Photochemical Synthesis of 1,2-Diazepines. V.[1] Synthesis and Rearrangements of 1,2-Diazepines

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A large-scale synthesis of 1-isopropoxycarbonyl-1,2-diazepine (**17**) was performed using a thin film ultraviolet reactor. 1,5-Disubstituted diazepines **10** and **12** and 1,3,7-trisubstituted 1,2-diazepine **14** have been prepared. Iron tricarbonyl complexes could be obtained only with diazepines which are unsubstituted on the butadiene moiety. Photosensitization of a 1-iminopyridinium ylide of type **1**, using triplet sensitizers, dramatically increased the photolytic N–N bond cleavage, a process which is in competition with the photoisomerization to 1,2-diazepines. A singlet excited state is postulated for the formation of 1,2-diazepines of type **3**. Base-induced ring opening of diazepine **17** led to the cis–cis dienaminonitrile **18** in good yield, whereas its pyrolysis led only to trace amounts of the isomeric dienaminonitriles **19** and **20**. Thermal rearrangement of **17** in *o*-xylene and in acetic acid solution gave 2-isopropoxycarbonylaminopyridine (**21**) and 1-isopropoxycarbonyliminopyridinium ylide (**15**), respectively, and suggests the existence of an equilibrium between diazepine **17** and its valence tautomer **16**. 2,3-Diaza-2-isopropoxycarbonyl[3.2.0]bicycloheptadiene (**22**) was obtained by a photoinduced disrotatory electrocyclic reaction of diazepine **17**.

1,2-Diazepines **3** can be obtained photochemically from 1-iminopyridinium ylides **1** on a preparative scale.[2-5] Several authors have postulated the heteroatomic norcaradienes, 1,7-diaza[4.1.0]bicycloheptadienes (**2**), as intermediates during these photoinduced rearrangements.

According to orbital symmetry conservation rules, 4-π-electron 1,3 dipoles of type A should undergo both thermal and photochemical intramolecular ring closure to the corresponding three-membered ring isomers of type B (see Scheme I). It can be seen that there are two possible modes for both ring closure and ring opening. Since thermodynamic parameters play no role in the Hoffmann–Woodward rules,[6] the direction of the equilibrium cannot be predicted by orbital symmetry considerations. The following examples serve to illustrate this point. Type I: Huisgen[7] showed that the aziridine **4** is much more stable than its isomeric azomethine ylide **5** which can only be formed and trapped when **4** is being heated above 100°. Type II: On the other hand, the dipolar nitrones **6** are much more stable than their isomeric oxaziridine counterparts **7**; thermally it is therefore impossible to ring close nitrones **6** into oxaziridines **7**; only the photoinduced ring closure operates, a reaction which has been discovered by Calvin.[8]

Greene[9] has given a brief account of the relative stability of 1,3-dipolar systems and of their three-membered carbon-, nitrogen-, and oxygen-containing analogs. 1-Iminopyridinium ylides **1**, being aromatic 1,3 dipoles,[10] belong to type II since their photoisomers **2** have no aromatic character and are thermally less stable compounds (*vide infra*). As a matter of fact, refluxing 1-iminopyridinium ylides **1** in solvents of any kind does not lead to the diazepines **3**.

We describe in this paper the synthesis of several 1,2-diazepines as well as a procedure for a large-scale synthesis of such a diazepine. Thermally and photochemically induced, as well as base-catalyzed, rearrangements of 1,2-diazepines reflect the peculiar reactivity of their seven-membered ring.

Synthesis of 1,2-Diazepines.—Although quite a few ring-substituted 1-iminopyridinium ylides have been investigated by Sasaki[3] and by Snieckus[4] since our original findings,[2] it seemed worthwhile to investigate the effect of the nature of the substituent in position 4 upon the photochemical reactivity of the corresponding pyridinium ylide. Unfortunately, the majority of C-4 substituted pyridines do not give the corresponding 1-iminopyridinium ylides. The 4-(4′-chloro)benzoyl-1-carbethoxyiminopyridinium ylide **8** does not lead to the corresponding 1,2-diazepine; instead, one gets photolytic cleavage of the N–N bond. 4-Methyl- and 4-phenylcarbethoxyiminopyridinium ylides **9** and **11** rearrange photochemically in good yields to the corresponding diazepines **10** and **12**; compound **10** has already been synthesized by Sasaki[3b] and by Snieckus.[4b] The iron tricarbonyl complexes, which we had obtained easily with unsubstituted 1,2-diazepines,[2,11] failed to form with **10** and **12**. Apparently substituents attached to the butadiene moiety prevent the formation of such complexes. For example, 1-acetyl-3-methyl-1,2-diazepine (**13**) leads to a tricarbonyl iron complex, whereas 1,7-dimethyl-1,2-diazepine (**14**) does not.

A large-scale synthesis of 1,2-diazepine **17** could be achieved by irradiation of **15** in thiophene-free benzene during 22 hr at 15–18° in a nitrogen atmosphere using a Pyrex circular-irradiating apparatus and high-pressure mercury lamps.[5] After evaporation of the solvent and chromatography on silica gel, a 90.3% yield of crystalline **17**, mp 54–56°, was obtained.

Triplet Photosensitization and Quenching of 1-Iminopyridinium Ylide 15.—In all photoinduced 1,2-diaze-

(1) Presented at the Spring Meeting of the Société Chimique de France, Organic Chemistry Section, Paris, March 13, 1971. Part IV: R. Gleiter, D. Schmidt, and J. Streith, *Helv. Chim. Acta*, in press.

(2) (a) J. Streith and J. M. Cassal, *Angew. Chem.*, **80**, 117 (1968); *Angew. Chem., Int. Ed. Engl.*, **7**, 129 (1968); (b) J. Strieth and J. M. Cassal, *Tetrahedron Lett.*, 4541 (1968); (c) J. Streith and J. M. Cassal, *Bull. Soc. Chim. Fr.*, 2175 (1969).

(3) (a) T. Sasaki, K. Kanematsu, and A. Kakehi, *Chem. Commun.*, 432 (1969); (b) T. Sasaki, K. Kanematsu, A. Kakehi, I. Ichikawa, and K. Hayakawa, *J. Org. Chem.*, **35**, 426 (Z970).

