Experimental Section

All photolyses were carried out in quartz reaction tubes in a Rayonet photochemical chamber using low-pressure mercury lamps which provide 84% of their emission at 2537 Å.

1-Adamantyl *p*-Nitrophenyl Carbonate (6).—To a solution of 1-adamantanol (3.0 g, 0.02 mol) and quinoline (2.4 ml, 0.02 mol) in 30 ml of methylene chloride was added a solution of *p*-nitrophenyl chloroformate (4.0 g, 0.02 mol) in 10 ml of methylene chloride over a 40-min period with stirring. The reaction mixture was allowed to stand at room temperature over the weekend, and extracted with two 100-ml aliquots of water and two 100-ml portions of 0.25 *N* hydrochloric acid. The organic phase was dried over magnesium sulfate and evaporated to give a crystalline solid, yield 6.1 g. This product was dissolved in 15 ml of hot methylene chloride, treated with Darco, and filtered. The filtrate was diluted with 25 ml of petroleum ether to afford crystals, yield 1.0 g, mp 132–136°. The infrared spectrum of this crop revealed it to be bis-*p*-nitrophenyl carbonate. The filtrate was evaporated to about 10 ml, diluted with 50 ml of petroleum ether, chilled, and filtered to give 2.8 g of product, mp 87–106°. The filtrate to this product was evaporated to 15 ml to give more crystals, yield 1.5 g, mp 101–106°. These two crops were combined, dissolved in 20 ml of methylene chloride, and applied to a column of acid-washed alumina (160 g). The column was eluted with 550 ml of methylene chloride and the eluate was evaporated to give a crystalline solid which was recrystallized from methylene chloride–petroleum ether: yield 3.3 g (52%), mp 115–118.5° (lit.[8] 106–108°). For analysis a small portion of this product was recrystallized from petroleum ether (melting point raised to 118.5–120°).

Anal. Calcd for $C_{17}H_{19}NO_5$: C, 64.3; H, 6.0; N, 4.4. Found: C, 64.6; H, 6.4; N, 4.7.

Adamantyl-1-carbazate (7).—1-Adamantyl *p*-nitrophenyl carbonate (3.8 g, 12 mmol) was added to 100 ml of methanol containing 1.0 ml (20 mmol) of hydrazine hydrate and refluxed for 3 hr on a steam bath. The reaction was evaporated to a yellow residue at reduced pressure and 100 ml of ether was added to give a yellow solid which was removed by filtration and discarded. The filtrate was warmed to effect solution and was extracted with six 75-ml aliquots of 10% sodium hydroxide solution and three 75-ml portions of water. After having been dried over magnesium sulfate, the ether was evaporated to afford a white, crystalline solid, yield 2.5 g (95%), mp 138–140° (lit.[8] 141–142°). For analysis a small portion of this crop was recrystallized from ethyl acetate (melting point unchanged).

Anal. Calcd for $C_{11}H_{18}N_2O_2$: C, 62.8; H, 8.6; N, 13.3. Found: C, 62.6; H, 8.6; N, 13.7.

Photolysis of 1-Adamantyloxycarbonylazide (8) in Cyclohexane.—Adamantyl-1-carbazate (4.3 g, 20.4 mmol) was dissolved in 60 ml of acetic acid followed by the addition of 200 ml of water and 13 ml of concentrated hydrochloric acid. The solution was chilled in an ice bath and a cold solution of sodium nitrite (1.5 g, 21.8 mmol) in 15 ml of water was added. The resulting azide was extracted into cyclohexane (500 ml total), washed with two 250-ml portions of cold 5% sodium bicarbonate followed by two 250-ml portions of water, and dried over magnesium sulfate. The magnesium sulfate was filtered off and the filtrate photolyzed for 15.5 hr. The solution was evaporated to dryness at reduced pressure and the oily crystalline residue was slurried in 50 ml of cyclohexane, chilled, and filtered to give 1.7 g (43%) of the oxazolidin-2-one **10**, mp 130–133.5°. A small portion of this product was recrystallized from ethyl acetate for analyses (mp raised to 134–136°): ir (KBr) 3.1, 5.7, and 5.8 μ; nmr ($CDCl_3$) δ 6.2 (NH), 3.7 (1 H adjacent to NH); mass spectrum *m/e* 193 (molecular ion).

Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.4; H, 7.8; N, 7.3. Found: C, 68.3; H, 7.7; N, 7.2.

The filtrate from above was concentrated to 20 ml to give more crystals, yield 0.95 g, mp 86–93°. Thin layer chromatography revealed this to be a mixture of compound **10** and another faster moving product. This compound was separated on Woelm alumina and crystallized from aqueous ethanol to afford 150 mg of carbamate **11**: mp 84–87°; ir (KBr) 3.0, 5.94 μ.

Anal. Calcd for $C_{17}H_{27}NO_2$: C, 73.6; H, 9.8; N, 5.1. Found: C, 73.2; H, 9.9; N, 5.2.

2-Amino-1-adamantanol Hydrochloride (12).—One gram (5.2 mmol) of the oxazolidinone **10** was added to 100 ml of 2 *N* hydrochloric acid and heated on a steam bath for 1.0 hr. The solution was filtered to remove a small amount of insoluble material and evaporated to a crystalline solid at reduced pressure with the aid of absolute ethanol. The compound was recrystallized from ethanol–ether to give a crystalline solid. The addition of ether to the filtrate gave more crystals. The infrared spectra and thin layer chromatograms of these two crops were identical. The total yield was 670 mg (63%): ir (KBr) 3.1, 5.05, 6.23, and 6.55 μ; nmr (D_6MSO) δ 8.1 (NH_3^+), 5.2 (OH), and 3.0 (H adjacent to NH_3^+); mass spectrum *m/e* 167 (molecular ion).

Anal. Calcd for $C_{10}H_{17}NO\cdot HCl$: C, 58.9; H, 8.9; N, 6.9; Cl, 17.4. Found: C, 59.3; H, 8.7; N, 7.1; Cl, 17.2.

2-Amino-1-chloroadamantane Hydrochloride (13).—Adamanto-[2,1-*d*]oxazolidin-2-one (**10**, 300 mg) was heated on a steam bath for 2.5 hr in 30 ml of concentrated hydrochloric acid and evaporated to dryness at reduced pressure. The residue was dissolved in 50 ml of absolute ethanol, evaporated to dryness, and redissolved in 15 ml of hot absolute ethanol. The solution was treated with Norit and filtered. The filtrate was diluted with 10 ml of ether and chilled, and the product was collected: yield 135 mg. Elemental analyses and ir and nmr spectra identified this product as 2-amino-1-adamantanol hydrochloride. The filtrate was evaporated to a volume of several milliliters and ether was addedto afford more crystals, yield 47 mg, mp 308° dec. Chlorine analyses, along with ir, nmr, and mass spectra, identified this product as 2-amino-1-chloroadamantane hydrochloride: ir (KBr) 3.45, 14.35 μ; nmr (D_6MSO) δ 8.6 (NH_3^+), 3.5 (H adjacent to NH_3^+); mass spectrum *m/e* 185 (molecular ion) 187 (M + 2 peak).

Anal. Calcd for $C_{10}H_{16}NCl\cdot HCl$: total Cl, 31.9; ionic Cl, 16.0%. Found: total Cl, 31.7; ionic Cl, 16.4.

Registry No.—**10**, 15252-86-5; **11**, 15215-43-7; **12**, 21347-36-4; **13**, 21371-75-5.

Acknowledgment.—We wish to thank Mr. L. Brancone and staff for the microanalyses, and Mr. W. Fulmor and staff for the spectral data reported herein.

