product compositions, and relative thermal conductivities were made using either 10% SE-30 silicone gum rubber on 60–80 Gas-Pack WAB columns or 15% Versamid 900 on 60–80 Gas-Pack WAB columns of various lengths and at appropriate temperatures. Elemental analyses were performed by M-H-W Laboratories, Garden City, Mich.

Registry No.—Isoprene, 78-79-5.

(18) H. C. Brown and W. A. Murphey, *J. Amer. Chem. Soc.*, **73**, 3308 (1951).

(19) S. Bank, C. A. Rowe, Jr., A. Schriesheim, and L. A. Naslund, *ibid.*, **89**, 6897 (1967).

The Chemistry of Diazepines. The Photochemical Intramolecular 1,3-Dipolar Cycloaddition of Substituted 1-Ethoxycarbonyliminopyridinium Ylides[1]

TADASHI SASAKI, KEN KANEMATSU, AKIKAZU KAKEHI, IZUO ICHIKAWA, AND KENJI HAYAKAWA

Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University, Chikusa, Nagoya, 464, Japan

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The photochemical intramolecular 1,3-dipolar cycloaddition of substituted 1-ethoxycarbonyliminopyridinium ylides produces 1H-1,2-diazepines. Structural elucidation of the diazepines was accomplished by spectral means and confirmed by Diels–Alder reactions with tetracyanoethylene (TCNE) and catalytic reduction.

Recently, increased attention has been paid to medium-sized cyclic nonbenzenoid heteroaromatic hydrocarbons such as azepines and oxepines.[2] Despite unabated interest in the theoretical and practical aspects of seven-membered heterocyclic chemistry, the diazepines have been incompletely defined, because until recently they have been known only in the form of condensed ring systems.[3] Recently, Streith, *et al.*,[4] reported the first synthesis of simple diazepines by the photochemical rearrangement of 1-ethoxycarbonyliminopyridinium ylides.

Independently, we have also reported the photochemical synthesis of 1H-1,2-diazepines by the same route.[1a] Since the photochemical behaviour of iminopyridinium ylides has not been so extensively investigated as that of aromatic amine oxides,[5] we have examined the solution-phase photolysis of α-, α,α′-, β-, and γ-substituted 1-ethoxycarbonyliminopyridinium ylides. This has led to a study of their catalytic reduction and their Diels–Alder reactions; the latter reactions appear to be the first in the diazepine series.

Results and Discussion

Syntheses of the Pyridinium Ylides.—The pyridinium ylides **3–11** were prepared by the reactions of α- and γ-picoline, 2,4-lutidine, β-picoline, 2,5-, 3,5-, 3,4-, and

(1) (a) For the preliminary communication, see T. Sasaki, K. Kanematsu, and A. Kakehi, *Chem. Commun.*, 432 (1969). (b) Studies on Heteroaromaticity. XXXIII. Part XXXII of this series: T. Sasaki, T. Yoshioka, and Y. Suzuki, *Bull. Chem. Soc. Jap.*, **42**, 3335 (1969).

(2) For a recent brief review in the azepine field, see I. C. Paul, S. M. Johnson, L. A. Paquette, J. H. Barrett, and R. J. Haluska, *J. Amer. Chem. Soc.*, **90**, 5023 (1968); for the oxepin field, see E. Vogel, *et al.*, *Angew. Chem.*, **76**, 535 (1968).

(3) For a recent brief review, see T. Takase, *J. Syn. Org. Chem. Jap.*, **26**, 807 (1968).

(4) J. Streith and J.-M. Cassal, *Angew. Chem.*, **80**, 117 (1968); *Tetrahedron Lett.*, 4541 (1968); J. Streith, A. Blind, J.-M. Cassal, and O. Sigwalt, *Bull. Soc. Chim. Fr.*, 948 (1969).

(5) (a) P. L. Kumler and O. Buchardt, *Chem. Commun.*, 1321 (1968); (b) E. C. Taylor and G. G. Spence, *ibid.*, 1037 (1968); (c) C. Kaneko, I. Yokoe, and S. Yamada, *Tetrahedron*, **25**, 295 (1969).

TABLE I

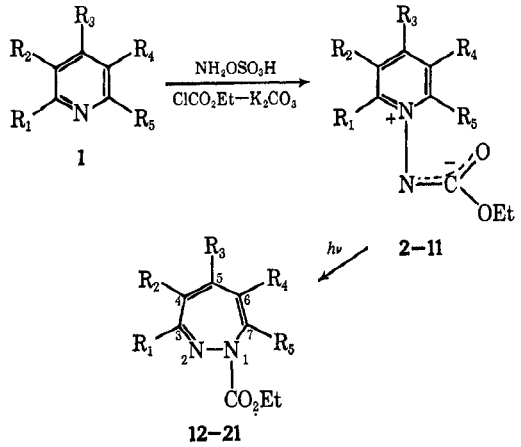
PHOTOISOMERIZATION OF YLIDES

Ylide	Solvent	Irradn time, hr	Method[a]	Diazepine[b]	Yield,[c] %	Mp, °C	$n^{22}D$	Appearance	$\nu_{C=O}^{KBr}$, cm^{-1}	λ_{max}^{EtOH}, mμ (log ε)	
2	Acetone	8	A	12	95		1.5218	Red oil[d]	1710	228 (4.03)	355 (2.38)
	Dioxane	19	B		85						
	Benzene	50	B		44						
3	Acetone	5.5	A	13	80		1.4992	Red oil[d]	1715	220 (3.99)	325 (2.63)
	Dioxane	12	B		43						
4	Acetone	10	A	14	74	51–53		Yellow prisms[e]	1700	220 (3.87)[f]	368 (2.43)[f]
	Dioxane	12	B		53						
5	Benzene	65	B	15	77		1.5203[g]	Orange oil[d]	1707	221 (3.94)	338 (2.63)
6	Acetone	6	A	16	75		1.5200	Yellow oil[d]	1710	218 (4.00)	341 (2.55)
	Benzene	48	B		16						
7	Benzene	43	B	17	51	88–89		Yellow prisms[e]	1695	221 (4.19)	344 (2.50)
	Acetone	6	A		70						
8	Acetone	4	A	18	84	42–43		Yellow prisms[e]	1690	219 (4.05)	350 (2.52)
	Benzene	44	B		44						
9	Acetone	47	B	19	80	89–90		Yellow prisms[e]	1690	217 (3.98)	320 (2.74)
10	Benzene	50	B	20	47		1.5191[g]	Yellow oil[d]	1700	221 (3.95)	339 (2.61)
11	Benzene	45	B	21	76	110		Yellow prisms[e]	1705	220 (3.95)	274 (3.48)[g]
	Acetone	45	B		87						

[a] See Experimental Section. [b] C, H, and N analyses were within ±0.35% for all diazepines (Editor). [c] Based on weight of material isolated from silica gel chromatography. [d] Purification by short-path distillation at 120–180° (0.5–0.6 mm) after separation by column chromatography. [e] Temperature 19°. [f] *n*-Hexane. [g] Shoulder.

