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.

Acknowledgment.—The authors are indebted to Dr. T. Nishida of the Nichiden Varian Co., Ltd., for the spin-decoupling experiments.

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

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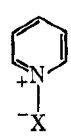
Received July 28, 1969

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).

(3) Such a comparison may be generalized; see H. Izawa, P. de Mayo, and T. Tabata, *Can. J. Chem.*, **47**, 51 (1969).

(4) (a) C. Kaneko, *J. Syn. Org. Chem. Jap.*, **26**, 758 (1968); (b) M. Ishikawa, C. Kaneko, I. Yokoe, and S. Yamada, *Tetrahedron*, **25**, 295 (1969), and references cited therein.

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

(6) For a comprehensive list of references, see E. C. Taylor and G. G. Spence, *Chem. Commun.*, 1037 (1968).

(7) W. E. Dolbier, Jr., and W. M. Williams, *J. Amer. Chem. Soc.*, **91**, 2818 (1969), and references cited therein.

(8) J. Streith and J.-M. Cassal, *C. R. Acad. Sci., Paris, Ser. C.*, **264**, 1307 (1967); J. Streith, B. Danner, and C. Sigwalt, *Chem. Commun.*, 979 (1967).

(9) The photolyses of several unusual N–N ylides have been reported: P. de Mayo and J. J. Ryan, *Tetrahedron Lett.*, 827 (1967); P. de Mayo and J. J. Ryan, *Can. J. Chem.*, **45**, 2177 (1967); M. G. Pleiss and J. A. Moore, *J. Amer. Chem. Soc.*, **90**, 4738 (1968).

(10) J. Streith and J.-M. Cassal, *Angew. Chem. Intern. Ed. Engl.*, **7**, 129 (1968); experimental details have appeared recently in J. Streith, A. Blind, J.-M. Cassal, and C. Sigwalt, *Bull. Soc. Chim. Fr.*, 948 (1969).

(11) J. Streith and J.-M. Cassal, *Tetrahedron Lett.*, 4541 (1968); J. Streith and J.-M. Cassal, *Bull. Soc. Chim. Fr.*, 2175 (1969).

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

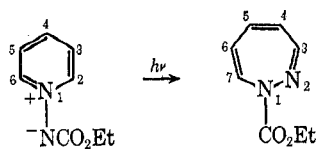
(13) V. Snieckus, *ibid.*, 831 (1969).

(14) Very few simple examples of the 1,2-diazepine system are known: F. D. Popp and A. C. Noble, *Advan. Heterocycl. Chem.*, **8**, 22 (1967); J. A. Moore and E. Mitchell, "Heterocyclic Compounds," Vol. 9, R. C. Elderfield, Ed., John Wiley & Sons, Inc., New York, N. Y., 1967, p 294 ff; see also T. Takase, *J. Syn. Org. Chem. Jap.*, **26**, 807 (1968).

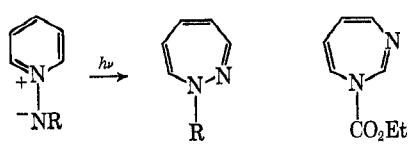
(15) L. A. Paquette, J. H. Barrett, and D. E. Kuhla, *J. Amer. Chem. Soc.*, **91**, 3616 (1969), and references cited therein; see also J. R. Wiseman and B. P. Chong, *Tetrahedron Lett.*, 1619 (1969).

(16) K. Dimroth, G. Arnoldy, S. von Eicken, and G. Schiffler, *Justus Liebigs Ann. Chem.*, **604**, 221 (1957), and references cited therein.

pounds **1** (X = $NCOCH_3$) and ring-methylated derivatives,[17] **2a**,[18] **4a**,[19] and **4b**[20]] have been reported. In our attempts to prepare a series of simple ylides, application of the methods of Hafner[18] or Curtius[20] gave uniformly poor yields (Table I, method A), and a new procedure was therefore devised. Treatment of substituted 1-aminopyridinium iodides with potassium hydroxide and ethyl chloroformate produced the corresponding ylides **2a–f** in fair to good yields (Table I, method B). With the exception of the precursor to **2f**, the 1-aminopyridinium iodide derivatives were prepared by a literature method.[21] Ylide **2g** could not be synthesized by this procedure but was obtained *via* the Hafner route.[18] The ylides **4a** and **4b** were readily available from the reaction of 1-aminopyridinium iodide with benzoyl chloride and *p*-toluenesulfonyl chloride, respectively (see Experimental Section).



