Anal. Calcd for $C_8H_9N_3O_3$: C, 49.23; H, 4.65; N, 21.53. Found: C, 49.10; H, 4.60; N, 21.66.

2-(*o*-Aminobenzoyl)-1-methylhydrazine (15). A 4.00-g (20.5 mmol) quantity of **14** in 40 ml of EtOH was hydrogenated in a Parr apparatus at 50 psi of hydrogen in the presence of 10% Pd/C (400 mg) for 90 min. Uptake of hydrogen (4 lb) was essentially complete after 10 min. The catalyst was removed by filtration and the filtrate was concentrated and triturated with ether. The resulting solid was collected to yield 3.00 g (89%) of **15** (mp 85–87 °C): mp 90–91 °C (hexane); ir (Nujol) 3430 and 3300 (NH), 1620 cm^{-1} (C=O); NMR ($CDCl_3$) δ 7.34–6.90 (m, 2, aromatic), 6.66–6.32 (m, 2, aromatic), 5.50 (broad s, 4, both NH groups and NH_2), 2.63 (s, 3, CH_3).

Anal. Calcd for $C_8H_{11}N_3O$: C, 58.16; H, 6.71; N, 25.44. Found: C, 57.90; H, 6.56; N, 25.23.

2-Methyl-3-(methylamino)-4(3*H*)-quinazolinone (11). A. From 9. A 1.00-g (4.83 mmol) quantity of **9** was mixed with 20 ml of 10% H_2SO_4, warmed on a hot plate until solution resulted, and then warmed at 80 °C for an additional 30 min. The solution was cooled, basified with NaOH, and extracted with CH_2Cl_2. The extract was dried (Na_2SO_4) and concentrated to yield 710 mg (78%) of **11**: mp 110–111 °C (EtOH); ir (Nujol) 3300 (NH) and 1660 cm^{-1}; (C=O); NMR ($CDCl_3$) δ 8.31–8.10 (m, 1, H ortho to C=O), 7.81–7.24 (m, 3, remaining aromatic), 5.78 (q, J = 6 Hz, 1, NH), 2.81 (d, J = 6 Hz, 3, NCH_3), 2.71 (s, 3, CCH_3). When the NMR sample was shaken with D_2O, the NH signal at δ 5.78 disappeared and the NCH_3 doublet at δ 2.81 collapsed to a singlet at δ 2.81; mass spectrum (70 eV) m/e 189 (molecular ion).

Anal. Calcd for $C_{10}H_{11}N_3O$: C, 63.47; H, 5.86; N, 22.21. Found: C, 63.60; H, 5.85; N, 22.07.

B. From 13. A 1.00-g (4.32 mmol) quantity of **13** was mixed with 10 ml of 10% H_2SO_4 and heated at 80–90 °C for 1 h. The solution was cooled, basified with NaOH, and extracted with CH_2Cl_2. The extracts were dried (Na_2SO_4) and concentrated to afford 480 mg (59%) of crude **11**, mp 97–99 °C, whose ir (Nujol) was identical with that of the material prepared in part A.

C. From 15. A 1.00-g (4.83 mmol) quantity of **15** in 20 ml of triethyl orthoacetate was heated at reflux for 12 h. The solution was concentrated and the resulting solid was crystallized (EtOH) to afford 450 mg (49%) of pure **11**, mp 110–111 °C, whose ir (Nujol) was identical with that of the material prepared in part A.

Registry No.—**1**, 3530-13-0; **2**, 38604-72-7; **3**, 931-54-4; **4**, 5790-59-0; **5**, 40028-55-5; **7**, 610-14-0; **8**, 59169-42-5; **9**, 59169-43-6; **10**, 118-48-9; **11**, 59169-44-7; **13**, 59169-45-8; **14**, 59169-46-9; **15**, 59169-47-0; methylhydrazine, 60-34-4; acetyl chloride, 75-36-5; methylhydrazine HCl, 7339-53-9; triethyl orthoacetate, 78-39-7.