(4) (a) V. Snieckus, *Chem. Commun.*, 831 (1969); (b) A. Balasubramanian, J. M. McIntosh, and V. Snieckus, *J. Org. Chem.*, **35**, 433 (1970).

(5) British Patent 1,212,330; Swiss patent 493,268.

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

(7) R. Huisgen, W. Scheer, G. Szeimies, and R. H. Huber, *Tetrahedron Lett.*, 397 (1966); R. Huisgen, W. Scheer, and R. H. Huber, *J. Amer. Chem. Soc.*, **89**, 1753 (1967).

(8) J. S. Splitter and M. Calvin, *J. Org. Chem.*, **23**, 651 (1958).

(9) F. D. Greene and S. S. Hecht, *ibid.*, **35**, 2482 (1970).

(10) R. Huisgen, *Proc. Chem. Soc.*, 365 (1961).

(11) R. Allmann, *Angew. Chem.*, **82**, 982 (1970).

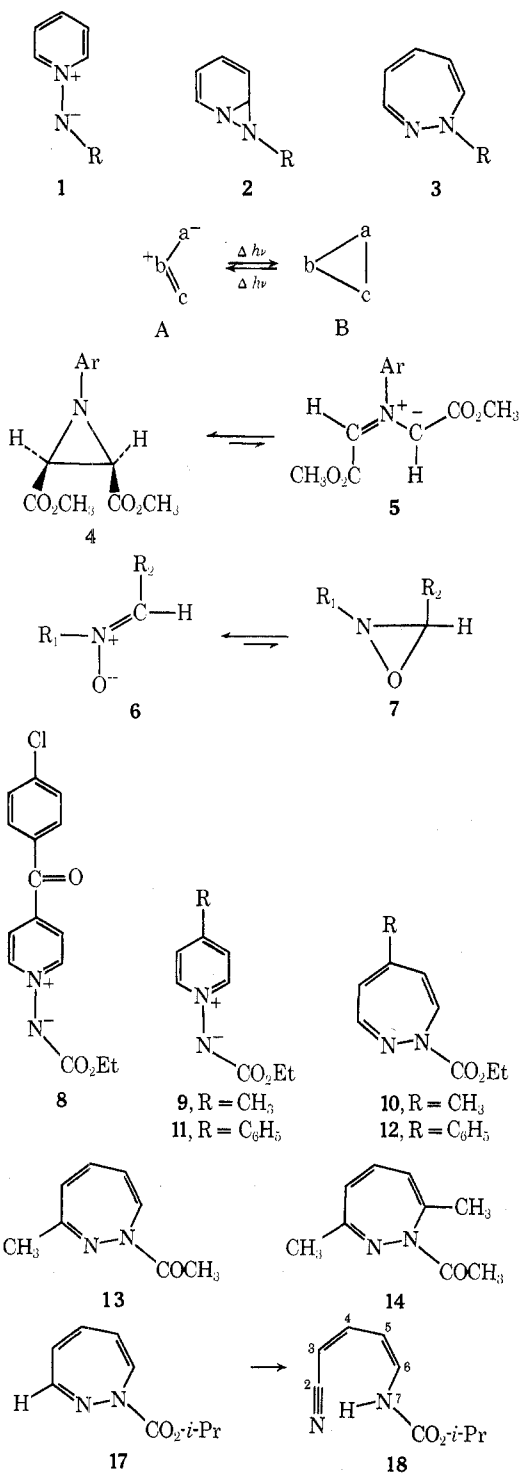
TABLE I

SENSITIZATION EXPERIMENTS OF IMINOPYRIDINIUM YLIDE 15[a]

Tube	Solvent	Sensitizer	λ_{max}, sens	ϵ, sens	E_T, sens	Filter	Atm	Pyridine formed, %
1	CH_2Cl_2					Pyrex	N_2	3.0
2	CH_2Cl_2					Pyrex	O_2	0.5
3	Acetone					Pyrex	N_2	5.0
4	Acetone	Eosine, 50 mg	538	67,000	43	GWV	N_2	58.0
5	CH_2Cl_2	3,4-Benzopyrene, 600 mg	296 320	5,800 2,800	42	Corex	N_2	33.0

[a] Experimental data obtained with a merry-go-round multitube reactor: λ_{max} in nm; E_T values expressed in kcal/mol; 25 mg of iminopyridinium ylide **15** in 15 ml of solvent for each tube.

SCHEME I



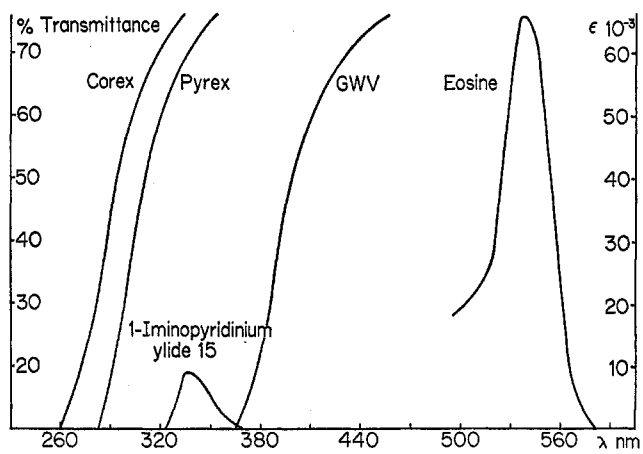


Figure 1.—Transmittance curves of some cut-off glass filters and absorption spectra of pyridinium ylide **15** and of eosine.

pine synthesis, we observed a minor competing process, namely photolytic N–N bond cleavage which gave the parent pyridines and led to nitrenes which reacted further with solvent molecules. When benzene was used as the solvent, formation of 1-substituted azepines had previously been observed.[2] These two competing processes have also been observed with pyridine *N*-oxides and with pyridinium dicyanomethylide.[12] We have recently demonstrated, through sensitization experiments, that photochemical-induced oxygen transfer from pyridine *N*-oxides toward solvent molecules occurs *via* an excited triplet state.[13] Analogously, photolysis of 1-iminopyridinium ylides in the presence of triplet sensitizers led to a notable increase of N–N bond cleavage (see Table I). Experiments have been conducted in a merry-go-round multitube photoreactor[14] under inert atmosphere until complete consumption of the starting material; formation of pyridine has been monitored by vpc. The most extensive cleavage was observed when eosine was used as a sensitizer. In this case the ylide was not excited directly, since a GWV glass cut-off filter was used (see Figure 1 for transmission curves of the various cut-off glass filters used).[15] In the presence of eosine, photolytic bond cleavage played the dominant

(12) J. Streith, A. Blind, J. M. Cassal, and C. Sigwalt, *Bull. Soc. Chim. Fr.*, 948 (1969).