Reaction of Cyanoacetamide and Some 2-Acylcyclanones

FILLMORE FREEMAN AND THOMAS I. ITO

Department of Chemistry, California State College, Long Beach, California 90801

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Although the literature abounds in examples of base-catalyzed condensations of cyanoacetamide (I) with 1,3-dicarbonyl compounds to give substituted pyridines, quinolines, isoquinolines, and 5H-1-pyrindines,[1-6] it appears that this facile reaction has not been used to prepare the difficultly accessible 5H-2-pyrindine and cycloalka[*c*]pyridine[7,8] ring systems. We wish to report that I reacts with 2-acylcyclanones,[9] in the presence of diethylamine, to give substituted 5H-2-pyrindines (II–IV) and substituted cycloalka[*c*]pyridines

(1) F. Freeman, D. K. Farquhar, and R. L. Walker, *J. Org. Chem.*, **33**, 3648 (1968).

(2) F. Brody and P. R. Ruby in "Heterocyclic Compounds," Part I, E. Kingsberg, Ed., Interscience Publishers, New York, N. Y., 1960, p 400.

(3) H. S. Mosher in "Heterocyclic Compounds," Vol. 1, R. C. Elderfield, Ed., John Wiley & Sons, Inc., New York, N. Y., 1950, p 469.

(4) G. N. Walker and B. N. Weaver, *J. Org. Chem.*, **25**, 484 (1960); **26**, 4441 (1961).

(5) H. Junek, *Monatsh. Chem.*, **95**, 1201 (1964).

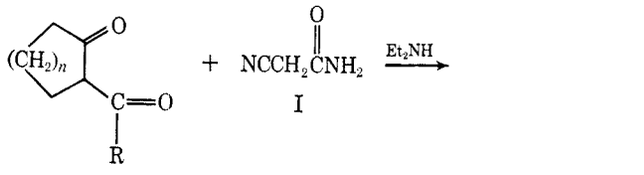
(6) H. K. Sen and U. Bose, *J. Indian Chem. Soc.*, **4**, 51 (1927).

(7) G. G. Hyist and K. Schofield, *J. Chem. Soc.*, 3445 (1960).

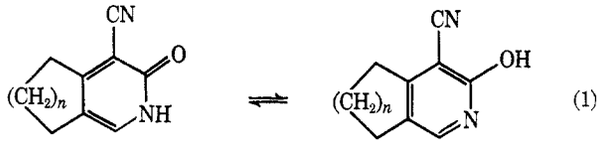
(8) A. T. Balaban and C. D. Nenitzescu, *ibid.*, 3561 (1961).

(9) 2-Acetylcyclohexanone has been reported[1] to give the same substituted 3-isoquinolinol with malononitrile or I. In contrast, Sen and Bose[6] reported that 2-acetylcyclohexanone and substituted 2-acetylcyclohexanones reacted with I to yield quinoline derivatives.

(V–VII) in good yields. This work describes a convenient and simple synthesis for the preparation of 5H-2-pyrindines and cycloalka[*c*]pyridines without contamination of the isomeric 5H-1-pyrindines and cycloalka[*b*]pyridines.[1,2] Compound VIII was also pre-



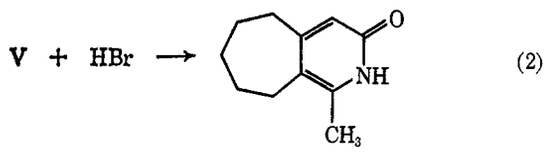
I



IV–II V–VII (1)

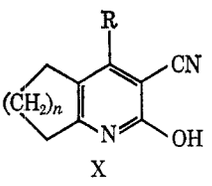
Compd	*n*	R	%	Compd	*n*	R	%
II	1	C_2H_5	60.1	V	3	CH_3	76.5
III	1	*n*-C_3H_7	50.7	VI	4	CH_3	60
IV	1	*i*-C_3H_7	55.5	VII	10	CH_3	49.6

pared in 71% yield, for spectral studies, by hydrolytic decarboxylation of V with 48% hydrobromic acid.[10]



VIII (2)

It has been suggested[1] that a probable mechanism for the condensation of I and 1,3-dicarbonyl compounds involves initial attack of the anion of I at the cyclic carbonyl carbon of the acylcyclanone[11] to form the cycloalkylidenecyanoacetamide which cyclizes and then eliminates water. Alternatively, initial attack at the acyl carbonyl carbon would lead to the isomeric 5H-1-pyrindines ($n = 1$) and cycloalka[*b*]pyridines ($n > 1$) X.