2,6-lutidine, and 2,4,6-collidine with hydroxylamine-O-sulfonic acid. These N-ylides showed strong carbonyl absorption in the range 1620–1640 cm^{-1} which shifted to 1730–1750 cm^{-1} in the corresponding picrates. The shift of the carbonyl absorption to lower wavenumber in the ylides may be due to the delocalization of the N lone pair, as shown in Scheme I. The uv spectra

SCHEME I

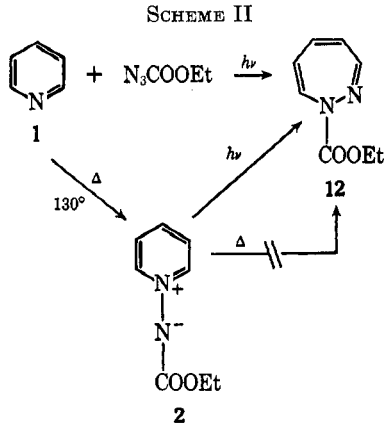


Ylide	Diazepine	R_1	R_2	R_3	R_4	R_5
2	12	H	H	H	H	H
3	13	CH_3	H	H	H	H
4	14	H	H	CH_3	H	H
5	15	CH_3	H	CH_3	H	H
6	16	H	CH_3	H	H	H
7	17	CH_3	H	H	CH_3	H
8	18	H	CH_3	H	CH_3	H
9	19	H	CH_3	CH_3	H	H
10	20	CH_3	H	H	H	CH_3
11	21	CH_3	H	CH_3	H	CH_3

of the ylides contained two maxima, one in the range of 228–243 mμ (log ε 3.3–4.0) and another at 304–318 mμ (log ε 3.0–3.7).

Photolysis of the N-Ylides and Structural Elucidation of the Products.—Irradiation of the ylides 2–11 in aprotic or protic solvents in Pyrex vessels using a 100-W high-pressure mercury lamp (>310 mμ) gave compounds 12–21 in 40–80% yields (Table I). When acetone was used as a solvent and irradiation was carried out with a 300-W high-pressure mercury lamp, the same products were obtained in 80–90% yields, suggesting that the photoisomerization may proceed *via* an excited triplet state. Irradiation of pyridine in acetone or in ethyl acetate in the presence of ethyl azidoformate at room temperature gave 1-ethoxycarbonyl-1H-1,2-diazepine in about 5% yield, while the thermal reaction of pyridine with ethyl azidoformate in ethyl acetate at 130° gave 1-ethoxycarbonyliminopyridinium ylide (2) in a yield of 60%. These findings indicate that 1-ethoxycarbonyl-1H-1,2-diazepine is formed only by the photochemical conversion of the ylide, as shown in Scheme II.

SCHEME II



In the uv spectral comparison between the ylides and their photoproducts 12–21, the decrease in the molecular extinction of longer wavelength absorption and the increase in that of shorter wavelength absorption suggest that the photoproducts exist as nonplanar molecules. The nmr spectra, which show long-range coupling between ring protons and methyl

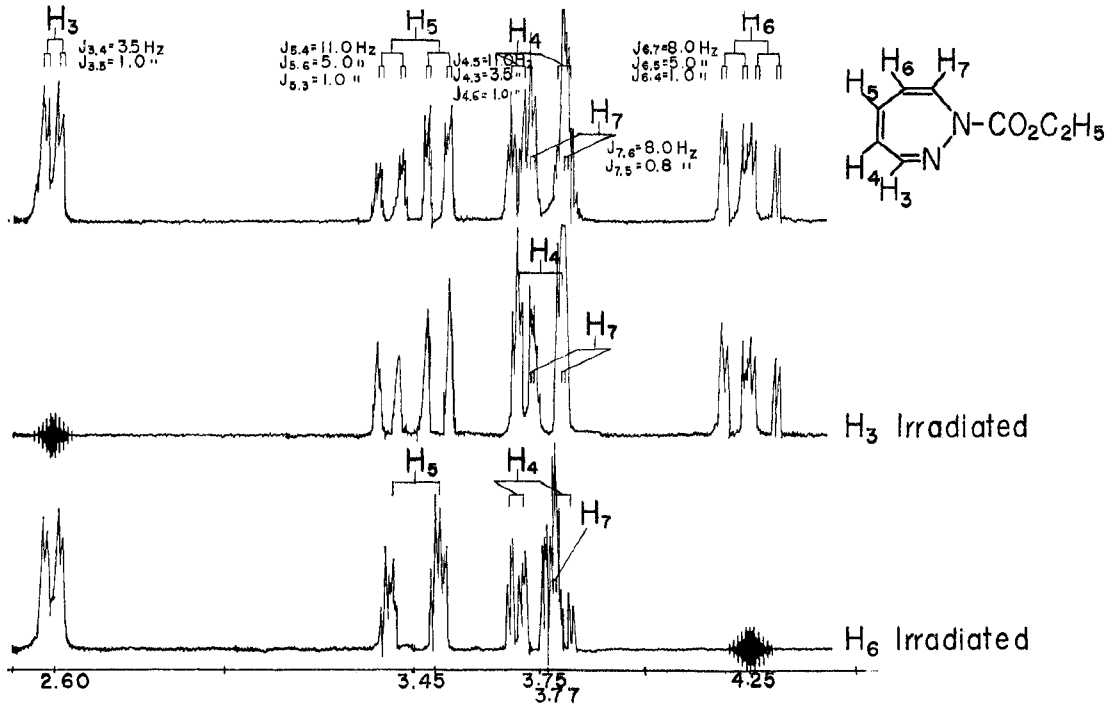


Figure 1.—100-Mc nmr spectra and spin decoupling of vinyl protons of 1-ethoxycarbonyl-1H-1,2-diazepine.