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(4) A. R. McCarthy, W. D. Ollis, A. N. M. Barnes, L. E. Sutton, and C. Ainsworth, *J. Chem. Soc. B*, 1185 (1969).
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(7) (a) M. Wilcox, *J. Med. Chem.*, **11**, 171 (1968); (b) French Patent 1 521 959 (1968); *Chem. Abstr.*, **71**, 3166k (1969); (c) G. Zinner and K. Dorschner, *Arch. Pharm. (Weinheim, Ger.)*, **306**, 35 (1973).
(8) 1-Methyl-4-phenylsemicarbazide (hydrochloride) has been prepared using less direct methods than the one described in Scheme II. 2-Phenyl-3-methyl-5-(phenyl)amino-1,3,4-oxadiazolium chloride, which was prepared from 1-benzoyl-1-methylhydrazine and phenyl isocyanide dichloride, was decomposed in methanol solution to yield **5** HCl.[9a] In addition, 1-methyl-3,3-pentamethylenediaziridine, prepared either from cyclohexanone, ammonia, and methylhydroxylamine-*O*-sulfonic acid or cyclohexanone, methylamine, and hydroxylamine-*O*-sulfonic acid,[9b] was reacted with phenyl isocyanate and subsequently hydrolyzed to **5**.[7c] In both of these syntheses, as in ours, the methylhydrazine derivative employed to introduce the methylhydrazine unit was one in which the *N*-methyl nitrogen was protected.
(9) (a) W. D. Ollis and C. Ramsden, *Chem. Commun.*, 1223 (1971); (b) E. Schmitz, R. Ohme, and R. D. Schmidt, *Chem. Ber.*, **95**, 2714 (1962).
(10) A mixture of hydrazide **15** and 1-(*o*-aminobenzoyl)-1-methylhydrazine were produced in a 15:85 ratio, respectively, by the reaction of isatoic anhydride with methylhydrazine in DMF. The authentic sample of **15** produced as shown in Scheme IV was used to identify its presence in the mixture.[11]
(11) S. Sunder, N. P. Peet, and D. L. Trepanier, *J. Org. Chem.*, preceding paper in this issue.
(12) F. E. Condon, *J. Org. Chem.*, **37**, 3615 (1972).
(13) Melting points are uncorrected. Ir spectra were recorded with a Perkin-Elmer 727B instrument; NMR spectra with a Varian T-60 spectrometer; and mass spectra with a Hitachi RMU-6D mass spectrometer. Combustion analyses were performed by Dow Analytical Laboratories.
(14) The procedure described is based on several reactions.
(15) The atmosphere in the reaction vessel is foggy during the addition. Vigorous stirring during the addition appears to increase the ratio of monoacylated to diacylated product. Midway through the addition a white precipitate is observed.
(16) The dried, white, crystalline solid is methylhydrazine hydrochloride, (mp 78–79.5 °C), weighing 80–82 g, and is analytically pure. Anal. Calcd for CH_7ClN_2: C, 14.55; H, 8.54; N, 33.93. Found: C, 14.50; H, 8.49; N, 34.28.
(17) The separation is easily effected with a 1 × 10 cm vacuum-jacketed Vigreux column (ca. three theoretical plates).
(18) The NMR spectrum of **1** indicated the presence of two conformers, with the inside, slightly more intense, set of singlets belonging to the methyl groups of one rotamer and the outside set to the methyl groups of the other. An NMR study on the conformer proportions of 1-acetyl-1-methylhydrazine in polar and nonpolar solvents is reported.[19] The NMR spectrum also indicated the absence of significant amounts of 1-acetyl-2-methylhydrazine, whose NMR spectrum ($CDCl_3$) is recorded.[3]
(19) P. Bouchet, J. Elquero, R. Jacquier, and J. M. Pereillo, *Bull. Soc. Chim. Fr.*, 2264 (1972).
(20) 1,2-Diacetylmethylhydrazine (bp 280 °C) has been prepared by reacting methylhydrazine with excess acetic anhydride: A. Michaelis and E. Hadanck, *Ber.*, **41**, 3285 (1908).
(21) The isatoic anhydride (mp 243–247 °C dec, colorless prisms) used in this reaction was prepared as described by N. P. Peet and S. Sunder, *J. Org. Chem.*, **39**, 1931 (1974), from methyl anthranilate.