(13) F. Bellamy, L. G. Ruiz-Barragan, and J. Streith, *Chem. Commun.*, 456 (1971).

(14) A Sem-Bruckl photochemical reactor of type PR-20 has been used. The original apparatus has been slightly modified in order to have all tubes under controlled atmosphere.

(15) The GWV cylindrical cut-off glass filter (Glaswerk, Wertheim, Germany) has been kindly provided by Dr. G. Pfundt of The Max Planck Institut für Kohlenforschung, Abteilung Strahlenchemie, Mülheim/Ruhr, Germany.

TABLE II

NMR SPECTRAL DATA OF ISOMERIC DIENAMINONITRILES 18, 19, AND 20 ($CDCl_3$)[a]

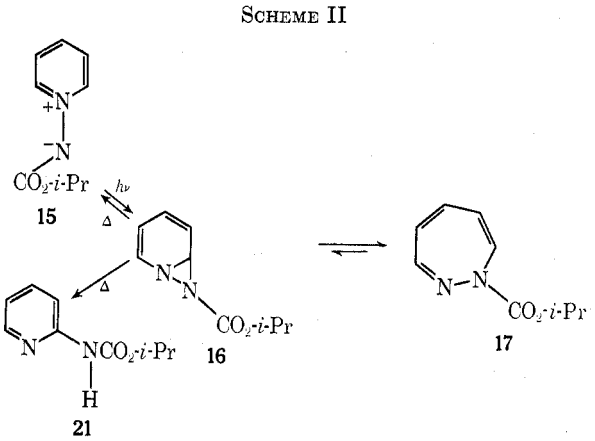
	H-2, τ	H-3, τ	H-4, τ	H-5, τ	H-6, τ
18 (cis–cis), mp 85–90°	4.94 ($J_{2,3}$ = 11.0)[b]	2.88 ($J_{2,3}$ = 11.0, $J_{3,4}$ = 12.0)	4.33 ($J_{4,3}$ = 12.0, $J_{4,5}$ = 9.0)	3.18 ($J_{5,4}$ = 9.0, $J_{5,6}$ = 11.5)	2.29 ($J_{5,6}$ = 11.5)
19 (cis–trans), mp 94–95°	5.0 ($J_{2,3}$ = 10.5)	3.08 ($J_{3,2}$ = 10.5, $J_{3,4}$ = 12)	3.75 ($J_{4,3}$ = 12, $J_{4,5}$ = 13)	2.73 ($J_{5,4}$ = 13, $J_{5,6}$ = 11)	2.3
20 (tran–trans), mp 113–114°	4.73 ($J_{2,3}$ = 16)	2.82 ($J_{3,2}$ = 16, $J_{3,4}$ = 11.5)	4.03 ($J_{4,3}$ = 11.5, $J_{4,5}$ = 14)	2.6 ($J_{5,4}$ = 14)	2.5

[a] Proton H-6 disappears after deuterium exchange. [b] J values in hertz.

role, whereas in the presence of oxygen it was almost totally suppressed. From these data we conclude that a triplet state of somewhat lower energy than 43 Kcal/mol is operative for the photolytic bond cleavage. Therefore, we assume that an excited singlet state gives rise to the isomerization process. A Pariser–Parr–Pople calculation, along with measurements of the absorption spectra of preoriented 1-iminopyridinium ylides **1** in polarized uv light, point to a π–π^* transition for the photoactive absorption band.[1]

Base-Catalyzed and Thermally Induced Rearrangements of Diazepine 17.—As pointed out previously the photochemical synthesis of diazepine **17**, starting with the pyridinium ylide **15**, was supposed to proceed *via* the bicyclic diaziridine **16**. Since valence tautomeric equilibria of, *e.g.*, epoxybenzene–oxepin, have been reported by various groups,[16] it seemed appropriate to investigate whether or not a valence tautomeric equilibrium occurred between diazepine **17** and diaziridine **16** (Scheme II). Nmr spectra taken at

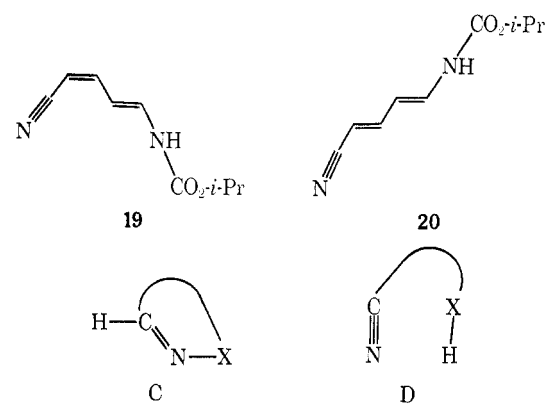
SCHEME II



various temperatures and concentrations of **17** did not permit us to detect the bicyclic tautomer **16**. Potassium hydroxide treatment of **17** led to the formation of 2-aminopyridine, a product which was initially thought to derive directly from the bicyclic diaziridine **16**. The following experiments disprove that hypothesis. Treatment of diazepine **17** in 2-propanol solution with sodium isopropoxide at 20° led, in a few minutes, to the formation of the isomeric dienaminonitrile **18** in 60% yield. The structure of **18** and its cis–cis geometry rest on the nmr data as indicated in Table II, as well as on its ir and uv spectra [ir ($CHCl_3$) ν 3420 (NH), 2210 (C≡N), 1730 (C=O), 1640 and 1590 (C=C), and δ (CH) out of plane at 690 cm^{-1}; uv (Et_2O) λ_{max} 298 nm (ϵ 29,500)].