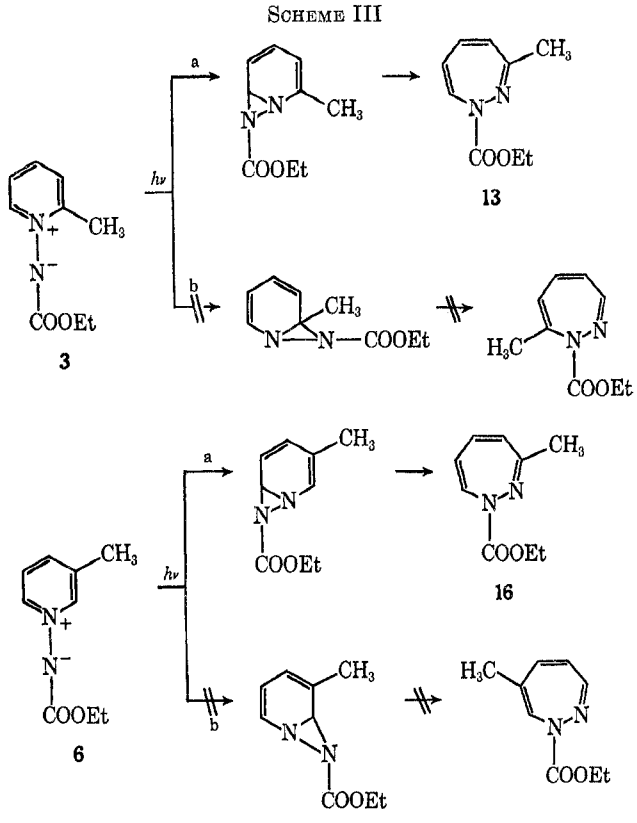
protons, confirm this conclusion. Recent studies on the molecular geometry of derivatives of 1H-azepine in the free and complexed state by X-ray analysis show that the molecule exists in a boat conformation (true polyenes).[2,6]

Structural elucidation of these photoproducts was accomplished by their nmr and mass spectral analyses. The spectral patterns of products **13**–**21** are grossly similar to each other, as seen from Table I. The nmr spectral and spin-decoupling data at 100 MHz for the parent diazepine **12** are shown in Figure 1.

Structural elucidation of the methyl-substituted diazepine derivatives was accomplished by the nmr spectral comparison with that of the parent compound **12**. Thus, compound **13** was assigned to be 1-ethoxycarbonyl-3-methyl-1H-1,2-diazepine from its nmr spectrum on the basis of absence of an absorption of the azomethine proton. Similarly, compound **16** was characterized as 1-ethoxycarbonyl-4-methyl-1H-1,2-diazepine on the basis of the nmr peaks which appeared at τ 2.69 (doublet, 1 H, H_3, J = 1.5 Hz owing to the azomethine proton, with the disposition of the C_3 and C_5 hydrogen atoms permitting long-range coupling), 3.63 (broad doublet, 1 H, H_5), 4.33 (broad triplet, 1 H, H_6), 3.78 (double doublets, 1 H, H_7), and 8.02 (doublet, 3 H, CH_3 at C_4, J = 1.5 Hz) in the ring protons. In particular, when acetone was used as a solvent and irradiation was carried out with a 300-W high-pressure mercury lamp (method A, see Experimental Section), the photoproduct **16** was obtained in 72.8% yield and no isomeric product could be detected by tlc or nmr analysis.

The mechanism by which these diazepines are produced is suggested to involve an intermediate diazabicyclo[4.1.0]heptadiene (Scheme III). On this basis, the results with ylide **3** indicate that initial 1,3-dipolar

SCHEME III



intramolecular cyclization on the less hindered α carbon is favored. This conclusion stands in contrast to results obtained by Okamoto[7a] and recently by us[7b] for the orientation of the ground-state 1,3-dipolar cycloaddition reactions of N-imines and the N-ylides with dipolarophiles (Scheme IV).

The above results are also interesting when com-

(6) X-Ray investigation of the iron–tricarbonyl complex of 1,2-diazepine has also been carried out by Professor Weiss; recent personal communication from Professor J. Streith.

(7) (a) T. Okamoto, M. Hirobe, Y. Tamai, and E. Yabe, *Chem. Pharm. Bull.* (Tokyo), **14**, 506 (1966); (b) T. Sasaki, K. Kanematsu, and Y. Yukimoto, unpublished work.

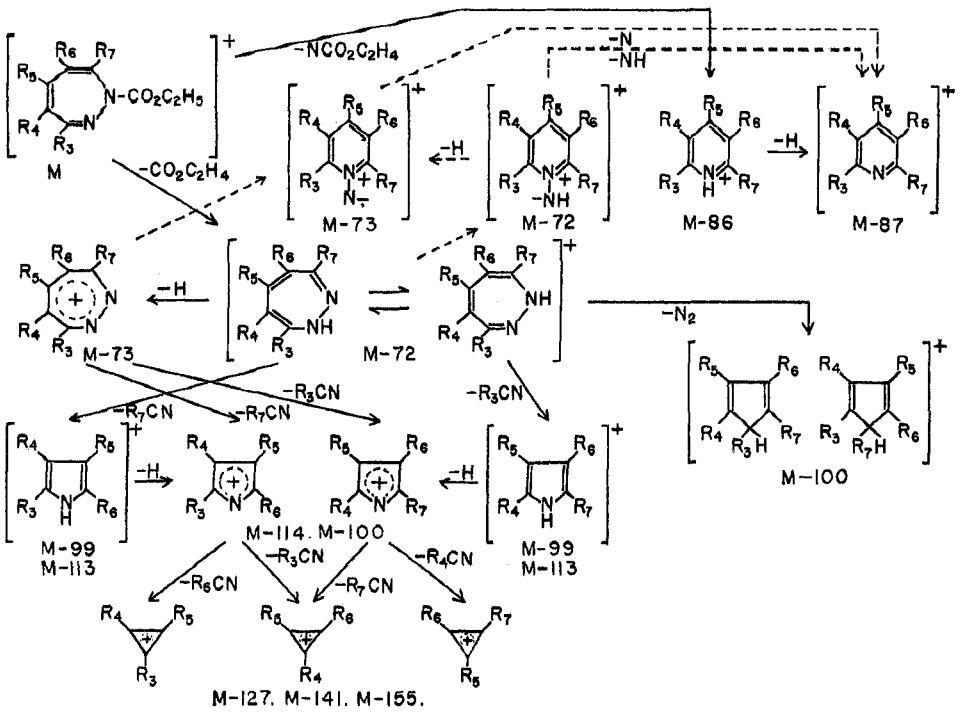
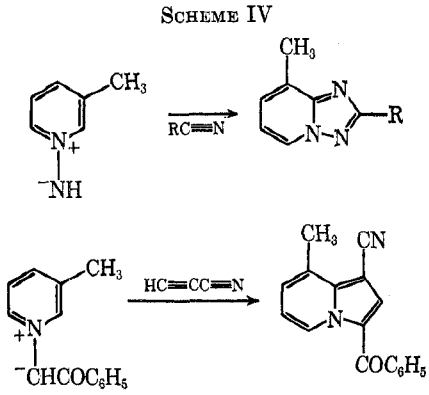
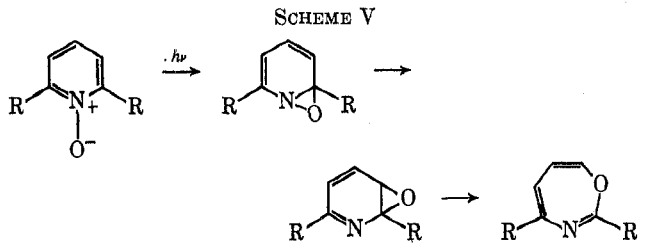


Figure 2.—Fragmentation paths of 1H-1,2-diazepines.