X

With the exception of 2-acetylcyclopentanone (XI), which gave a mixture of 5H-1- and 5H-2-pyrindines, the size of R had little effect on the yield. In contrast, the yields were lower with the larger cycloalkyl rings of the other 2-acetylcyclanones.

Support for the proposed structures (II–VIII) is obtained from the uv spectra, which are similar to pyridones[12] (217–240 mμ), to pyridines[13] (250 mμ), and to 3-isoquinolinols[1,14,15] (340 mμ). Although the absorption intensity is only decreased slightly, it is seen that the absence of the nitrile group causes a hypsochromic shift in VIII (201, 237, 244, and 305 mμ).

The ir spectra of II–VIII [3100–3300 (NH), 1630–1650, 1570, 1515 (pyridone amide C=O), 2232–2262 cm^{-1} (nitrile)] are also very similar, and are completely compatible with the proposed structures.[1,13,16,17] The amide C=O and NH stretching vibration bands suggest that the compounds exist predominantly in the amide form.[13,16,17]

No products were obtained from the reaction of XI with malonoamide or ethyl acetoacetate; malononitrile and ethyl cyanoacetate gave unresolvable product mixtures.

Experimental Section

All melting points were determined on a Thomas–Hoover apparatus and are uncorrected. Infrared spectra were taken on a Baird-Atomic spectrophotometer, and ultraviolet spectra were taken on a Beckman DK-2A. Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich.

The acylcyclanones were prepared according to published procedures.[18]

6,7-Dihydro-4-cyano-1-ethyl-3-hydroxy-5H-2-pyrindine (II).—A solution of 8.842 g (0.07 mol) of 2-propionylcyclopentanone, 2.94 g (0.035 mol) of I (Aldrich), 75 ml of 95% ethanol, and 2 ml of diethylamine (Eastman) was stirred for 24 hr and filtered; the solid was washed with cold ethanol and dried. The filtrate and washings were combined, stirred for 24 hr, and filtered; the solid was treated as described previously. The resulting filtrate and washings were combined and treated as described above. Recrystallization of the combined solids from absolute ethyl alcohol gave a 60.1% yield of II: mp 317–317.5° dec; uv max (95% EtOH) 220 mμ (log ε 4.27), 240 (3.80), 223 (4.29), 340 (4.07); ir (KBr) 3355, 3185 (NH), 2262 (CN), 1639, 1567 (C=O), 840, 772, 711 cm^{-1} (cycloalkyl).

Anal. Calcd for $C_{11}H_{12}N_2O$: C, 70.19; H, 6.43; N, 14.89. Found: C, 70.24; H, 6.37; N, 14.92.

6,7-Dihydro-4-cyano-3-hydroxy-1-*n*-propyl-5H-2-pyrindine (III).—2-*n*-Butyrylcyclopentanone was treated with I as described above to give III in 50.7% yield: mp 245–245.5°; uv max (95% EtOH) 218 mμ (log ε 4.26), 241 (3.77), 223 (4.28), 341 (4.08); ir (KBr) 3378, 3194 (NH), 2262 (CN), 1647, 1567 (C=O), 847, 771, 730 cm^{-1} (cycloalkyl).

Anal. Calcd for $C_{12}H_{14}N_2O$: C, 71.26; H, 6.98; N, 13.85. Found: C, 71.32; H, 6.98; N, 13.81.