The facile base-catalyzed ring opening of 1,2-diazepines which bear a hydrogen atom in the C-3 position should be expected, since many heterocyclic systems, having an sp^2 nitrogen attached to an electron-withdrawing heteroatom or group of the type C, open up with base to give nitriles of type D (see Scheme III).[17]

SCHEME III



The presence of a hydrogen atom in position 3 is mandatory. Treatment of 1-acetyl-3-methyl-1,2-diazepine (**13**) with sodium isopropoxide does not lead to any nitrile isomer. Nevertheless, H-3 atoms do not have a pronounced acidic character since no deuterium exchange could be detected by nmr spectroscopy after a prolonged treatment in heavy water. The cis–cis nitrile **18**, when treated once more with sodium isopropoxide for a longer period, gave 2-aminopyridine in good yield. When the diazepine **17** was refluxed in *o*-xylene at 140°, the geometric isomers cis–trans **19** [for nmr data see Table II; ir ν 3420 (NH), 2210 (C≡N), 1730 (C=O), 1640 and 1600 (C=C), δ 985 and 690 cm^{-1} (CH); uv (Et_2O) λ_{max} 290 nm (ϵ 36,700)] and trans–trans **20** [for nmr data see Table II; ir ν 3420 (NH), 2210 (C≡N), 1730 (C=O), δ 985 cm^{-1} (CH); uv (Et_2O) λ_{max} 289 nm (ϵ 27,000)] were obtained in poor yield,

(16) E. Vogel and H. Günther, *Angew. Chem.*, **79**, 429 (1967); *ibid., Int. Ed. Engl.*, **6**, 385 (1967); H. Prinzbach, D. Stusche, and R. Kitzing, *Angew. Chem.*, **82**, 393 (1970); G. Maier, *ibid.*, **79**, 446 (1967); *ibid., Int. Ed. Engl.*, **6**, 402 (1967); M. Görlitz and H. Günther, *Tetrahedron*, **25**, 4467 (1969).

(17) (a) For isoxazoles see R. B. Woodward and R. A. Olofson, *ibid., Suppl.*, **7**, 415 (1966); (b) for isoxazolium salts see R. B. Woodward and D. J. Woodman, *J. Amer. Chem. Soc.*, **88**, 3169 (1966); (c) for isoxazolines see G. W. Moersch, E. L. Wittle, and W. A. Neuklis, *J. Org. Chem.*, **30**, 1272 (1965); (d) for pyrazoles see R. Fusco, V. Rosnati, and G. Pagani, *Tetrahedron Lett.*, 1739 (1966); (e) for pyrazolines see G. L. Closs and H. Heyn, *Tetrahedron*, **22**, 463 (1966); (f) for triazoles see R. M. Carmann, D. J. Brecknell, and H. C. Deeth, *Tetrahedron Lett.*, 4387 (1966).

along with trace amounts of the 2-isopropoxycarbonylaminopyridine (**21**). Pyrolysis of **17**, at 170° under nitrogen atmosphere, led mainly to tar formation. Careful chromatography of the reaction mixture led to the isolation of isomer **21** in 10% yield.

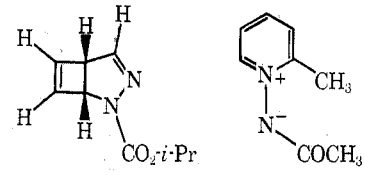
A definite proof for the existence of the diaziridine **16** has been found by refluxing diazepine **17** in acetic acid, a reaction which led to the parent 1-iminopyridinium ylide **15** in 55% yield (see also ref 2c). Thermal rearrangement of diazepine **17** to 2-isopropoxycarbonylaminopyridine (**21**), and even more interestingly to the parent pyridinium ylide **15**, is in good agreement with the 1,7-diaza[4.1.0]bicycloheptadiene intermediate **16** and fits with the original reaction scheme as depicted in Scheme I. For the time being we do not have any rational explanation for the two different pathways when using acetic acid instead of *o*-xylene. The base-catalyzed ring closure of the cis–cis dienaminonitrile **18**, followed by the saponification of the carbamoyl ester which led to the formation of 2-aminopyridine, cannot occur with the isomers **19** and **20** because of their cis–trans and trans–trans geometry, respectively.

Photochemical Isomerization of Diazepine 17.—In view of the thermal rearrangements of 1,2-diazepines which we have just described, it seemed of interest to test whether a photochemically induced rearrangement would also take place. Photoinduced electrocyclic reactions of seven-membered trienes are well known and proceed by a disrotatory course, leading to [3.2.0] bicycloheptadienes. For example, cycloheptatriene, tropones, and tropolones give [3.2.0] bicycloheptatrienes,[18] 2,7-dimethyloxepine gives 1,5-dimethyl-2-oxa[3.2.0]bicycloheptadiene,[18] and 1-carbethoxyazepine leads to 2-carbethoxy-2-aza[3.2.0]bicycloheptadiene.[19] Although earlier attempts to effect photocyclization of diazepine **17** in benzene solution did not succeed, ultraviolet irradiation of **17** in methylene chloride under nitrogen atmosphere, using a high-pressure mercury lamp in a Pyrex reactor, led to a slow disappearance of the starting material and to the formation of a major product. Column chromatography followed by vacuum distillation led to the isolation of a pale yellow photoisomer in 40% yield. The structure of this compound, 2,3-diaza-2-isopropoxycarbonyl[3.2.0]bicycloheptadiene (**22**), has been deduced from its uv, ir, and nmr spectra. The uv spectrum of this photoisomer shows two absorption bands [λ_{max} (EtOH) 249 nm (ϵ 6450) and 316 (25)] tailing out in the visible region. The infrared spectrum agrees with the proposed structure **22**: ν 1720 (C=O), 1680 (C=N), and 1580 cm^{-1} (C=C); δ (CH) out of plane at 730 cm^{-1} characteristic of a cis-disubstituted double bond in a strained ring. Making use of Paquette's interpretation of some [3.2.0] bicycloheptadiene nmr spectra[19,20] and applying the double resonance technique, we could ascertain structure **22** unambiguously (Table III). In a preceding paper we made the statement that the bicyclic photoisomer **22** could not be obtained;[2] as a matter of fact irradiation of **17** in benzene led only to trace amounts of compound **22** which could not be isolated for analytical purposes. Methylene chloride is the solvent of choice in order to obtain photoisomer **22**.