Synthesis of 3,4-Dihydro- and 1,4-Dihydro-5*H*-1,3,4-benzotriazepin-5-ones

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2-Aminobenzoic acid 1-methylhydrazides (**1**) react with ortho esters to yield 3,4-dihydro-(**2a–o**) and 1,4-dihydro-5*H*-1,3,4-benzotriazepin-5-ones (**3a–h**). Proton magnetic resonance studies were employed to define the predominant tautomer in the tautomeric members of the benzotriazepine class.

The synthetic interest in benzodiazepines arising from their well-established role as potential psychotherapeutics has prompted investigations into their nitrogen homologues, the benzotriazepines. Several studies have reported the preparation of members of the 1,3,4-benzotriazepine family[1–6] but the synthetic methods were not unambiguous and could easily have generated isomeric five- or six-membered heterocyclics. In fact, several of these earlier syntheses were recently called into question and the alternate structures established.[7]

The availability of authentic 2-aminobenzoic acid 1-methylhydrazides[8] ensures that cyclization with a one carbon insertion unit will involve the ortho amino and the β nitrogen

Table I. 2-Aminobenzoic Acid 1-Methylhydrazides

Registry no.	Compd	X	R	Yield, %	Bp, °C (mm) (mp, °C)	Formula	Anal.[a]
59169-69-6	1a[b]	H	H	84.5	154–155 (0.35)	$C_8H_{11}N_3O$	CHN
59169-70-9	1b[b]	Cl	H	82.5	162–163 (0.20)	$C_8H_{10}ClN_3O$	CHN
59169-71-0	1c	Br	H	67.3	(100.0–100.5)[c]	$C_8H_{10}BrN_3O$	CHN
59169-72-1	1d	NO_2	H	69.5	(160.0–160.5)[d]	$C_8H_{10}N_4O_3$	CHN
59169-73-2	1e[b]	H	CH_3	86.0	157–158 (0.80)	$C_9H_{13}N_3O$	CHN
59169-74-3	1f	Cl	CH_3	81.2	160–163 (0.07)	$C_9H_{12}ClN_3O$	CH
59169-75-4	1g	NO_2	CH_3	58.0	(189.0–189.5)[d]	$C_9H_{12}N_4O_3$	CHN

[a] Analytical data were within ±0.3% for indicated elements. Ed. [b] Previously reported: R. W. Leiby and N. D. Heindel, *Synth. Commun.*, in press. [c] Recrystallized from 95% ethanol. [d] Recrystallized from dioxane.

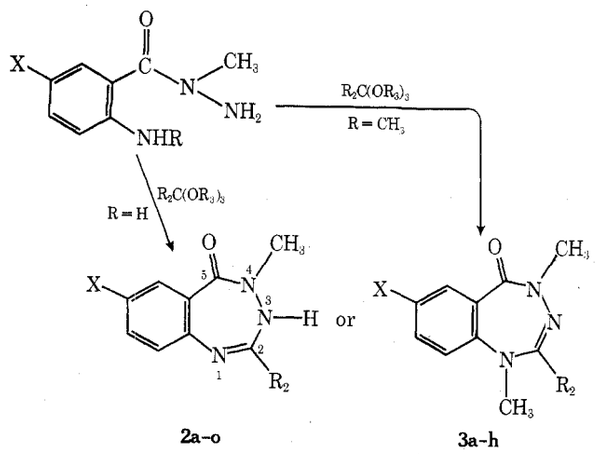
Table II. Benzotriazepinones[a]