6,7-Dihydro-4-cyano-3-hydroxy-1-isopropyl-5H-2-pyrindine (IV).—2-Isobutyrylcyclopentanone was treated with I to give IV: mp 312.5–313°, in 55.5% yield; uv max (95% EtOH) 218 mμ (log ε 4.27), 240 (3.81), 223 (4.28), 340 (4.09); ir (KBr) 3222, 3205 (NH), 2257 (CN), 1642, 1567 (C=O), 845, 770, 710 cm^{-1} (cycloalkyl).

Anal. Calcd for $C_{12}H_{14}N_2O$: C, 71.26; H, 6.98; N, 13.85. Found: C, 71.04; H, 6.93; N, 13.95.

6,7,8,9-Tetrahydro-4-cyano-3-hydroxy-1-methyl-5H-cyclohepta[*c*]pyridine (V).—I and 2-acetylcycloheptanone gave V, mp 266.5–267° dec, in 76.5% yield: uv max (95% EtOH) 218 mμ (log ε 4.21), 244 (infl, 3.85), 222 (4.21), 252 (3.73), 341 (4.11); ir (KBr) 3322, 3145 (NH), 2252 (CN), 1636, 1538 (C=O), 833, 780, 765 cm^{-1} (cycloalkyl).

Anal. Calcd for $C_{12}H_{14}N_2O$: C, 71.26; H, 6.98; N, 13.85. Found: C, 71.01; H, 6.91; N, 14.02.

6,7,8,9,10-Pentahydro-4-cyano-2-hydroxy-1-methyl-5H-cycloocta[*c*]pyridine (VI).—The procedure described above was used to prepare VI from 2-acetylcyclooctanone in 60% yield: mp 280–280.5° dec; uv max (95% EtOH) 217 mμ (log ε 4.25), 242 (infl, 3.82), 222 (4.24), 249 (3.67), 342 (4.09); ir (KBr) 3246, 3115 (NH), 2232 (CN), 1629, 1529 (C=O), 820, 811 (doublet), 790, 772 cm^{-1} (cycloalkyl).

Anal. Calcd for $C_{13}H_{16}N_2O$: C, 72.14; H, 7.46; N, 12.96. Found: C, 72.25; H, 7.38; N, 13.01.

(10) V. Prelog and O. Metzler, *Helv. Chim. Acta*, **29**, 1170 (1946).

(11) Cyclic ketones generally react faster than acyclic ketones in carbonyl addition reactions: A. Lapworth and R. H. F. Manske, *J. Chem. Soc.*, 2533 (1928); 1976 (1930).

(12) R. A. Jones and B. D. Roney, *ibid.*, *B*, 84 (1967).

(13) E. M. Godar and R. P. Mariella, *Appl. Spectrosc.*, **15**, 29 (1961).

(14) H. E. Baumgarten, W. F. Murdock, and J. E. Dirks, *J. Org. Chem.*, **26**, 803 (1961).

(15) D. A. Evans, G. F. Smith, and M. A. Wahid, *J. Chem. Soc.*, *B*, 590 (1967).

(16) S. F. Mason, *ibid.*, 4874 (1957).

(17) A. R. Katritzky and R. A. Jones, *ibid.*, 2947 (1960).

(18) R. M. Manyik, F. C. Frostick, J. J. Sandstrom, and C. R. Hauser, *J. Amer. Chem. Soc.*, **75**, 5030 (1953).

5,6,7,8,9,10,11,12,12,14-Decahydro-3-hydroxy-1-methylcyclododeca[c]pyridine-4-carbonitrile (VII).—2-Acetylcyclododecanone was treated as described above except the reaction time was 72 hr. VII, mp 281.5–282° dec, was obtained in 49.6% yield: uv max (95% EtOH) 217 mμ (log ε 4.29), 239 (infl, 3.83), 221 (4.29), 249 (3.59), 341 (4.10); ir (KBr) 3311, 3156 (NH), 2237 (CN), 1631, 1534 (C=O), 829, 778, 769 cm^{-1} (cycloalkyl).

Anal. Calcd for $C_{17}H_{24}N_2O$: C, 74.96; H 8.88; N, 10.29. Found: C, 75.04; H, 8.70; N, 10.27.