TABLE III

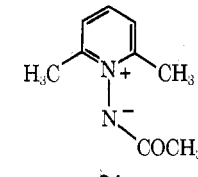
NMR SPECTRUM OF COMPOUND **22** RING PROTONS ($CDCl_3$)

Hydrogen atoms	Chemical shifts in τ units, ppm	Coupling constants, Hz
H-1	5.0	$J_{1,5} = 4.0$, $J_{1,6} = 2.0$
H-4	3.1	$J_{4,5} = 1.4$
H-5	5.92	$J_{5,1} = 4.0$, $J_{5,4} = 1.4$, $J_{5,7} = 1.0$, $J_{5,6} = 0.5$
H-6	3.68	$J_{6,7} = 2.8$, $J_{6,1} = 2.0$, $J_{6,5} = 0.5$
H-7	3.93	$J_{7,6} = 2.8$, $J_{7,5} = 1.0$



22

23



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In addition to the five ring protons reported in Table III, the typical isopropyl bands appear at τ 8.68 (doublet; 6 protons, J = 7 Hz) and 4.95 (multiplet, 1 proton, J = 7 Hz). Compound **22** is thermally stable up to 150°; when heated in diphenyl ether at 170° it reverts quantitatively back to the parent 1,2-diazepine **17**. Since the electrocyclic thermal ring opening of a substituted cyclobutene proceeds by a conrotatory mode, the first diazepine to be formed by such a process should have the enormously strained cis–cis–trans or the cis–trans–cis geometry; such geometries would immediately isomerize to the *all-cis*-diazepine.

Experimental Section

Microanalysis were performed by the Service Central de Microanalyse du C.N.R.S., divisions of Strasbourg and Lyon. Melting points were measured on a Leitz apparatus and are uncorrected. Infrared spectra were determined with Beckman IR-5 A and IR-12 instruments in chloroform solution, unless otherwise indicated. Ultraviolet spectra were recorded on a Beckman DB spectrophotometer. Nuclear magnetic resonance spectra were obtained with Varian A-60A and T-60 spectrometers in deuteriochloroform solution using tetramethylsilane as an internal standard (d = doublet; t = triplet; q = quartet; o = octet; m = multiplet; chemical shifts are given in τ values). Column, thin, and thick layer chromatographies were carried out with silica gel (Merck, Darmstatt). Gas–liquid chromatography was performed with a Carlo-Erba Fractovap apparatus, using a flame ionization detector. Solvents were reagent grade and distilled before use. Photochemical reactions were carried out in a Pyrex glass vessel unless otherwise indicated, reactors being of the Hanovia internal cooling finger type.

Synthesis of 1-Iminopyridinium Ylides. Method A.[21] Synthesis of *N*-Isopropoxycarbonyliminopyridinium Ylide (15).—A solution of 19 g of isopropyl azidoformate in 40 g of pyridine was heated for 70 hr at 100°, the nitrogen evolution being measured with a gas buret. Excess pyridine was removed *in vacuo* and the dark residue was taken up in 1 l. of boiling methanol and treated several times with charcoal. The filtrate was evaporated to dryness and the solid material recrystallized three times from benzene–hexane to yield 16 g of ylide **15**, mp 96°. This procedure was repeated five times in order to get 80 g of ylide **15**: nmr 1.14 (q, 2 H, J = 2 and 7 Hz), 2.34 (m, 3 H, J = 2 and 7 Hz); ir ν 1640 cm^{-1} (C=O); uv (C_6H_6) λ_{max} 344 nm (ϵ 11,600) and 282 (2900).

Anal. Calcd for $C_9H_{12}N_2O_2$: C, 59.98; H, 6.71; N, 15.55. Found: C, 60.2; H, 6.6; N, 15.3.

(18) O. L. Chapman, *Advan. Photochem.*, **1**, 323 (1963).

(19) L. A. Paquette and J. L. Barrett, *J. Amer. Chem. Soc.*, **88**, 1718 (1966).

(20) L. A. Paquette, J. H. Barrett, R. P. Spitz, and R. Pitcher, *ibid.*, **87**, 3417 (1965).

(21) T. Curtius and G. Kraemer, *J. Prakt. Chem.*, **125**, 303 (1930); K. Hafner, D. Zinser, and K. L. Moritz, *Tetrahedron Lett.*, 1733 (1964).

Synthesis of 4-(4′-Chloro)benzoyl-1-carbethoxyiminopyridinium Ylide (8).—Method A was used. A solution of 16 g of ethyl azidoformate in 63 g of 4-(4′-chloro)benzoylpyridine (mp 110°) was heated at 120° for 92 hr. Excess solid 4-(4′-chloro)benzoylpyridine was removed by dissolving it in hexane. After the standard treatment with charcoal, recrystallization from acetone gave 1.3 g of ylide **8** (pale yellow crystals): mp 203–204°; nmr 0.86 (d, 2 H, J = 7 Hz), 2.40 (d, 2 H, J = 7 Hz), 2.4 (m, 4 H); ir ν 1650 cm^{-1} (C=O); uv (C_6H_6) λ_{max} 395 nm (ϵ 17,900).

Anal. Calcd for $C_{15}H_{13}O_3N_2Cl$: C, 59.12; H, 4.30; N, 9.19; Cl, 11.64. Found: C, 59.1; H, 4.3; N, 9.2; Cl, 12.1.