SCHEME IV



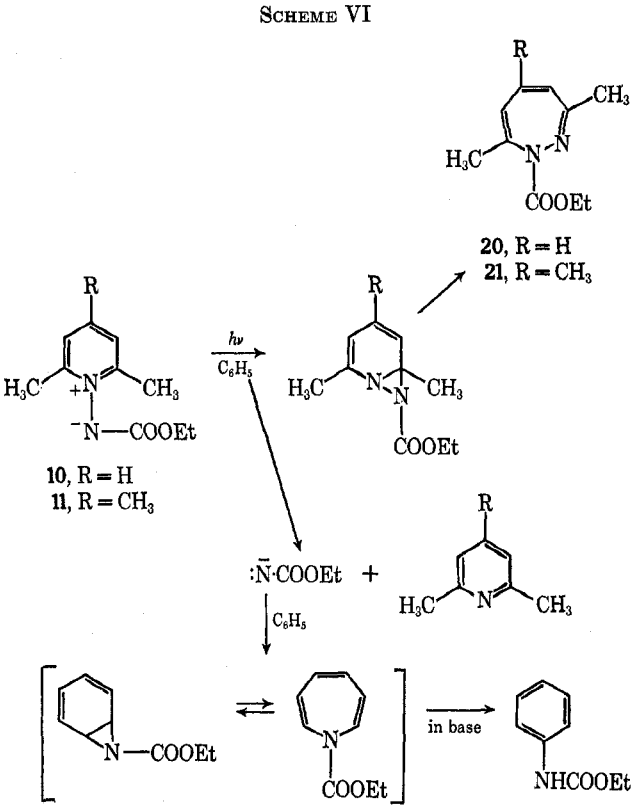
SCHEME V



pared with the formation of the 1,3-oxazepine ring system by photolysis of α,α'-substituted aromatic amine N-oxides and the mechanisms for their formation *via* oxaziridines and oxiranes[5] (Scheme V).

In contrast, in the case of 1-ethoxycarbonylimino derivatives of 2,6-lutidine and 2,4,6-collidine whose α and α' positions are occupied with methyl groups, the 1,3-dipolar intramolecular photocycloaddition reactions in benzene gave 1H-1,2-diazepine compounds **20** and **21**, and phenylurethan in yields of 47, 76, and *ca.* 2–5%, respectively. These findings suggest that ethoxycarbonyl nitrene is formed by photochemical cleavage of α,α'-disubstituted pyridinium ylides, which presumably add to benzene to give N-ethoxycarbonylazepine, which in turn rearranges to phenylurethan, since the azepine is known to rearrange to phenylurethan easily on treatment with base[8] (Scheme VI).

SCHEME VI



The structures of diazepines **20** and **21** were assigned on the basis of their nmr spectra. The nmr spectrum of **20** in deuteriochloroform exhibits signals at τ 3.60, 3.58, 4.15, and 7.82 with relative intensities of 1:1:1:6,

(8) (a) K. Hafner, D. Zinser, and K.-L. Moritz, *Tetrahedron Lett.*, 1733 (1964); (b) W. Lwowski, *Angew. Chem. Intern. Ed. Engl.*, **6**, 897 (1967).

TABLE II

NMR SPECTRA OF DIAZEPINES[a]

Diazepine	Ring protons and ring methyl protons, τ ($CDCl_3$)
13	3.60–3.67 (m, 3 H, H_4, H_5, H_7), 4.31 (dq, 1 H, H_6, $J_{6,7}$ = 7.5 Hz, $J_{6,5}$ = 4.5 Hz, $J_{6,4}$ = 2.0 Hz), 7.89 (s, 3 H, C_3 CH_3)
14	2.73 (br d, 1 H, H_3, $J_{3,4}$ = 3.0 Hz), 3.80 (d, 1 H, H_7, $J_{7,6}$ = 7.2 Hz), 3.95 (m, 1 H, H_4), 4.43 (dd, 1 H, H_6, $J_{6,7}$ = 7.2 Hz, $J_{6,4}$ = 2.0 Hz), 8.08 (d, 3 H, C_5 CH_3, J = 0.5 Hz)
15	3.73 (d, 1 H, H_7, $J_{7,6}$ = 7.5 Hz), 3.88 (br s, 1 H, H_4), 4.49 (dd, 1 H, H_6, $J_{6,7}$ = 7.5 Hz, $J_{6,4}$ = 1.5 Hz), 7.88 (s, 3 H, C_3 CH_3), 8.09 (d, 3 H, C_5 CH_3, J = 1.0 Hz)
16	2.69 (d, 1 H, H_3, $J_{3,5}$ = 1.5 Hz), 3.63 (br d, 1 H, H_5, $J_{5,6}$ = 5.0 Hz), 3.78 (dd, 1 H, H_7, $J_{7,6}$ = 8.0, $J_{7,5}$ = 0.8 Hz), 4.33 (br t, 1 H, H_6), 8.02 (d, 3 H, C_4 CH_3, J = 1.5 Hz)
17	3.63 (br s, 2 H, H_4, H_5), 3.86 (br s, 1 H, H_7), 7.90 (s, 3 H, C_3CH_3), 8.18 (d, 3 H, C_6 CH_3, J = 1.5 Hz)
18	2.89 (s, 1 H, H_3), 3.80 (br s, 1 H, H_5), 4.06 (br s, 1 H, H_7), 8.09 (d, 3 H, C_4 CH_3, J = 1.5 Hz), 8.23 (d, 3 H, C_6 CH_3, J = 1.5 Hz)
19	2.88 (s, 1 H, H_3), 3.84 (d, 1 H, H_7, $J_{7,6}$ = 7.5 Hz), 4.49 (d, 1 H, H_6, $J_{6,7}$ = 7.5 Hz), 8.16 (s, 6 H, C_4 and C_5 CH_3)
20	3.42–3.75 (m, 2 H, H_4, H_5), 4.15 (m, 1 H, H_6), 7.82 (br s, 6 H, C_3 and C_7 CH_3)
21	3.87 (br s, 1 H, H_4), 4.33 (br s, 1 H, H_6), 7.87 (br s, 6 H, C_3 and C_7 CH_3), 8.07 (s, 3 H, C_5 CH_3)

[a] Multiplicity is indicated as follows: s, singlet; d, doublet; dd, double doublet; m, multiplet; t, triplet; q, quartet; br, broad.