6,7,8,9-Tetrahydro-3-hydroxy-1-methyl-5H-cyclohepta[c]pyridine (VIII).—VIII was prepared from V according to the procedure of Prelog and Metzler.[10] Recrystallization from dilute ethanol gave VIII: mp 256.5–257°, in 71% yield; uv max (95% EtOH) 201 mμ (log ε 4.19), 237 (infl, 3.79), 244 (3.72), 305 (3.88); ir (KBr) 3367 (NH), 1650, 1541 (C=O), 842, 759 cm^{-1} (cycloalkyl).

Anal. Calcd for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.71; H, 8.56; N, 7.95.

Registry No.—I, 107-91-5; II, 21297-71-2; III, 21298-56-6; IV, 21298-57-7; V, 21298-58-8; VI, 21298-59-9; VII, 21298-60-2; VIII, 21298-61-3.

Acknowledgment.—We express our thanks to Kay-Fries Chemicals, Inc., for generous samples of malononitrile and malonoamide.

The Reaction of 1-Trimethylsilyl-1,4-dihydropyridine with Ethyl Azidoformate and *p*-Tosyl Isocyanate[1]

EMIL J. MORICONI AND ROBERT E. MISNER[2]

Department of Chemistry, Fordham University, New York, New York 10458

Received January 31, 1969

The recently reported synthesis of 1-trimethylsilyl-1,4-dihydropyridine (**1**) and its base-catalyzed methanolysis product 1,4-dihydropyridine (**2**)[3] should have normally spurred an intense study of the chemistry of these very reactive substrates.[4] To date, we have not seen any study reported.[6]

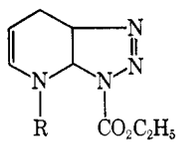
In this Note we report on two reactions of **1** with electrophiles to give ultimately substitution products at different sites. Thus, treatment of **1** with ethyl azidoformate followed by methanolysis led to a 40–55% yield of the tautomeric mixture **3a** ⇌ **3b**.[7] In the infrared the mixture displayed both free (5.79 μ) and bonded (5.90 μ) carbonyl absorptions.

Treatment of 1-phenyl-1,4-dihydropyridine (**6**) with ethyl azidoformate led only to the single product, 1-phenyl-2-carbethoxyimino-1, 2, 3, 4-tetrahydropyridine (**7**) in 35% yield.[8] Adduct **7** is incapable of tautomerism; hence the infrared showed only a single carbonyl absorption at 5.93 μ.

Hydrogenation of **3a** ⇌ **3b** led expectedly to the tautomeric mixture **4a**[9] ⇌ **4b** ($\lambda_{C=O}^{KBr}$ 5.78 and 5.98 μ), while dehydrogenation of **3a** ⇌ **3b** over Pd–C afforded the known ethyl 2-pyridinecarbamate (**5**) (53%)[10] prepared independently from ethyl chloroformate and 2-aminopyridine.[10b]

Treatment of **1** with *p*-tosyl isocyanate afforded N-*p*-tosyl-1-trimethylsilyl-1,4-dihydronicotinamide (**8**), in addition to large amounts of an insoluble, unidentified material (Scheme I).

Generally, dihydropyridines are obtainable from pyridine quaternary salts *via* sodium amalgam or borohydride reductions.[5,11,12] Thus, Saunders and Gold[5] obtained 1-phenyl-1,2-dihydropyridine (60%) on sodium or potassium borohydride reduction of 1-phenylpyridinium chloride (**12**), and the 1,4 isomer (**6**, 70%) using sodium amalgam.[13] In an effort to prepare 1-benzyl-1,4-dihydropyridine (**11**) as a substrate for reactions previously discussed, the benzylpyridinium cation (**9**) was reduced with sodium amalgam. The only product isolated was 1,1′-dibenzyltetrahydro-4,4′-bipyridyl (**10**),[14] further hydrogenation of which led to the known 1,1′-dibenzyl-4,4′-bipiperidyl.[15] A repetition of the Saunders and Gold effort[5] using Karrer's work-up procedure[13] expectedly led to **6**, in addition to 1,1′-diphenyltetrahydro-4,4′-bipyridyl (**13**, 7%). Sodium borohydride reduction of **9** gave the known 1-benzyl-1,2,5,6-tetrahydropyridine (**14**)[16] and smaller amounts of 1-benzylpiperidine (**15**). Catalytic reduction of **14** afforded **15**.