Synthesis of 4-Methyl-1-ethoxycarbonyliminopyridinium Ylide (9).—Method A was used by replacing pyridine with 4-picoline. Three recrystallizations from benzene–hexane gave ylide **9** as colorless crystals: mp 150° (lit.[4b] 151.5–152.5°); uv (EtOH) λ_{max} 243 nm (ϵ 5600) and 314 (5400); uv (C_6H_6) λ_{max} 341 nm (ϵ 9400); yield 6%.

Synthesis of 4-Phenyl-1-ethoxycarbonyliminopyridinium Ylide (11).—Method A was used by replacing pyridine with 4-phenylpyridine. Three recrystallizations from acetone–hexane gave colorless crystals: yield 9%; mp 163° (ylide **11**); nmr 1.28 (d, 2 H, J = 7.5 Hz), 2.36 (d, 2 H, J = 7.5 Hz), 2.5 (m, 5 H); ir ν 1640 cm^{-1} (C=O); uv (C_6H_6) λ_{max} 370 nm (ϵ 19,000).

Anal. Calcd for $C_{14}H_{14}N_2O_2$: C, 69.40; H, 5.83; N, 11.56. Found: C, 69.36; H, 5.76; N, 11.57.

Method B.[22,23] Synthesis of 2-Methyl-1-acetyliminopyridinium Ylide (23).—A stirred solution of 25 g (0.106 mol) of 1-amino-2-picolinium iodide in 250 ml of acetic anhydride was heated for 2 hr at 95°. After 2 days at normal temperature, yellow crystals had formed which were filtered off and washed with diethyl ether. Yield of acetylamino-2-picolinium iodide so obtained was 85%, mp 187°.

A solution of 7 g of iodide in 500 ml of ethanol was run through an ion exchange column IRA 410 which had been pretreated with sodium hydroxide. After removal of ethanol under vacuum and chromatography over silica gel, one obtained 3.4 g of 2-methyl-1-acetyliminopyridinium ylide as hygroscopic needles: yield 90%; uv (C_6H_6) λ_{max} 336 nm (ϵ 5600); picrate mp 166–167° (lit. 167°).

Synthesis of 2,6-Dimethyl-1-acetyliminopyridinium Ylide (24).—Method B was used. Purification was achieved by *in vacuo* sublimation and yielded colorless and hygroscopic crystals, mp 65°, for which no good microanalytical values could be obtained: nmr 2.3 (m, 3 H), 7.33 (s, 6 H), 7.88 (s, 3 H); ir ν 1574 cm^{-1} (C=O); uv (C_6H_6) λ_{max} 280 nm (ϵ 5800) and a shoulder at 340 (1800); mass spectrum m/e 164 (parent ion).

Anal. Calcd for $C_9H_{12}N_2O$: C, 65.83; H, 7.37; N, 17.06. Found: C, 65.7; H, 7.5; N, 17.2.

Photochemical Synthesis of 1-Isopropoxycarbonyl-1,2-diazepine (17). Standard Procedure.—A solution of 3.44 g (0.019 mol) of pyridinium ylide **15** in 900 ml of benzene was irradiated under nitrogen with a Philips HPK 125 mercury high-pressure lamp until the photoactive absorption band of **15** had disappeared. After 12 hr the solvent was removed *in vacuo* and the oily residue was chromatographed over 300 g of silica gel with cyclohexane–ethyl acetate 6:4; 3.1 g of the crystalline diazepine **17** was obtained: mp 55°; yield 90%; nmr 2.60 (q, 1 H, J = 1 and 3 Hz), 3.6 (m, 3 H), 4.30 (m, 1 H); ir ν 1700 (C=O), and 1640 cm^{-1} (C=N); uv (C_6H_6) λ_{max} 370 nm (ϵ 230) and 278 (530).

Anal. Calcd for $C_9H_{12}N_2O_2$: C, 59.98; H, 6.71; N, 15.55. Found: C, 60.2; H, 6.6; N, 15.3.

Large-Scale Synthesis Using a Pyrex Circular-Irradiating Apparatus.—A solution of 27.0 g (0.147 mol) of pyridinium ylide **15** in 6 l. of thiophene-free benzene was irradiated under nitrogen atmosphere during 22 hr at 15–16° in a Pyrex circular-irradiating apparatus with two 2000-W mercury high-pressure lamps. The reaction was followed spectrophotometrically. The dark red solution was evaporated to dryness under reduced pressure at 15–20°. The brown and slowly crystallizing residue weighed 30.3 g. This crude product was filtered over a 10 times excess of silica gel (deactivated by addition of 5% water) using cyclohexane–ethyl acetate 7:3; 24.4 g of the crystalline diazepine **17** was obtained, mp 54–56° (yield 90.3%). This latter procedure was performed at the CIBA-Basel plant by Dr. N. Tarkoy and C. Campana.

Iron Tricarbonyl Complex of Diazepine 17.—To a solution of 500 mg of diazepine **17** (2.8 mmol) in 100 ml of benzene, 1.5 g of $Fe_2(CO)_9$ was added and the resulting suspension was stirred under nitrogen for 4 hr at normal temperature. After filtration of the excess iron carbonyl reagent, the solvent was evaporated *in vacuo*. From the brown residue 400 mg of yellow crystals was isolated by preparative thick layer chromatography (elution with cyclohexane–ethyl acetate 6:4), followed by a vacuum sublimation: mp 106°; yield 45%; nmr 2.99 (d, 1 H, J = 6.5 Hz, H_3), 3.69 (q, 1 H, J = 7 and 2 Hz, H_7), 4.9 (m, 1 H, J = 7 and 2 Hz, H_5), 5.4 (m, 1 H, J = 7 Hz, H_6), 6.65 (q, 1 H, J = 6.5 and 7 Hz, H_4); ir ν 2060, 1990, and 1710 cm^{-1} (C=O).

Anal. Calcd for $C_{12}H_{12}N_2O_5Fe$: C, 45.03; H, 3.78; N, 8.75; Fe, 17.45. Found: C, 45.1; H, 3.8; N, 8.8; Fe, 17.6.