2a, unsubstituted — **3a**, unsubstituted
b, 2-CH_3 — **b**, 3-CH_3
c, 4-CH_3 — **c**, 5-CH_3
d, 3,5-diCH_3 — **d**, 4,6-diCH_3
e, 2,6-diCH_3 — **e**, 3,7-diCH_3
f, 4-$N(CH_3)_2$ — **f**, 5-$N(CH_3)_2$
g, 4-CO_2Et



4a, R = COPh — **5a**, R = COPh — **6**
b, R = $SO_2C_7H_7$ — **b**, R = $SO_2C_7H_7$

The ir, uv, and nmr spectral data for these compounds are summarized in Tables I and II. Carbonyl absorption at 1630–1640 cm^{-1} in the infrared spectrum and ultraviolet maxima at >310 mμ were diagnostic for the characterization of these ylides and agreed with earlier reports of these properties for the related 1-acetyliminopyridinium systems.[17]

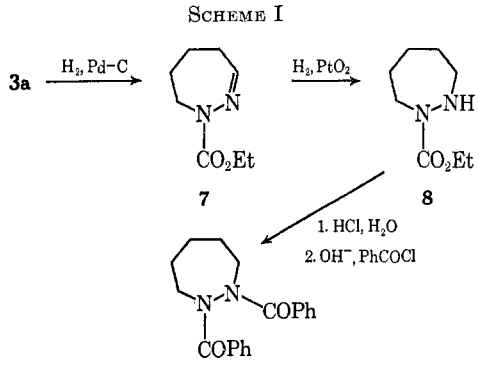
Photolysis of **2a** in methylene chloride solution at 3500 Å gave a single isomeric product. At this stage of our work, Streith and Cassal reported their preliminary results[10] and assigned structure **3a** to the photoproduct on the basis of spectral properties. Although our spectral data were in reasonable agreement with those presented by Streith, we had already undertaken a course of action initiated by the following analysis. As mentioned previously, a photochemical analogy between **2a** and the pyridine N-oxides could be drawn, and on this basis several possible structures could be formulated for the photoproduct. The spectral properties of the photoproduct, in particular the nmr spectrum, ruled out most of these and left structures **3a** and **6** for consideration.[22] The observed low-field signal at τ 2.56 could be associated with an azomethine proton in either of the two structures, but its multiplicity and coupling constants strongly favored the 1(1H),2-diazepine structure **3a** for the photoproduct. Determination of the 100-MHz nmr spectrum with appropriate decoupling experiments led to a complete first-order analysis in terms of the structure **3a** (Table III).[23] Confirmation was obtained by degradation of **3a** to the known[24] 1,2-dibenzoyl-1,2-hexahydrodiazepine **9** shown in Scheme I.

TABLE I
PREPARATION AND INFRARED AND ULTRAVIOLET SPECTRA OF PYRIDINIUM YLIDES

Ylide	Prepn method[a]	Yield, %	$\nu_{max}^{CHCl_3}$, cm^{-1} [b]	λ_{max}^{MeOH}, mμ (ϵ)[c]
2a	A	17	1641	228 (6600)
	B	48	1606	315 (5530)
2b	A	0	1632	242 (5300)
	B	47[d]	1610	270 (sh, 3810)
				277 (sh, 3350)
				310 (2050)
2c	A	3	1638	230 (5490)
	B	29	1620	245 (5880)
				312 (4620)
2d	A	9	1633	233 (5630)
	B	51	1611	282 (3420)
				311 (3670)
2e	B	49[d]	1632	243 (4960)
			1614	274 (4940)
				281 (sh, 4320)
				305 (sh, 970)
2f	B	53	1655	298 (23,460)
			1565	
2g	A	1	1720	231 (sh, 6460)
			1640	274 (4340)
			1610	350 (9900)
4a	B	83	1621 (w)	233 (13,530)
			1592	317 (4850)
			1551	
4b	A	14	1601 (w)	240 (14,000)
	B	57		317 (2180)

[a] See Experimental Section. [b] w = weak. [c] Liquid samples were handled by microtechniques described in P. L. Kirk, "Ultramicroanalysis," John Wiley & Sons, Inc., New York, N. Y., 1950. sh = shoulder. [d] Yield of picrate derivative.

SCHEME I



(17) T. Okamoto, M. Hirobe, and A. Ohsawa, *Chem. Pharm. Bull.* (Tokyo), **14**, 518 (1966).
(18) K. Hafner, D. Zinser, and K.-L. Moritz, *Tetrahedron Lett.*, 1733 (1964).
(19) T. Okamoto, M. Hirobe, C. Mizushima, and A. Ohsawa, *Yakugaku Zasshi*, **83**, 308 (1963); *Chem. Abstr.*, **59**, 5130b (1963).
(20) T. Curtius and G. Kraemer, *J. Prakt. Chem.*, **125**, 303 (1930).
(21) R. Gosl and A. Meuwsen, *Chem. Ber.*, **92**, 2521 (1959).
(22) This point has been made recently by Kaneko; *cf.* ref 4a.
(23) Computer-simulated analysis of the nmr spectra of **3a** and related diazepines is in progress.
(24) G. Zinner and W. Deucker, *Arch. Pharm.* (Weinheim), **295**, 526 (1962). We thank Dr. Zinner for correspondence.