Registry no.	Compd	X	R_2	Yield, %	Mp, °C	Formula
59169-76-5	2a	H	H	89	162.0–162.5	$C_9H_9N_3O$
59169-77-6	2b	Cl	H	72	222.0–223.5	$C_9H_8ClN_3O$
59169-78-7	2c	Br	H	73	256.5–257.0	$C_9H_8BrN_3O$
59169-79-8	2d	NO_2	H	71	270.5–271.0	$C_9H_8N_4O_3$
59169-80-1	2e	H	CH_3	58	133.0–133.5	$C_{10}H_{11}N_3O$
59169-81-2	2f	Cl	CH_3	61	227–228	$C_{10}H_{10}ClN_3O$
59169-82-3	2g	Br	CH_3	58	226–227	$C_{10}H_{10}BrN_3O$
59169-83-4	2h	NO_2	CH_3	84	277–278	$C_{10}H_{10}N_4O_3$
59169-84-5	2i	Cl	C_2H_5	68	167–168	$C_{11}H_{12}ClN_3O$
59169-85-6	2j	Br	C_2H_5	46	176.0–176.5	$C_{11}H_{12}BrN_3O$
59169-86-7	2k	NO_2	C_2H_5	85	203–205	$C_{11}H_{12}N_4O_3$
59169-87-8	2l	H	C_6H_5	68	165–166	$C_{15}H_{13}N_3O$
59169-88-9	2m	Cl	C_6H_5	64	240–241	$C_{15}H_{12}ClN_3O$
59169-89-0	2n	Br	C_6H_5	51	247–248	$C_{15}H_{12}BrN_3O$
59169-90-3	2o	NO_2	C_6H_5	69	295–296	$C_{15}H_{12}N_4O_3$
59169-91-4	3a	H	H	53	102.5–103.5	$C_{10}H_{11}N_3O$
59169-92-5	3b	Cl	H	61	166.0–166.5	$C_{10}H_{10}ClN_3O$
59169-93-6	3c	NO_2	H	57	225–227	$C_{10}H_{10}N_4O_3$
59169-94-7	3d	H	CH_3	77	150.5–151.5	$C_{11}H_{13}N_3O$
59169-95-8	3e	Cl	CH_3	64	131–132	$C_{11}H_{12}ClN_3O$
59169-96-9	3f	NO_2	CH_3	44	185.5–186.0	$C_{11}H_{12}N_4O_3$
59169-97-0	3g	NO_2	C_2H_5	42	149.5–150.0	$C_{12}H_{14}N_4O_3$
59169-98-1	3h	Cl	C_6H_5	27	104.0–105.5	$C_{16}H_{14}ClN_3O$

[a] Analytical data were within ±0.3% for C, H, N. Ed. All components were recrystallized from ethanol except **3c**, which was sublimed in vacuo, and **2o**, which was recrystallized from dioxane.

of the hydrazide and produce a benzotriazepine. Treatment of these substituted 2-aminobenzoic acid 1-methylhydrazides (**1a–g**) (see Table I) with ortho esters resulted in 3,4-dihydro- (**2a–o**) and 1,4-dihydro-5*H*-1,3,4-benzotriazepin-5-ones (**3a–h**) (Scheme I).

Scheme I[a]

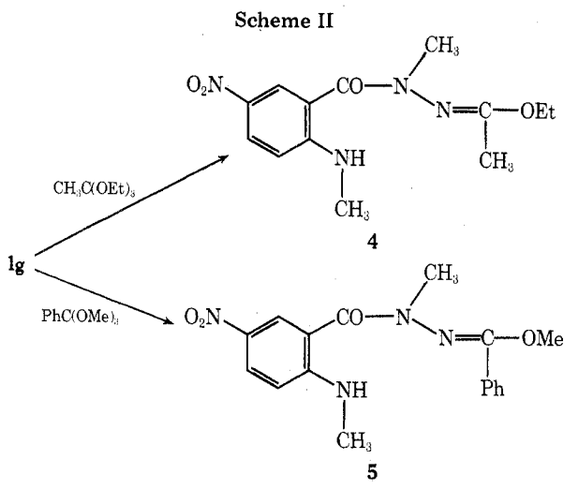


[a] Ortho esters employed were triethyl orthoformate, triethyl orthoacetate, triethyl orthopropionate, and trimethyl orthobenzoate.