Photochemical Synthesis of 1-Acetyl-3-methyl-1,2-diazepine (13).—The standard procedure was repeated with a solution of 3.5 g of pyridinium ylide **23** (0.023 mol) in 2.6 l. of benzene with a Hanovia 450-W mercury high-pressure lamp. After 12 hr all starting material had disappeared and the solution was evaporated to dryness. The only residue was chromatographed over 300 g of silica gel with cyclohexane–ethyl acetate 6:4 and yielded 2.8 g of diazepine **13** (yield 80%) as an orange oil: nmr 3.53 (m, 3 H), 4.23 (m, 1 H), 7.78 (s, 3 H), 7.86 (s, 3 H); ir ν 1650 cm^{-1} (C=O); uv (C_6H_6) λ_{max} 368 nm (ϵ 270) and 279 (2700); mass spectrum m/e 150 (parent ion).

Anal. Calcd for $C_8H_{10}N_2O$: C, 63.98; H, 6.71; N, 18.65. Found: C, 64.1; H, 6.8; N, 18.8.

Iron Tricarbonyl Complex of Diazepine 13.—The same procedure as above was used with 500 mg of diazepine **13**. Yellow crystals were obtained after chromatography and *in vacuo* sublimation: mp 110°; yield 92%; nmr 3.51 (q, 1 H, J = 6.5 and 2 Hz, H_7), 4.82 (o, 1 H), J = 7, 4.5, and 2 Hz, H_5), 5.32 (o, 1 H, J = 6.5, 4.5, and 1.5, H_6), 6.77 (q, 1 H, J = 7 and 1.5 Hz, H_4); ir ν 2060 and 1675 cm^{-1} (C=O).

Anal. Calcd for $C_{11}H_{10}N_2O_4Fe$: C, 45.50; H, 3.47; N, 9.66; Fe, 19.25. Found: C, 45.8; H, 3.5; N, 9.6; Fe, 19.4.

Photochemical Synthesis of 1-Acetyl-3,7-dimethyl-1,2-diazepine (14).—The standard procedure was repeated with 1.5 g of pyridinium ylide **24** in 2.75 l. of benzene using a Hanovia 450-W mercury high-pressure lamp for 3 hr and yielded 312 mg of diazepine **14** as a red oil: yield 21%; nmr 3.5 (m, 2 H), 4.0 (m, 1 H), 7.78 (s, 3 H), 7.80 (s, 3 H), 7.82 (s, 3 H); ir ν 1660 cm^{-1} (C=O); uv (C_6H_6) λ_{max} 356 nm (ϵ 350) and 279 (1900).

Anal. Calcd for $C_9H_{12}N_2O$: C, 65.83; H, 7.37; N, 17.06. Found: C, 65.6; H, 7.4; N, 16.7.

Photochemical Synthesis of 1-Carbethoxy-5-methyl-1,2-diazepine (10).—The standard procedure was repeated with 1 g of pyridinium ylide **9** (5.6 mmol) in 1.4 l. of benzene using a Hanovia 450-W mercury high-pressure lamp for 6 hr. Diazepine **10** (750 mg) was isolated as yellow crystals, mp 52° (lit.[3b,4b] 51–53°).

Photochemical Synthesis of 1-Carbethoxy-5-phenyl-1,2-diazepine (12).—The standard procedure was repeated with 190 mg (0.78 mmol) of pyridinium ylide **11** in 25 ml of benzene, using a Philips HPK 125 mercury high-pressure lamp for 10 hr, and yielded 171 mg of diazepine **12** as orange crystals after chromatography and recrystallization: mp 86–87°; nmr 2.43 (d, 1 H, J = 4 Hz), 2.50 (s, 5 H), 3.43 (q, 1 H, J = 4 and 2 Hz), 3.51 (d, 1 H, J = 7 Hz), 3.97 (q, 1 H, 7 and 2 Hz); ir ν 1715 cm^{-1} (C=O); uv (C_6H_6) λ_{max} 375 nm (ϵ 510) and 279 (12,000); mass spectrum m/e 242 (parent ion).

Anal. Calcd for $C_{14}H_{14}N_2O_2$: C, 69.40; H, 5.83; N, 11.56. Found: C, 69.5; H, 5.9; N, 11.4.

Thermal Rearrangements of 1-Isopropoxycarbonyl-1,2-diazepine (17). Reflux in o-Xylene.—A 2-g solution of diazepine **17** (11.1 mmol) in 50 ml of *o*-xylene was refluxed for 17 hr at 144°. The reaction was followed by tlc. After removal of the solvent *in vacuo*, chromatography of the residue over 350 g of silica gel (elution with cyclohexane–ethyl acetate 5:5) led to the isolation of products with the following order of elution: 1.2 g of diazepine **17**; 500 mg of a mixture of nonidentified compounds; 120 mg of a colorless compound A, mp 94–95°; 60 mg of a colorless compound B, mp 113–114°; 40 mg of a third colorless compound C, mp 80–81°.

Compound A was identified as cis–trans dienaminonitrile **19**. For spectral data see Table II and data previously given for **19**; mass spectrum m/e 180 (parent ion).

Anal. Calcd for $C_9H_{12}O_2N_2$: C, 59.98; H, 6.71; N, 15.55. Found: C, 60.0; H, 6.7; N, 15.3.

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

(23) (a) T. Okamoto, M. Hirobe, C. Mizushima, and A. Ohsawa, *Yakugaku Zasshi*, **83**, 308 (1963); *Chem. Abstr.*, **59**, 5103*b* (1963); (b) T. Okamoto, M. Hirobe, and A. Osawa, *Chem. Pharm. Bull. Jap.*, **14**, 518 (1966).

Compound B was identified as trans–trans dienaminonitrile **20**. For spectral data see Table II and data previously given for **20**; mass spectrum *m/e* 180 (parent ion).

Anal. Calcd for $C_9H_{12}O_2N_2$: C, 59.98; H, 6.71; N, 15.55. Found: C, 59.5; H, 6.7; N, 15.2.