TABLE II

NMR SPECTRA OF PYRIDINIUM YLIDES[a]

Ylide	Aromatic and ring methyl protons	$CO_2CH_2CH_3$[b]	$CO_2CH_2CH_3$[b]
2a	1.34 (d, 2, J = 6 Hz, H_2, H_6), 2.14–2.59 (m, 3, H_{3-5})	5.85	8.68
2b	1.38 (br d, 1, J = 8 Hz, H_6), 2.02–2.61 (m, 3, H_{3-5}), 7.22 (s, 3, C_2 CH_3)	5.80	8.62
2c	1.54 (br d, 2, J = 6 Hz, H_2, H_6), 2.60 (br d, 2, J = 6 Hz, H_3, H_5), 7.41 (s, 3, C_4 CH_3)	5.80	8.62
2d	1.61 (br s, 2, H_2, H_6), 2.70 (br s, 1, H_4), 7.62 (s, 6, C_3, C_5 CH_3)	5.87	8.71
2e	1.70–2.60 (m, 2, H_{3-5}), 7.30 (s, 6, C_2, C_6 CH_3)	5.82	8.62
2f	1.84 (br d, 2, J = 7.5 Hz, H_2, H_6), 3.38 (br d, 2, J = 7.5 Hz, H_3, H_5), 6.83 [s, 6, $N(CH_3)_2$]	5.88	8.70
2g	1.05 (br d, 2, J = 6 Hz, H_2, H_6), 1.97 (br d, 2, J = 6 Hz, H_3, H_5)	5.69[c]	8.70[d]
4a	1.07 (br d, 2, J = 7 Hz, H_2, H_6), 1.77–2.67 (m, 8, H_{3-5}, COPh)		
4b	1.40 (br d, 2, J = 7 Hz, H_2, H_6), 2.73 (br d, 2, J = 8 Hz, $H_{2'}$, $H_{6'}$[e]), 1.92–2.45 (m, 3, H_{3-5}), 2.63 (br d, 2, J = 8 Hz, $H_{3'}$, $H_{5'}$[e]), 7.57 (s, 3, $C_{4'}$ CH_3[e])		

[a] Tabulation follows the order chemical shift (τ value), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), number, coupling constant, and assignment of protons. [b] J = 6–7 Hz. [c] Two overlapping quartets, 4 H. [d] Two overlapping triplets, 6 H. [e] Protons of the $-SO_2C_7H_7$ function.

TABLE III

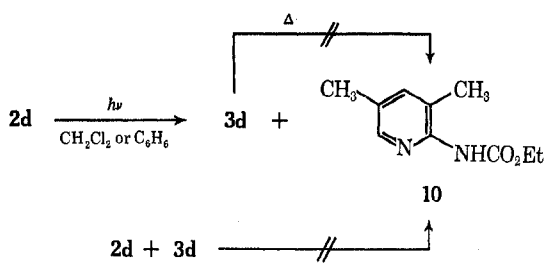
100-MHz NMR SPECTRUM OF 1-ETHOXYCARBONYL-1(1H),2-DIAZEPINE (3a)

Proton	τ	Multiplicity	Coupling constants, Hz
H_3	2.56	dd	$J_{3,4}$ = 3, $J_{3,5}$ = 1
H_4	3.70	m	$J_{4,3}$ = 3, $J_{4,5}$ = 11
H_5	3.40	m	$J_{5,3}$ = 1, $J_{5,4}$ = 11, $J_{5,6}$ = 5, $J_{5,7}$ = 1
H_6	4.20	m	$J_{6,4}$ = 1, $J_{6,5}$ = 5, $J_{6,7}$ = 7.5
H_7	3.71	m	$J_{7,5}$ = 1, $J_{7,6}$ = 7.5
$CO_2CH_2CH_3$	5.75	q	J = 7.0
$CO_2CH_2CH_3$	8.67	t	J = 7.0

Stepwise reduction to the hexahydro derivative **8** was followed by acid hydrolysis and Schotten–Baumann reaction with benzoyl chloride to yield compound **9**.

Irradiation of the ylides **2b**, **2c**, **2e**, **2f**, **4a**, and **4b** produced the corresponding diazepine derivatives **3b**, **3c**, **3e**, **3f**, **5a**, and **5b** in good yields (see Experimental Section). The structures of the photoproducts have been assigned by comparison of the spectral data with that of compound **3a**. In particular, the nmr spectra confirmed the structural assignments, although their complexity allowed calculation of coupling constants only in the cases of simple spin systems[23] (Table IV). The ir and uv data for these compounds are summarized in Table V (Experimental Section). It is to be noted that the unsymmetrical ylide **2b** rearranges exclusively to yield the diazepine **3b**; no isomeric product could be detected by tlc or nmr analysis.

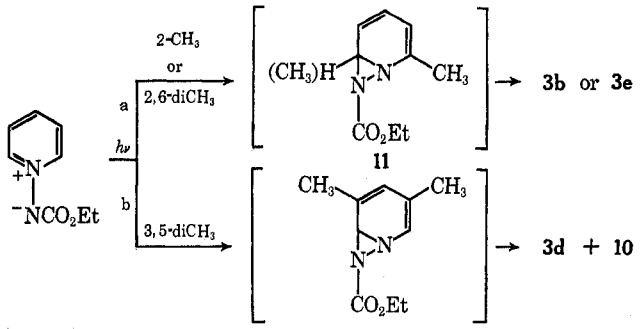
More interesting results were obtained when 3,5-dimethyl-1-carbethoxyiminopyridinium ylide **2d** was irradiated in methylene chloride solution. Besides the normal photoproduct **3d** (41%), characterized mainly by its nmr spectrum (Table IV), a 31% yield of 2-carbethoxyamino-3,5-dimethylpyridine (**10**) was obtained. The latter was identified by comparison with an authentic sample prepared by a known route. The same two products were produced by irradiation in benzene; however, the yields were different, **3d** (80%) and **10** (10%). It was shown that **10** did not arise from **3d** either by a thermal process or by a base-promoted rearrangement of **3d** (ylide **2d** acting as base) during the photolysis[25] (see Experimental Section). Therefore, compound **10** is a true photoproduct.