while that of **21** appears at τ 3.87, 4.33, 7.87, and 8.07 with relative intensities of 1:1:6:3, as shown in Table II. In addition, chemical-shift values of methyl protons at τ 7.82 ($2CH_3$) in **20**, and 7.87 ($2CH_3$) and 8.07 in **21** could be correlated with those of methyl-substituted 1H-1,2-diazepines **13–19**. Here, isomeric structures, 2-methyl-1H-1,3-diazepine derivatives for these products, are ruled out, since methyl protons attached to C_2 of the 1,3-diazine skeleton would appear at lower fields, as in 2-methylimidazole (τ 7.58).[9]

Mass Spectra of Diazepines.—Since the mass spectra of the diazepines have yet not been reported, the spectra of compounds **12–21** were examined and are characterized by fragment ion peaks at M − 72, M − 73, M − 86, M − 87, M − 99, M − 100, M − 113, M − 114, M − 127, and M − 141, as shown in Table III, and mechanisms for some of these fragmentation processes are proposed in Figure 2. Striking differences were observed in the base peaks between the spectra of the parent diazepine **12** and the methyl-substituted diazepines **13–21**. Base peaks (relative intensity 100) appear at *m/e* 166 (M^+), 67, 80, 29, 80, 29, 29, 29, 28, and 29 in the diazepines **12–21**, respectively. The ions at M − 72 and M − 73 are readily formed from the molecular ion and fragment to M − 99 and M − 113 ions. Apparently, the presence of the methyl group at C_3 or C_7 favors major fragmentation to the pyrrole ions at M − 113 and M − 114. In comparison, compound **12** and the methyl-substituted diazepines at C_4, C_5, and C_6 lose HCN, as observed by appearance of intense peaks at M − 99 and M − 100. The peaks at M − 127 or M − 141 presumably arise from loss of HCN or CH_3CN depending on the substitution pattern.

Diels–Alder Reactions of Diazepines.—For further structural elucidation, the diene reactivity of diazepines **12–21** was studied. The additions of dienophiles to medium-sized ring polyenes such as cycloheptatriene, oxepine, and azepine frequently lead to abnormal products.[10] Thus, cycloheptatriene and dimethyl acetylenedicarboxylate give rise to the tricyclic adduct formally derived from norcaradiene, and, similarly, oxepine and maleic anhydride also give a tricyclic adduct. Recently, a bicyclic 1,4-cycloaddition structure has been assigned to the product for the reaction between 1H-azepines and tetracyanoethylene.[11] More recently, the unusual 1,6-cycloaddition reaction of N-ethoxycarbonylazepine with nitrosobenzene was reported by Murphy and McCarthy.[12] A thermally induced, 6 + 2 cycloaddition is not permissible according to the Hoffmann–Woodward correlations.[13] The diazepines **12–15**, **17**, and **19** proved to be inert to reaction with maleic anhydride, dimethylacetylene dicarboxylate, or diethyl azodicarboxylate, but they did react readily with tetracyanoethylene (TCNE) in benzene solution even at room temperature to give

TABLE III

MASS SPECTRAL FRAGMENTATION IN DIAZEPINES

	Rel intensity									
Ion	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**[a]
M	100	21	5	59	54	44	42	50	53	35[a]
M − 72	96	59	42	40	64	29	31	42	20	19
M − 73	42	31	12	32	33	40	46	33	21	35
M − 86	74	26	20	24	18	12	14	15	13	11
M − 87	39	50	20	27	20	21	17	21	16	11
M − 99	61	60	39	27	79	29	35	36	11	32
M − 100	56	95	100	50	100	49	66	69	12	36
M − 113	17	100	9	30	14	15	11	14	18	48
M − 114	17	41	13	56	8	31	22	22	29	37
M − 127	91	85	69	15	60	14	21	21	4	18
M − 141	...	38	10	48	42	42	30	31	14	24
77	...	92	31	27	19	21	17	20	8	11

[a] In this case, "M" refers to a fragment ion 14 mass units ($-CH_2$) below the molecular ion; the latter had a relative intensity of 4%.

(9) Chemical shifts of methyl protons of imidazoles are given in the literature; see G. S. Reddy, R. T. Hobgood, Jr., and J. H. Goldstein, *J. Amer. Chem. Soc.*, **84**, 336 (1962).

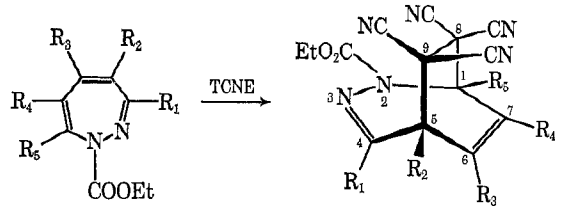
(10) A. S. Kende, P. T. Izzo, and J. E. Lancaster, *ibid.*, **87**, 5044 (1965).

(11) J. H. van den Hende and A. S. Kende, *Chem. Commun.*, 384 (1965).

(12) W. S. Murphy and J. P. McCarthy, *ibid.*, 1155 (1968).

(13) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

TABLE IV



Diazepine	Adduct[a]	R_1	R_2	R_3	R_4	R_5	Temp,[b] °C	Time, hr	Yield, %	Mp, °C
12	22	H	H	H	H	H	80	6	56	148.5–150.5
							25	72	10	
13	23	CH_3	H	H	H	H	25	72	53	177–179
14	24	H	H	CH_3	H	H	80	3	64	161–164
15	25	CH_3	H	CH_3	H	H	25	24	54	210 dec
16	26	H	CH_3	H	H	H	80	5	7	161–163
17	27	CH_3	H	H	CH_3	H	25	24	46	188–189
18	28	H	CH_3	H	CH_3	H	80	6	1.5	167–170
19	29	H	CH_3	CH_3	H	H	25	24	55	164–165

[a] C, H, and N analyses were within ±0.3% for all compounds (Editor). [b] 80° was refluxing benzene temperature; 25° was room temperature.