Compound C was identified with 2-isopropoxycarbonylaminopyridine (**21**). **21** was synthesized as follows. To a solution of 2 g of 2-aminopyridine (0.021 mol) in 100 ml of isopropyl alcohol, 4 g of sodium bicarbonate (0.048 mol) and 3.7 g of isopropyl chloroformate were added successively. Once the CO_2 evolution had ceased the solution was refluxed for 16 hr. Evaporation to dryness followed by a chromatography over silica gel with cyclohexane–ethyl acetate 4:1 led to the isolation of 1.6 g of crystals identical in all respects with compound C (melting point, mixture melting point, and ir and uv spectra).

Anal. Calcd for $C_9H_{12}O_2N_2$: C, 59.98; H, 6.71; N, 15.55. Found: C, 60.3; H, 6.7; N, 15.6.

Reflux in Acetic Acid.—A solution of 300 mg of diazepine **17** (1.67 mmol) in 5 ml of acetic acid was refluxed for 1 hr under nitrogen. After evaporation to dryness the residue was treated several times with ether in order to eliminate the remaining diazepine. Thick layer chromatography over neutral alumina with ethyl acetate yielded pyridinium ylide **15** (165 mg, yield 55%), mp 96°.

Pyrolysis at 170°.—A 2-g batch of diazepine **17** was pyrolyzed under nitrogen for 20 min at 170°. The black residue was chromatographed over silica gel thick layer; 206 mg of 2-isopropoxycarbonylaminopyridine (**21**) was obtained (yield 10%).

Treatment of 1-Isopropoxycarbonyl-1,2-diazepine (17) with Sodium Isopropoxide.—To a solution of 3 g (16.7 mmol) of diazepine **17** in 60 ml of isopropyl alcohol was slowly added a solution of sodium isopropoxide (30 mmol) in 150 ml of isopropyl alcohol at room temperature. After a few minutes a change in color had occurred and aqueous hydrochloric acid was added until neutralization. The solvent was removed *in vacuo* at a temperature not exceeding 45° after the usual extraction procedure, and the residue was chromatographed over 300 g of neutral alumina with cyclohexane–ethyl acetate 4:1. Besides 157 mg of 2-aminopyridine, mp 57°, 1.8 g of colorless crystals (yield 60%) was isolated and identified as cis–cis dienaminonitrile **18**, mp 85–90°. For spectral data see data previously given for **18**; mass spectrum *m/e* 180 (parent ion).

Anal. Calcd for $C_9H_{12}O_2N_2$: C, 59.98; H, 6.71; N, 15.55. Found: C, 59.9; H, 6.4; N, 15.5.

Base-Induced Ring Closure of Cis–Cis Dienaminonitrile 18.—To a solution of 200 mg of dienaminonitrile **18** (1.11 mmol) in 20 ml of isopropyl alcohol, a solution of sodium isopropoxide (2 mmol) in isopropyl alcohol was added. After 15 min at room temperature the starting material had disappeared. Removal of the solvent *in vacuo* and thick layer chromatography over neutral alumina yielded 57 mg of 2-aminopyridine (yield 55%).

Sensitization and Quenching of the 1-Iminopyridinium Ylide 15 Triplet State.—A Sem-Bruckl merry-go-round multitube photoreactor was used.[14] The 15-ml quartz tubes were surrounded by various cylindrical cut-off glass filters. A Philips HPK 125 mercury high-pressure lamp, placed into a water-cooled quartz jacket, was positioned along the rotation axis of the apparatus. Each tube was placed under controlled atmosphere and was stirred magnetically. Acetone and methylene chloride were used as solvents, tubes being irradiated until complete disappearance of the starting material (control by tlc). Pyridine formation was determined quantitatively by vpc (Carbowax 20M on 10% Chromosorb W). For quantitative results see Table I.

Electrocyclic Photoisomerization of 1-Isopropoxycarbonyl-1,2-diazepine (17) into 2-Isopropoxycarbonyl-2,3-diaza[3.2.0]bicycloheptadiene (22).—A 2-g solution of diazepine **17** (11 mmol) in 1 l. of methylene chloride was irradiated according to the standard procedure under nitrogen atmosphere using a Hanovia 450-W mercury high-pressure lamp. After 92 hr diazepine **17** had disappeared; formation of a major product was detected by tlc. Evaporation of the solvent *in vacuo*, followed by a chromatography of the residue over 200 g of silica gel with cyclohexane–ethyl acetate 1:1, yielded a yellow liquid which was distilled under vacuum (70°, 0.2 mm), overall yield 40%. This yellow and viscous oil was identified as being 2-isopropoxycarbonyl-1,2-diaza[3.2.0]bicycloheptadiene (**22**). For spectroscopic data see Table III and the data previously given for **22**; mass spectrum *m/e* 180 (parent ion).

Anal. Calcd for $C_9H_{12}N_2O_2$: C, 59.98; H, 6.71; N, 15.55. Found: C, 60.1; H, 6.7; N, 15.4.

Thermal Rearrangement of 2-Isopropoxycarbonyl-2,3-diaza-[3.2.0]bicycloheptadiene (22) into 1-Isopropoxycarbonyl-1,2-diazepine (17).—A solution of 50 mg of photoisomer **22** in 10 ml of diphenyl ether was heated during 18 hr under nitrogen at 135°; no reaction occurred. At 180° a quantitative reaction leading to a single product occurred after 2 hr. Chromatography of the preceding solution over silica gel with cyclohexane–ethyl acetate 1:1 yielded 45 mg of 1-isopropoxycarbonyl-1,2-diazepine (**17**) (melting point, mixture melting point; ir and tlc data identical with an authentic sample of **17**).

Registry No.—**8,** 31020-21-0; **9,** 22928-85-4; **11,** 31020-23-2; **12,** 31020-24-3; **13,** 23882-04-4; **13** iron tricarbonyl complex, 12524-67-3; **14,** 23922-05-6; **15,** 31020-27-6; **17,** 31020-28-7; **17** iron tricarbonyl complex, 12524-66-2; **18,** 31020-29-8; **19,** 31020-30-1; **20,** 31020-31-2; **21,** 31020-32-3; **22,** 31020-33-4; **23,** 7584-27-2; **24,** 31020-35-6; acetylamino-2-picolinium iodide, 7583-98-4; 2-aminopyridine, 504-29-0.

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