The effect of electronic factors on the photolytic process is illustrated dramatically by the behavior of ylides **2f** and **2g**. Whereas **2f** rearranged cleanly to **3f**, **2g** was stable to irradiation in methylene chloride or benzene solution.

The results may be summarized by the mechanism outlined in Scheme II. When dealing with a 2-methyl-substituted ylide (**2g**), rearrangement goes exclusively to the least hindered side, forming the hypothetical diaziridine intermediate **11** which then undergoes valence isomerization to the diazepine **3b**; however, 2,6-dimethyl substitution (**2e**) does not hinder the ring expansion to **3e** (path a). 3,5-Dimethyl substitution forces a cleavage process to compete with ring expansion (path b).

SCHEME II



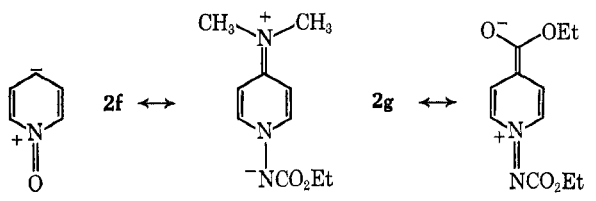
(25) We thank Professor J. A. Moore for discussion concerning these experiments.

TABLE IV
60-MHz NMR SPECTRA OF DIAZEPINES[a,b]

Diazepine	Aromatic and ring methyl protons	$CO_2CH_2CH_3$[c]	$CO_2CH_2CH_3$[c]
3b	3.44–3.74 (m, 3, H_4, H_5, H_7), 4.31 (m, 1, H_6), 7.90 (s, 3, C_3 CH_3)	5.70	8.67
3c	2.70 (d, 1, $J_{3,4}$ = 4 Hz, H_3) 3.73–4.07 (m, 2, H_4, H_7), 4.43 (dd, 1, $J_{6,4}$ = 1.5 Hz $J_{6,7}$ = 8 Hz, H_6), 8.10 (d, 3, C_5 CH_3)	5.67	8.67
3d	2.76 (d, 1, $J_{3,5}$ = 1.5 Hz, H_3), 3.73 (br s, 1, H_5), 3.99 (br s, 1, H_7), 8.07 (d, 3) and 8.21 (d, 3, C_4, C_6 CH_3)	5.70	8.68
3e	3.43–3.76 (m, 2, H_4, H_5), 4.17 (m, 1, H_6), 7.83 (s, 6, C_3, C_7 CH_3)	5.72	8.65
3f	2.75 (d, 1, $J_{3,4}$ = 5.5 Hz, H_3), 3.77 (d, 1, $J_{7,6}$ = 8.5 Hz, H_7), 4.35 (dd, 1, $J_{6,7}$ = 8.5 Hz, $J_{6,4}$ = 2.5 Hz, H_6), 5.20 (q, 1, $J_{4,3}$ = 5.5 Hz, $J_{4,6}$ = 2.5 Hz, H_4), 7.13 [s, 6, $N(CH_3)_2$],	5.72	8.67
5a	2.23–2.70 (m, 6, H_3, COPh), 3.15–3.80 (m, 3, H_4, H_5, H_7), 4.12 (m, 1, H_6)		
5b	2.16 (d, 2, J = 8 Hz, $H_{2'}$, $H_{6'}$[d]), 2.69 (d, 2, J = 8 Hz, $H_{3'}$, $H_{5'}$[d]), 2.74 (d, 1, hidden H_3), 3.24–3.92 (m, 2) and 4.06–4.49 (m, 2, H_{4-7}), 7.55 (s, 3, $C_{4'}$ CH_3[d])		

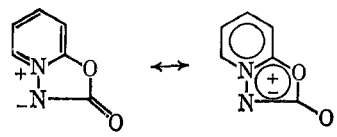
[a] See footnote *a*, Table II. [b] See ref 23. [c] J = 7.0 Hz. [d] See footnote *e*, Table II.