TABLE V

NMR DATA OF DIELS–ALDER ADDUCTS

Adduct	Ring protons and ring methyl protons, τ (DMSO-d_6)
22	2.98 (d, 1 H, H_4, $J_{4,5}$ = 6.0 Hz), 3.09 (br t, 1 H, H_6, $J_{5,6}$ = 8.0 Hz, $J_{6,7}$ = 8.0 Hz), 3.43 (br t, 1 H, H_7, $J_{7,1}$ = 7.0 Hz, $J_{7,6}$ = 8.0 Hz), 3.94 (dd, 1 H, H_1, $J_{1,7}$ = 7.0 Hz, $J_{1,6}$ = 1.5 Hz), 5.70 (m, 1 H, H_5)
23	3.10 (br t, 1 H, H_6, $J_{6,5}$ = 7.0 Hz, $J_{6,7}$ = 8.0 Hz), 3.41 (br t, 1 H, H_7, $J_{7,6}$ = 8.0 Hz, $J_{7,1}$ = 7.5 Hz), 3.91 (dd, 1 H, H_1, $J_{1,7}$ = 7.5 Hz, $J_{1,6}$ = 1.5 Hz), 5.64 (dd, 1 H, H_5, $J_{5,6}$ = 7.0 Hz, $J_{5,7}$ = 1.0 Hz), 7.88 (s, 3 H, C_4 CH_3)
24	3.00 (d, 1 H, H_4, $J_{4,5}$ = 6.5 Hz), 3.69 (m, 1 H, H_7), 4.06 (d, 1 H, H_1, $J_{1,7}$ = 8.0 Hz), 5.72 (dd, 1 H, H_5, $J_{5,4}$ = 6.5 Hz, $J_{5,7}$ = 1.0 Hz), 7.97 (d, 3 H, C_6 CH_3, J = 1.5 Hz)
25	3.80 (m, 1 H, H_7), 4.03 (d, 1 H, H_1, $J_{1,7}$ = 8.0 Hz), 5.67 (d, 1 H, H_5, $J_{5,7}$ = 2.0 Hz) 7.88 (s, 3 H, C_4 CH_3), 7.95 (d, 3 H, C_6 CH_3, J = 1.5 Hz)
26	3.19 (s, 1 H, H_4), 3.46 (dd, 1 H, H_6, $J_{6,7}$ = 8.0 Hz, $J_{6,1}$ = 1.5 Hz), 3.94 (t, 1 H, H_7, $J_{7,1}$ = 8.0 Hz, $J_{7,6}$ = 8.0 Hz), 4.16 (dd, 1 H, H_1, $J_{1,7}$ = 8.0 Hz, $J_{1,6}$ = 1.5 Hz), 8.27 (s, 3 H, C_5 CH_3)
27	3.48 (m, 1 H, H_6), 4.13 (d, 1 H, H_1, $J_{1,6}$ = 1.5 Hz), 5.73 (d, 1 H, H_5, $J_{5,6}$ = 8.0 Hz), 7.92 (s, 3 H, C_6 CH_3), 7.95 (d, 3 H, C_7 CH_3, J = 1.5 Hz)
28	3.19 (s, 1 H, H_4), 3.72 (m, 1 H, H_6), 4.11 (d, 1 H, H_1, $J_{1,6}$ = 1.5 Hz), 7.99 (d, 3 H, C_7 CH_3, J = 1.5 Hz), 8.33 (s, 3 H, C_5 CH_3)
29	3.22 (s, 1 H, H_4), 3.66 (m, 1 H, H_7), 4.03 (d, 1 H, H_1, $J_{1,7}$ = 8.0 Hz), 7.98 (d, 3 H, C_6 CH_3, J = 1.5 Hz), 8.23 (s, 3 H, C_5 CH_3)

the crystalline 1:1 adducts **22–25**, **27**, and **29**, respectively, in *ca.* 50% yields (Table IV). On the other hand, compounds **16** and **18** reacted with TCNE in benzene only on heating, to afford the corresponding 1:1 adducts **26** and **28** in very low yields, and **20** and **21** were inert to the Diels–Alder reaction. The nmr data are summarized in Table V; spectral assignments were derived by comparison with those of the carbethoxyazepine–tetracyanoethylene adduct.[10,14] Each adduct displayed characteristic ir bands for C=O (1700–1718 cm^{-1}), C≡N (2280 cm^{-1}), and C=C (1620–1638 cm^{-1}). Furthermore, the mass spectra of these adducts showed a molecular ion and strong peak at M − 128 by the loss of a C_6N_4 molecule from the molecular ion; this fragment may arise from a retro Diels–Alder fragmentation. As shown in Table VI, the fragment ion peaks at M − 128 for the adducts, with the exception of **26**, were observed as the base peaks.

(14) Computer-simulated analysis of the 100-MHz nmr spectrum of the adducts is now in progress.

TABLE VI

MASS SPECTRAL FRAGMENTATION IN DIELS–ALDER ADDUCTS

	Rel intensity						
Peak	**22**	**23**	**24**	**25**	**26**	**27**	**29**
Base	166	180	180	194	108	194	194
M	5	15	16	13	24	9	15
M − 128	100	100	100	100	89	100	100
128	28	17	37	74	76	18	27
76[a]	12	7	35	36	37	22	19

[a] A peak at *m/e* 76 might be assignable to the fragment TCNE − 2CN.

Catalytic Hydrogenation of Diazepines.—The diazepines **12–21** were hydrogenated over 5% palladium on carbon at atmospheric pressure. Reduction of compounds **14**, **18**, and **19** gave good yields of the corresponding hexahydro diazepines. These compounds showed ir absorption at 3340 cm^{-1} (NH). On the other hand, in agreement with Streith's observation,[4] the reduction of **12**, **13**, **15–17**, **20**, and **21** gave a mixture of the corresponding hexahydrodiazepines and tetrahydrodiazepines which could not be separated

by fractional distillation. These mixtures showed absorption owing to amino (3340 cm^{-1}) and imino bands (1630–1650 cm^{-1}) in their ir spectra.

Experimental Section[15]

Preparation of 1-Ethoxycarbonyliminopyridinium Ylides (2–11).[16] **1-Ethoxycarbonyliminopyridinium Ylide (2) (Method A).**—A solution of hydroxylamine-O-sulfonic acid (HAS) (5.7 g, 0.05 mol) in water (50 ml) was neutralized with aqueous potassium hydroxide (2.8 g, 0.05 mol, in 10 ml of water). To this solution was added pyridine (20 g, 0.25 mol). The solution was stirred at room temperature for 1 day and then potassium carbonate (6.9 g, 0.05 mol) was added. Water and unreacted pyridine were removed *in vacuo* below 50°. The residue was treated with ethanol (100 ml), and the insoluble precipitate was removed by filtration. To this filtrate ethyl chloroformate (5.4 g, 0.05 mol) and excess potassium carbonate (10 g, 0.07 mol) were added and the resulting solution was stirred at room temperature overnight. After filtration of the solution, the filtrate was concentrated *in vacuo*. Purification by chromatography (alumina) using benzene as an eluent followed by recrystallization from benzene gave **2** (3.4 g, 41%) as colorless crystals, mp 108–109° (lit.[8] mp 109°).

1-Ethoxycarbonylimino-2-methylpyridinium Ylide (3) (Method A).—From 14 g (0.15 mol) of α-picoline there was obtained 7.0 g (78%) of **3** as a pale yellow oil: picrate mp 145–147°, $\nu_{C=O}^{KBr}$ 1750 cm^{-1}.

Anal. Calcd for $C_{15}H_{15}N_5O_9$ (picrate): C, 44.01; H, 3.69; N, 17.11. Found: C, 44.08; H, 3.71; N, 17.20.

When an aqueous solution of HAS and α-picoline was heated at 70–80° in a water bath for 1 hr, only 50% **3** was obtained.