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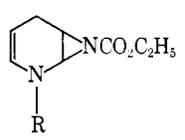
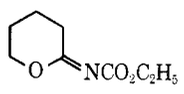


II



III

(1) This research was supported by the Department of the Army, U. S. Army Research and Development Command Office, Office of the Surgeon General, under Contract DA-49-193-MD-2992, and by Public Health Service Research Grant 5 R01 AI-08063-01 from the National Institute of Allergy and Infectious Diseases. This is Contribution No. 533 to the Army Research Program on Malaria.

(2) Abstract from the Ph.D. Thesis of R. E. Misner.

(3) N. C. Cook and J. E. Lyons, *J. Amer. Chem. Soc.*, **88**, 3396 (1966); **87**, 3283 (1965).

(4) For example, these planar 6 π electron heterocycles contain the elements of a cross-conjugated dienamine, and both they and their salts should be responsive to electrophiles and nucleophiles, respectively. Alkylation, however, of 1-phenyl-1,4-dihydropyridine with methyl iodide led only to 1-phenylpyridinium iodide.[5]

(5) M. Saunders and E. H. Gold, *J. Org. Chem.*, **27**, 1439 (1962).

(6) We perhaps can understand why: the reaction of **1** with Br_2, 70% perchloric acid, methyl iodide, ethyl acrylate, chlorosulfonyl isocyanate, carbenes, and Simmons–Smith reagent led to no isolable products.

(7) *Cf.* similar tautomerism observed with 2-amino- and 2-alkylaminotetrahydropyridines [T. B. Grave, *J. Amer. Chem. Soc.*, **46**, 1460 (1924); M. Freifelder, R. W. Mattoon, and Y. H. Ng, *J. Org. Chem.*, **29**, 3730 (1964)].

(8) Mechanistically, products **3** and **7** could be accounted for *via* collapse of such initial adducts as the triazoline I and aziridine II. No such intermediates were experimentally observed, however.

(9) The oxygen analog of **4a**, III, was spectrally inferred as the primary product of the thermal reaction between dihydropyran and ethyl azidoformate. The nmr spectrum of III was quite similar to that of **4a** ⇌ 4b [I. Brown and O. E. Edwards, *Can. J. Chem.*, **43**, 1266 (1965)].

(10) (a) R. L. Shriner and R. G. Child, *J. Amer. Chem. Soc.*, **74**, 549 (1952); (b) A. R. Katritzky, *J. Chem. Soc.*, 2063 (1956).

(11) R. A. Barnes, "Pyridine and its Derivatives," Part I, Vol. 14, E. Klingsberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 77.

(12) F. Liberatore, V. Carelli, and M. Cardellini, *Tetrahedron Lett.*, 4735 (1968).

(13) P. Karrer, G. Schwarzenbach, and G. E. Utzinger, *Helv. Chim. Acta*, **20**, 72 (1937).

(14) A. W. Hoffman, *Ber.*, **14**, 1497 (1881); B. Emmert, *ibid.*, **42**, 1997 (1909).

(15) H. Ochai and K. Kataoka, *J. Pharm. Soc. Jap.*, **62**, 241 (1942).

(16) A. N. Kost, L. G. Yudin, and A. E. Shipov, *Chem. Abstr.*, **52**, 9115*b* (1948); P. S. Anderson, Ph.D. Thesis, University of New Hampshire, Durham, N. H., 1963; V. Petrov and O. Stephenson, *J. Pharm. Pharmacol.*, **14**, 306 (1962).