The results with ylides **2f** and **2g** are partially understood if reference may be made to the thoroughly investigated ultraviolet spectral characteristics of the isoelectronic pyridine N-oxides.[1a] In these systems, evidence is available which indicates that contributing resonance forms in which oxygen has lost most of its negative charge, *e.g.*, **12**, are important in excited-state considerations. Assuming that these considerations apply to the N–N ylides, the excited states of **2f** and **2g** may be described by the resonance forms **13** and **14**, respectively. Thus photochemical lability (**2f**) and stability (**2g**) may be associated with the amount of negative charge on exocyclic nitrogen. Information concerning the detailed mechanism, in particular evidence for the diaziridine intermediate **11**, is not yet available, although the attention of Streith toward the solution of this problem is to be noted.[10,11]



12 **13** **14**

Finally, the very similar uv spectrum [uv max (CH_2Cl_2) 271, 308 mμ] of an unusual, rigid carboxypyridinium ylide, pyrido[2,1-*b*]-1,3,4-oxadiazolone-2 (**15**),[26]



15

to that of the simple case **2a** led to a brief investigation of its photochemical behavior. It was found that compound **15** was stable to irradiation at 3500 and 3000 Å in methylene chloride solution for at least 24 hr. Sensitization with benzophenone also proved fruitless in that starting material was recovered unchanged after lengthy irradiation times at 3500 Å. The stability of **15** may be due to its inability to form a (strained) diaziridine intermediate which, in turn, is possibly associated with the highly delocalized (aromatic) nature of the compound.[26]

(26) K. Hoegele, *Helv. Chim. Acta*, **41**, 548 (1958).

Experimental Section

Microanalyses were performed by A. B. Gygli, Microtech Laboratories, Toronto, and Uniroyal Laboratories, Guelph. Melting points were measured on a Fisher-Johns apparatus and are uncorrected. Infrared spectra were determined with Beckmann IR-5A, -9, and -10 instruments in chloroform solution unless otherwise indicated. Ultraviolet spectra were recorded on Hitachi EPS-3T and Beckman DB-G spectrophotometers in methanol solution. Nuclear magnetic resonance spectra were obtained with JEOL C-60, Varian T-60, and Varian HA-100 spectrometers in deuteriochloroform solution using tetramethylsilane as internal standard. Column, thin layer, and thick layer chromatography was carried out with silica gel obtained from Brinkmann (Canada) Ltd.; Woelm alumina (basic, grade III) was used for the purification of the ylide picrates. Solvents were reagent grade and distilled before use; unless otherwise indicated, petroleum ether of boiling range 60–80° was used. A Rayonet photochemical reactor equipped with sixteen 3500-Å lamps was used; photolyses were carried out in Pyrex vessels and cooled internally to 10–20° by a cold finger.

The Preparation of 1-Ethoxycarbonyliminopyridinium Ylides (2a–g). 1-Ethoxycarbonyliminopyridinium Ylide (2a). Method A.—A three-necked round-bottom flask equipped with a condenser and an addition funnel was charged with 70 g of freshly distilled pyridine and 10 g of ethyl azidoformate. The condenser was attached to a gas buret in order to measure the nitrogen evolution. The reaction was initiated by immersing the flask into an oil bath at 105° and stirring. In 12 hr, 1.9 l. of nitrogen were evolved (theoretical: 1.94 l.). Excess pyridine was removed *in vacuo* and the dark residue was taken up in 75 ml of boiling chloroform and treated with charcoal. The filtrate was concentrated and recrystallized twice from benzene and twice from tetrahydrofuran to yield 2.50 g (17.4% based on ethyl azidoformate) of **2a**, mp 108–109° (lit.[18] mp 109°).

Method B.—To a stirred solution of 1.60 g (7.55 mmol) of 1-aminopyridinium iodide[21] in 50 ml of ethanol were added dropwise and concurrently from two addition funnels solutions of 0.69 g (15.0 mmol) of potassium hydroxide in 50 ml of ethanol and 1.61 g (14.7 mmol) of ethyl chloroformate in 10 ml of ethanol. The additions were carried out in such a manner as to maintain a basic solution, indicated by the persistence of a purple color in the reaction mixture. After the additions, the resulting pale yellow solution was further stirred for 70 min. Evaporation to dryness yielded a yellow residue which was dissolved in 20 ml of a 10% aqueous sodium carbonate solution and extracted with methylene chloride. The extracts were dried (Na_2SO_4) and concentrated to yield 761 mg of crystalline material. Recrystallization from tetrahydrofuran gave colorless flakes of **2a**, 575 mg (48%), identical with material prepared by method A.

The following compounds were prepared by methods A and B as indicated in Table I.

2-Methyl-1-ethoxycarbonyliminopyridinium Ylide (2b).—A pale yellow, hygroscopic oil was obtained. Further purification was accomplished *via* the picrate. Recrystallization from benzene–

methanol gave yellow needles, mp 139–142.5°. For the purpose of photolysis, the ylide **2b** was regenerated by passing a chloroform solution of the picrate through a short column of basic alumina. Purity was established by ir and uv spectroscopy and tlc homogeneity in several solvent systems.

The picrate was recrystallized from benzene for the analytical sample, mp 141–142°.

Anal. Calcd for $C_{15}H_{16}N_8O_9$: C, 44.02; H, 3.69; N, 17.11. Found: C, 44.12; H, 3.92; N, 17.04.