3-Ethoxycarbonylimino-4-methylpyridinium Ylide (4) (Method A).—From 8 g (0.09 mol) of γ-picoline there was obtained 5.4 g (60%) of **4** as yellow crystals: mp 148–151°, $\nu_{C=O}^{KBr}$ 1640 cm^{-1}.

Anal. Calcd for $C_9H_{12}N_2O_2$: C, 59.98; H, 6.71; N, 15.55. Found: C, 59.57; H, 6.82; N, 15.39.

When an aqueous solution of HAS and γ-picoline was heated at 70–80° for 1 hr, only 23% **4** was obtained.

1-Ethoxycarbonylimino-2,4-dimethylpyridinium Ylide (5) (Method A).—From 8 g (0.06 mol) of 2,4-lutidine there was obtained 6.1 g (63%) as a yellow oil, and this compound was used in the following reactions without further purification (one spot by tlc).

1-Ethoxycarbonylimino-3-methylpyridinium Ylide (6) (Method B).—A solution of HAS (5.7 g, 0.05 mol) in water (50 ml) was neutralized with aqueous potassium hydroxide (2.8 g, 0.05 mol, in 10 ml of water) under cooling. To this solution there was added β-picoline (10 g, 0.11 mol). The resulting solution was heated at 70–80° for 3 hr and cooled to room temperature with stirring. Potassium carbonate (6.9 g, 0.05 mol) was then added to the solution. Water and unreacted β-picoline were removed from the solution *in vacuo* below 50°. The residue was treated with chloroform (100 ml), and the insoluble precipitate was removed by filtration. To this filtrate ethyl chloroformate (5.4 g, 0.05 mol) and excess potassium carbonate (10 g, 0.07 mol) were added, and the resulting solution was stirred at room temperature overnight. After filtration the filtrate was concentrated *in vacuo*. Purification by chromatography (alumina) using benzene as an eluent followed by recrystallization from benzene gave **6** (4 g, 44%) as yellow crystals: mp 100–101°, $\nu_{C=O}^{KBr}$ 1630 cm^{-1}; picrate mp 141–143°, $\nu_{C=O}^{KBr}$ 1730 cm^{-1}.

Anal. Calcd for $C_9H_{12}N_2O_2$: C, 59.98; H, 6.71; N, 15.55. Found: C, 59.83; H, 6.81; N, 15.50.

1-Ethoxycarbonyl-2,5-dimethylpyridinium Ylide (7) (Method B).—From 10 g (0.09 mol) of 2,5-lutidine there was obtained 3.3 g (34%) of **7** as hygroscopic yellow flakes after purification by chromatography (silica gel) using benzene as an eluent.

1-Ethoxycarbonyl-3,5-dimethylpyridinium Ylide (8) (Method B).—From 10 g (0.09 mol) of 3,5-lutidine there was obtained 4.4 g (45%) of **8** as colorless crystals: mp 132–134°, $\nu_{C=O}^{KBr}$ 1620 cm^{-1}.

Anal. Calcd for $C_{10}H_{14}N_2O_2$: C, 61.83; H, 7.27; N, 14.42. Found: C, 62.16; H, 7.46; N, 14.61.

1-Ethoxycarbonylimino-3,4-dimethylpyridinium Ylide (9) (Method B).—From 10 g (0.09 mol) of 3,4-lutidine there was obtained 4.5 g (46%) of **9** as yellow-brown crystals: mp 90–91°, $\nu_{C=O}^{KBr}$ 1625 cm^{-1}; picrate mp 154–155°.

Anal. Calcd for $C_{10}H_{14}N_2O_2$: C, 61.83; H, 7.27; N, 14.42. Found: C, 61.27; H, 7.30; N, 14.61.

1-Ethoxycarbonylimino-2,6-dimethylpyridinium Ylide (10) (Method A).—From 7.0 g (0.07 mol) of 2,6-lutidine there was obtained *ca.* 4.1 g (43%) of **10** as hygroscopic yellow needles. This compound was used for photolysis without further purification.

1-Ethoxycarbonylimino-2,4,6-trimethylpyridinium Ylide (11) (Method A).—From 6.0 g (0.06 mol) of 2,4,6-collidine there was obtained 1.5 g (14%) of **11** as colorless crystals, mp 137–140°.

Anal. Calcd for $C_{11}H_{16}N_2O_2$: C, 63.44; H, 7.74; N, 13.49. Found: C, 63.21; H, 7.55; N, 13.44.

However, this compound was not obtained by method B.

Preparation of the Diazepines (12–21). General Method.—A solution of the pyridinium ylides (2–11) in acetone or benzene was irradiated under nitrogen and cooling internally to 20–25° by a cold finger with (A) a 300-W high-pressure mercury lamp (volume 800 ml), or (B) a 100-W high-pressure mercury lamp (volume 400 ml). The solution was then concentrated *in vacuo* and purified by silica gel chromatography. Furthermore, the crude compound was purified by short-path distillation or recrystallization from *n*-hexane. These data are summarized in Table I. The crude products (strong pyridine odor)[17] from photolysis of compounds **11** and/or **12** were chromatographed using benzene as an eluent. After separation of the diazepine compounds **20** and **21**, elution with 10% benzene–chloroform solution yielded *ca.* 2–5% phenylurethan, characterized by identical ir and nmr spectra with those of an authentic sample.

Reactions of Pyridine with Ethyl Azidoformate. A. Photochemical.—A solution of ethyl azidoformate (6.0 g, 0.05 mol) and pyridine (15 g, 0.19 mol) in acetone (250 ml) was irradiated at room temperature for 36 hr by method A. The solution was concentrated *in vacuo*, and the residue was then purified by column chromatography (silica gel). 1-Ethoxycarbonyl-1*H*-1,2-diazepine (**12**)[4] was obtained in 5% yield. However, the yield when ethyl acetate was employed as a solvent instead of acetone was only 2%.

B. Thermal.—A mixture of ethyl azidoformate (2.0 g, 0.017 mol) and pyridine (10 g, 0.13 mol) was heated at 130° for 1 hr in a sealed tube. The reaction mixture was then purified by column chromatography (alumina) and recrystallized from benzene to yield 1.7 g (59%), mp 108–109°. This compound was found to be identical with 1-ethoxycarbonyliminopyridinium ylide (**2**), prepared by the method described above.

Diels–Alder Reactions of Diazepines (22–29).—The general procedure is illustrated for the preparation of **2-ethoxycarbonyl-8,8,9,9-tetracyano-2,3-diazabicyclo[3.2.2]nona-3,6-diene (22).** A solution of **12** (471 mg, 2.8 mmol) and TCNE (354 mg, 2.8 mmol) in dry benzene (30 ml) was refluxed for 6 hr and then cooled. The solution was concentrated *in vacuo* and the residue was recrystallized from ethanol to yield 471 mg (56.5%) of colorless crystals, mp 148.5–150.5°. However, when the reaction was carried out at room temperature for 3 days, the yield was only 9.7%.