4-Methyl-1-ethoxycarbonyliminopyridinium Ylide (2c).—Method A was modified in that toluene was used as a solvent for the reaction and the w/w ratio of pyridine derivative to ethyl azidoformate was reduced to 3:1. Recrystallization from tetrahydrofuran and benzene yielded **2c**. Further recrystallization from carbon tetrachloride furnished an analytical sample, mp 151.5–152.5°.

Anal. Calcd for $C_9H_{12}N_2O_2$: C, 59.99; H, 6.71; N, 15.55. Found: C, 59.66; H. 6.80; N, 15.57.

3,5-Dimethyl-1-ethoxycarbonyliminopyridinium Ylide (2d).—Method A was modified as in the case of **2c**. Three recrystallizations from benzene gave colorless crystals of **2d**, mp 138–140°.

Anal. Calcd for $C_{10}H_{14}N_2O_2$: C, 61.84; H, 7.27; N, 14.42. Found: C, 61.71; H, 7.31; N, 14.46.

2,6-Dimethyl-1-ethoxycarbonyliminopyridinium Ylide (2e).—The picrate, mp 153–155° from ethanol, was treated as in the case of **2b**. Recrystallization from petroleum ether–benzene gave **2e** as pale yellow needles, mp 101–102°.

Anal. Calcd for $C_{10}H_{14}N_2O_2$: C, 61.84; H, 7.27; N; 14.42. Found: C, 61.93; H, 7.28; 6, 14.49.

4-Dimethylamino-1-ethoxycarbonyliminopyridinium Ylide (2f).—4-Dimethylamino-1-aminopyridinium iodide was prepared in 13% yield according to the procedures of Gosl[21] and Okamoto.[27] Two recrystallizations from ethanol gave colorless needles, mp 201.5–202.5°.

Anal. Calcd for $C_7H_{12}N_3I$: C, 31.72; H, 4.57; N, 15.85; I, 47.87. Found: C, 31.73; H. 4.63; N, 15.84; I, 47.71.

The above compound, when treated with ethyl chloroformate according to method B, gave **2f**. Three recrystallizations from benzene furnished colorless needles, mp 183–185°.

Anal. Calcd for $C_{10}H_{15}N_3O_2$: C, 57.40; H, 7.23; N, 20.08. Found: C, 57.31; H, 7.24; N, 20.31.

4-Ethoxycarbonyl-1-ethoxycarbonyliminopyridinium Ylide (2g).—Method A was modified as in the case of **2c**. Concentration *in vacuo* gave a viscous oil which was triturated with ether to yield pale yellow needles, mp 162–163.5°.

Anal. Calcd for $C_{11}H_{14}N_2O_4$: C, 55.46; H. 5.92; N, 11.76. Found: C, 55.19; H, 5.93; N, 11.62.

1-Benzoyliminopyridinium Ylide (4a).—In following method B, 2 equiv of benzoyl chloride instead of ethyl chloroformate was used. Recrystallization from benzene–petroleum ether gave tan needles of **4a**, mp 179–180.5° (lit.[19] mp 177.5°).

1-*p*-Toluenesulfonyliminopyridinium Ylide (4b).—Method B was followed except that 2 equiv of *p*-toluenesulfonyl chloride instead of ethyl chloroformate was used. Two recrystallizations from methanol yielded colorless rectangles, mp 215–217° (lit.[20] mp 210°).

Preparation of 1(1H),2-Diazepine Derivatives (3a–f). General Photolysis Procedure.—A 0.25% solution (w/v) of the ylide in methylene chloride was irradiated and the reaction was followed by the disappearance of the high-wavelength absorption in the uv spectrum (see Table I). In general, photolysis was complete in 10–12 hr for 100-mg samples. Evaporation of solvent *in vacuo*, chromatography over silica gel (elution with benzene and benzene–chloroform mixtures), and recrystallization or distillation yielded **3a–f**, **5a**, and **5b**. The yields of products and physical and analytical data are collected in Tables V and VI.

Photolysis of 1-Ethoxycarbonyliminopyridinium Ylide (2a) and Its Degradation to 1,2-Dibenzoyl-1,2-hexahydrodiazepine (9).—A solution of **2a** (399 mg, 2.5 mmol), in 90 ml of methylene chloride solution was photolyzed for 24 hr. The solvent was removed *in vacuo* and the resulting 370 mg of brown oil was hydrogenated at 1 atm in ethanol over 5% palladium on charcoal. After uptake of 101 ml (1.95 mmol) of hydrogen, the reaction was stopped and worked up in the usual way. A 130-mg portion of the crude product was chromatographed on silica gel (ether eluent) and yielded 60 mg of **1-ethoxycarbonyl-4,5,6,7-tetrahydrodiazepine (7)** as a pale yellow oil: ir (CCl_4) 1705 (C=O) and 1630 (C=N) cm^{-1}; nmr τ 2.92 (t, 1, C_3 H), 5.83 (q, 2, $CO_2CH_2CH_3$), 6.28 (br m, 2, C_4 H), 7.58 (br m, 2, C_7 H), 8.26 (br m, 4, C_5, C_6 H), and 8.68 (t, 3, $CO_2CH_2CH_3$). The remainder of the material was directly hydrogenated in ethanol over platinum oxide and yielded, after chromatography, 217 mg (55%) of oily **1-ethoxycarbonyl-1,2-hexahydrodiazepine (8)**: ir (CCl_4) 1700 cm^{-1} (C=O); nmr τ 5.80 (br, 1, NH, exchanged with D_2O), 5.87 (q, 2, $CO_2CH_2CH_3$), 6.53 (m, 2, C_7 H), 7.11 (m, 2, C_3 H), 8.36 (m, 6, C_4, C_5, C_6 H), and 8.73 (t, 3, $CO_2CH_2CH_3$).

Anal. Calcd for $C_8H_{16}N_2O_2$: C, 55.79; H, 9.36; N, 16.27. Found: C, 55.71; H, 9.30; N, 16.66.

Compound **8** was dissolved in 7 ml of concentrated hydrochloric acid and the resulting solution was refluxed for 10 hr. Evaporation *in vacuo* gave a residue which was dissolved in alcoholic potassium hydroxide solution (10 g in 80 ml) and refluxed for 30 min. The solution was concentrated and extracted with large amounts of warm ether. Concentration of the ether extract to 25 ml was followed by additions of 50 ml of pyridine and 4 g of benzoyl chloride. After standing overnight, the mixture was concentrated *in vacuo* and the product was isolated in the usual way. Two recrystallizations from ethanol yielded **1,2-dibenzoyl-1,2-hexahydrodiazepine (9)**, mp 156–157°, which was characterized by identical ir spectrum, melting point, and mixture melting point with those of an authentic sample prepared according to Zinner and Deucker.[24]

Photolysis of 3,5-Dimethyl-1-ethoxycarbonyliminopyridinium Ylide (2d).—The crude product from photolysis in methylene chloride solution was chromatographed. After separation of **4,6-dimethyl-1-ethoxycarbonyl-1(1H),2-diazepine (3d)**, elution with 7% methanol–chloroform solution yielded 31% **10**, characterized by identical ir, uv, and nmr spectra, melting point, and mixture melting point with those of an authentic sample prepared as described below.

Preparation of 2-Carbethoxyamino-3,5-dimethylpyridine (10).—2-Amino-3,5-dimethylpyridine was prepared[28] in 20% yield: bp 98–100° (5–6 mm); ir (CCl_4) 3505, 3405, and 1616 cm^{-1}; uv max 235 mμ (ϵ 10,440) and 304 (5310); nmr τ 2.23 (br s, 1, H_6), 2.91 (br s, 1, H_4), 5.72 (br s, 2, NH_2, exchanged with D_2O), 7.84 (s, 3, C_5 CH_3), and 7.92 (s, 3, C_3 CH_3). This compound was treated with pyridine and ethyl chloroformate according to the procedure of Katritzky.[29] Compound **10** was obtained in 38% yield: mp 113–117.5°; ir (CCl_4) 3420, 3175 (NH), and 1740 cm^{-1} (C=O); uv max 226 mμ (ϵ 9200) and 274 (5000); nmr τ 1.93 (d, 1, J = 2 Hz, H_6), 2.44 (br, 1, NH, exchanged with D_2O), 2.63 (d, 1, J = 2 Hz, H_4), 5.98 (q, 2, $CO_2CH_2CH_3$), 7.70 (s, 6, C_3, C_5 CH_3), and 8.65 (t, 3, $CO_2CH_2CH_3$). Recrystallization from ethanol–water gave an analytical sample, mp 115.5–116.5°.

Anal. Calcd for $C_{10}H_{14}N_2O_2$: C, 61.84; H, 7.27; N, 14.42. Found: C, 61.93; H, 7.28; N, 14.49.

Methylene chloride solutions of **3d** and a mixture of **2d** with **3d** (1:1) were left standing at room temperature in the dark for 24 hr. In both cases, tlc analysis showed that no decomposition and no generation of **10** had occurred.

TABLE V

INFRARED AND ULTRAVIOLET SPECTRA OF DIAZEPINES

Diazepine	$\nu_{max}^{CHCl_3}$, cm^{-1} [a]	λ_{max}^{MeOH}, mμ (ϵ)[b]
3a	1700	221 (11,440)
	1609	255 (sh, 3560)
3b	1706	224 (12,380)
	1631	256 (sh, 3460)
3c	1711	220 (12,670)
	1633	242 (sh, 7260)
3d	1717	222 (8790)
	1632	250 (sh, 5840)
3e	1697	226 (8330)
	1641	242 (6990)
3f	1695	271 (14,200)
	1650	352 (3440)
5a	1651	227 (13,350)
	1611	285 (sh, 5400)
5b	1615 (w)	226 (16,050)
	1598 (w)	276 (sh, 1950)

[a] See footnote *b*, Table I. [b] See footnote *c*, Table I.