Catalytic Hydrogenation of the Diazepines. General Method.—The diazepines in methanol (20 ml) were hydrogenated over 5% Pd–C with stirring at room temperature for 15-hr work-up in the normal way followed by short-path distillation at 70–100° (1–2 mm).

Registry No.—3, 22928-83-2; **3** picrate, 22928-84-3; **4,** 22928-85-4; **6,** 22928-86-5; **6** picrate, 22979-16-4;

(15) The melting points were measured with a Yanagimoto micromelting point apparatus and are uncorrected. Microanalyses were performed on a Yanagimoto C.H.N.-Corder, Model MT-1. The uv spectra were determined with a JASCO Model ORD/UV-5 recorder. The nmr spectra were taken with a Japan Electric Optics Laboratory Co., Ltd., Model JNM-MH-60 nmr spectrometer and with a Varian A-60 recording spectrometer with tetramethylsilane as an internal standard. The chemical shifts are expressed in τ values. The mass spectra were obtained on a Hitachi RMU-D double-focusing mass spectrometer operating at an ionization potential of 70 eV. The solid samples were ionized by electron bombardment after sublimation directly into the electron beam at 100–150°. The ir spectra were taken with a JASCO Model IR-S spectrophotometer. Thin layer chromatography (tlc) was carried out on alumina and silica plates by using benzene–methanol mixtues as developing solvents and iodine as a developing reagent.

(16) R. Gösl and A. Meuwsen, *Chem. Ber.*, **92**, 2521 (1959).

(17) 2,6-Lutidine and 2,4,6-collidine were characterized by glpc comparison with authentic samples.

8, 22928-87-6; **9**, 22979-17-5; **9** picrate, 22928-88-7; **11**, 22979-18-6; **12**, 17377-08-1; **13**, 22928-90-1; **14**, 22928-91-2; **15**, 22928-92-3; **16**, 22928-93-4; **17**, 22928-94-5; **18**, 22928-95-6; **19**, 22928-96-7; **20**, 22928-97-8; **21**, 22928-98-9; **22**, 22958-19-6; **23**, 22958-16-3; **24**, 22958-17-4; **25**, 22958-18-5; **26**, 22929-03-9; **27**, 22979-19-7; **28**, 22929-04-0; **29**, 22929-05-1.

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The Photoisomerization of 1-Iminopyridinium Ylides to 1(1H),2-Diazepines[1]

A. BALASUBRAMANIAN, JOHN M. MCINTOSH, AND VICTOR SNIECKUS

Department of Chemistry, University of Waterloo, Waterloo, Canada

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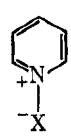
Irradiation of 1-iminopyridinium ylides **2a–f** and **4a** and **b** in methylene chloride solution produces 1(1H),2-diazepines **3a–f** and **5a** and **b** in good yields. The majority of the ylides were best prepared by a new method from the corresponding 1-aminopyridinium iodides and acylating agent. Structure **3a** was deduced from the first-order analysis of its 100-MHz nmr spectrum and was confirmed by its degradation to **9**. The second major photoproduct of the ylide **2d** was shown to be **10** by synthesis. Whereas ylide **2f** rearranged to **3f**, **2g** was photochemically stable; it is suggested that this may be due to large contributions of **13** and **14** to the respective excited states of the two ylides. Compound **15** was stable to irradiation at 3000 and 3500 Å.

Over the years, some of the most intriguing and fruitful heterocyclic chemistry has been associated with the three classes of compounds defined by structure **1** (X = O, CR_2, and NR). Although examples of each class have been known for over 50 years, their chemistry has been explored only relatively recently.[2] The isoelectronic nature of these systems has invited comparison of their ground-state chemical



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reactivity. A similar comparison in their photochemical reactivity is predicted to be instructive,[3] and thus it is not surprising that examples of all three types have been investigated from this point of view. Emphasis has been placed mainly on the irradiation of the readily available[2a] quinoline and pyridine N-oxides,[4-6] but more recently other aromatic amine N-oxides have received attention.[7] On the other hand, a single but interesting example of the pyridinium ylide **1** (X = CR_2) has been irradiated.[8] The corresponding N–N ylides remained unexplored[9] until Streith and Cassal made the important observation[10] that the irradiation of the system **1** (X = NCO_2Et) gives 1-ethoxycarbonyl-1(1H),2-diazepine (*vide infra*). More recently, the French workers[11] and a Japanese group[12] broadened the scope of this photochemical rearrangement. As part of a detailed investigation of the 1-iminopyridinium ylides **1** (X = NR), we have independently irradiated a series of ring-substituted 1-ethoxycarbonylimino- and 1-acetyliminopyridinium ylides **1** (X = NCO_2Et and $NCOCH_3$, respectively) as well as several related single examples. Preliminary observations concerning the system **1** (X = $NCOCH_3$) have appeared.[13] Herein we report on the photochemistry of the ylides **2a–g**, **4a**, **4b**, and **15**. Our results are complementary to the work of Streith[10,11] and Sasaki,[12] but differ in several aspects and extend the scope of the general photochemical synthesis of 1(1H),2-diazepines to include new functionalized derivatives of this largely unexplored class of compounds.[14] Furthermore, in view of the interest in the theoretical aspects of cycloaddition reactions as they apply to the related oxepin and azepine systems,[15] a detailed presentation of the preparation and physical properties of the new 1(1H),2-diazepines would seem to have timely utility. In this connection, it is to be noted that diazepine–tetracyanoethylene adducts have been described by Sasaki very recently.[12]

Whereas many complex 1-phenyliminopyridinium ylides have been known for some time,[16] only a few examples of simple 1-iminopyridinium ylides [com-

(1) Presented at the 52nd Meeting of the Chemical Institute of Canada, Montreal, May 25, 1969.

(2) Summaries follow. (a) **1** (X = O): E. Ochiai, "Aromatic Amine Oxides," Elsevier Publishing Co., Amsterdam, 1967. (b) **1** (X = CR_2): F. Krohnke, *Angew Chem.*, **75**, 317 (1963). (c) **1** (X = NR): T. Okamoto and M. Hirobe, *J. Syn. Org. Chem. Jap.*, **26**, 746 (1968).

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(5) O. Buchardt and P. L. Kumler, *Acta Chem. Scand.*, **23**, 159 (1969), and references cited therein.

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(12) S. Sasaki, K. Kanematsu, and A. Kaheki, *Chem. Commun.*, 432 (1969).

(13) V. Snieckus, *ibid.*, 831 (1969).

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(15) L. A. Paquette, J. H. Barrett, and D. E. Kuhla, *J. Amer. Chem. Soc.*, **91**, 3616 (1969), and references cited therein; see also J. R. Wiseman and B. P. Chong, *Tetrahedron Lett.*, 1619 (1969).

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