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TABLE VI

PHYSICAL AND ANALYTICAL DATA OF DIAZEPINES

Diazepine	Yield, %[a]	Physical state[b]	$n^{25}D$ or mp, °C	Molecular formula	Analysis,[c] % Calcd C	Calcd H	Calcd N	Found C	Found H	Found N
3a	97	Red oil	1.5400	$C_8H_{10}N_2O_2$	57.82	6.07	16.86	57.40	5.93	16.44
3b	84	Yellow oil	1.5276	$C_9H_{12}N_2O_2$	59.99	6.71	15.55	60.05	6.96	15.38
3c	98	Pale yellow needles[d]	55.5–56	$C_9H_{12}N_2O_2$	59.99	6.71	15.55	59.74	6.93	15.59
3d	41	Yellow oil	1.5065	$C_{10}H_{14}N_2O_2$	61.84	7.27	14.42	61.44	7.26	14.20
3e	72	Yellow oil	1.5140	$C_{10}H_{14}N_2O_2$	61.84	7.27	14.42	61.50	7.33	14.20
3f	65	Yellow needles[e]	90–91	$C_{10}H_{15}N_3O_2$	57.40	7.23	20.08	57.05	7.20	19.80
5a	64	Orange needles[c]	52–54	$C_{12}H_{10}N_2O$	72.71	5.08	14.13	72.71	5.23	14.00
5b	61	Pale yellow crystals[f]	173–175 dec	$C_{12}H_{12}N_2O_2S$[g]	58.06	4.87	11.28	58.37	4.77	11.06

[a] After chromatography. [b] Purification of the oily diazepines was achieved by short-path distillation at 45–60° (0.1–0.5 mm). [c] Owing to volatility and instability, analytical data on the oily compounds was difficult to obtain and the values given are the best of at least quadruplicate determinations. [d] From benzene–petroleum ether. [e] From ether–petroleum ether (bp 35–60°). [f] From benzene. [g] Calcd: S, 12.89. Found: S, 13.08.

Registry No.—**2a**, 23025-55-0; **2b**, 22928-83-2; **2b** picrate, 22928-84-3; **2c**, 22928-85-4; **2d**, 22928-87-6; **2e**, 23025-59-4; **2f**, 23025-60-7; **2g**, 23025-61-8; **3a**, 17377-08-1; **3b**, 22928-90-1; **3c**, 22928-91-2; **3d**, 22928-95-6; **3e**, 22928-97-8; **3f**, 23025-66-3; **4a**, 23031-08-5; **4b**, 23025-67-4; **5a**, 20169-43-1; **5b**, 23025-45-8; **7**, 20169-37-3; **8**, 20169-38-4; **10**, 22931-88-0.

Acknowledgments.—We express our gratitude to the National Research Council of Canada for the support of this work. Thanks are due to Mr. D. Burkholder and Mr. M. Stanton for able technical assistance and to Professor G. L. Lange for the use of the 3000-Å lamps and the nmr spectrometer in critical times. We are especially indebted to Mr. Brian Sayer for the 100-MHz nmr spectrum and to the Uniroyal Laboratories for analytical data on the oily diazepines. Finally, we wish to thank Professor T. Sasaki for an exchange of information and for graciously agreeing to simultaneous publication of results.

Synthesis of 4,5-Disubstituted Pyrimidines

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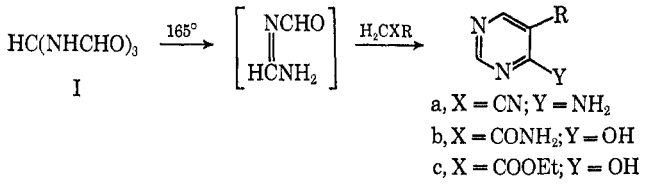
Received June 9, 1969

Several new 4-amino (or hydroxy) 5-substituted pyrimidines are prepared by the reaction of trisformylaminomethane with various substituted acetonitriles, acetamides, and corresponding esters, and the reaction results are discussed.

In a previous paper,[2] the synthesis of 4-amino (or hydroxy) 5-substituted pyrimidines by the reaction of trisformylaminomethane (I) with phenylacetonitriles (a) or *p*-nitrophenylacetamide (b) having an active methylene group was reported.



I

a, X = CN; Y = NH_2
b, X = $CONH_2$; Y = OH
c, X = COOEt; Y = OH

Pyrimidines of similar structure, with different substituent R, have been prepared by other workers.[3-7]

In this paper, the possibility of synthesis of 4-hydroxy-5-phenylpyrimidine from phenylacetamide, having a less active methylene group than *p*-nitrophenylacetamide, as well as the synthesis of 4-hydroxypyrimidines from the corresponding esters (c), were studied. Furthermore, in order to prepare new 4-amino (or hydroxy) 5-substituted pyrimidines and to extend the application of this synthetic method, substituted acetonitriles, acetamides, and the corresponding esters, with both electron-attracting and -releasing substituents, were used.

The reactions were carried out under the same conditions, using formamide as a solvent and *p*-toluenesulfonic acid as a catalyst.[8] However, the presence of formamide and the catalyst has been found to be unnecessary. The results of these reactions are presented in Table I.

Some 4-hydroxypyrimidines were also prepared by acid hydrolysis of the corresponding 4-aminopyrimidines. The results of the replacement reactions are summarized in Table II.

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