Although the hydrazides normally yield the benzotriazepines directly, it appears that the stepwise mechanism for the cyclization involves initial condensation with the more nucleophilic hydrazide nitrogen with subsequent closure by the anilino nitrogen on the ortho ring position. In **1g** the reduced nucleophilicity of the ortho amino and a degree of steric hindrance imparted by the *N*-methylamino substituent and the choice of ortho ester permitted the isolation of two noncyclized adducts. Reaction of 2-methylamino-5-nitrobenzoic acid 1-methylhydrazide (**1g**) with triethyl orthoacetate and trimethyl orthobenzoate was found to give 2-methylamino-5-nitrobenzoic acid 2-*N*-(1-ethoxy)ethylidene-1-*N*-methylhydrazide (**4**) and 2-methylamino-5-nitrobenzoic acid 2-*N*-(1-methoxy)benzylidene-1-*N*-methylhydrazide (**5**), respectively (Scheme II). In addition to the orthoacetate intermediate (**4**), the benzotriazepine (**3f**) was also isolated. These compounds displayed characteristic N–H absorbances at 3380 cm^{-1} and strong C–O ether absorptions at 1300 cm^{-1} in the infrared. The ^1H NMR spectra displayed the 2-methylamino methyl protons as doublets and the corresponding amine protons as quartets. The expected resonances for the ethoxy and methoxy groups were also present in the respective ^1H NMR spectral data.

Assignment of the potentially tautomeric nitrogen–carbon double bond in the benzotriazepines **2a–o** can be made by spectral comparisons with model compounds. Benzotriazepines **3a–h** derived from the 2-*N*-methylaminobenzoic acid hydrazides, with the unsaturation at C_2–N_3, show N_4-methyl

Scheme II

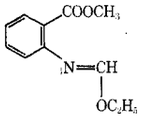


resonances at δ 3.32 ± 0.06 ppm whereas the corresponding methyl signal appears at 3.14 ± 0.05 in the noncyclic *N*-2-methylaminobenzoic acid hydrazide precursors. In **4** and **5** the hydrazide *N*-methyl signal was located at 3.30 ppm. The downfield shift of approximately 10 Hz which was observed for the N_4-methyl resonance in each compound is in accord with the expected additional deshielding provided by the adjacent C_2–N_3 double bond.

The benzotriazepines (**2a–o**) prepared from the 2-aminobenzoic acid hydrazides might be 3,4-dihydro or 1,4-dihydro tautomers. The assignment as 3,4-dihydro-5*H*-1,3,4-benzotriazepin-5-ones **2** is based on the position of their N_4-methyl signals (3.19 ± 0.06 ppm) compared to those in the noncyclic hydrazide precursors (3.14 ± 0.05 ppm). This deshielding presumably arises from the more rigid geometry in the heterocyclic product which constrains the NCH_3 to the nodal plane of the hydrazide carbonyl. In earlier studies on the cyclization of *N*-methylanthranilamides to quinazolinones[9] we observed a similar downfield shift of the amidic *N*-methyl of approximately 3 Hz in the cyclized product compared to the acyclic precursor. Much greater deshielding of the N_4-methyl resonance in the benzotriazepines would be expected if the tautomeric double bond localized at the C_2–N_3 locus.

Ultraviolet spectra (see Table III) of a fixed bond isomer (**3a**), a potentially tautomeric compound (**2a**), and a synthetic

Table III. Ultraviolet Spectral Data

Compd	λ, nm	Log ε
2a	331	2.76
	282	3.63
	251	4.28
	233	4.47
3a	320	2.86
	278	3.70
	257	4.15
	237	4.40
	338	3.62
	312	3.72
	253	4.14
	227	4.62

6

model with imino unsaturation at the ortho-amino function (**6**) also indicate the N_1–C_2 tautomer. Not only does **2a** have a longer λ_{max} (in accord with the expected benzenoid overlap of its potential N_1–C_2 unsaturation), but it also displays a closer spectral similarity to the imino model than does **3a**.

Experimental Section

Infrared spectra were obtained in KBr on a Perkin-Elmer 257 spectrophotometer. A Hitachi Perkin-Elmer R20A nuclear magnetic resonance spectrometer was employed to obtain the ^1H NMR spectra. Combustion analyses were provided by Dr. G. I. Robertson, Florham Park, N.J.

Preparation of 2-Aminobenzoic Acid 1-Methylhydrazides (1). The ring opening of isatoic anhydrides by methylhydrazine to yield **1a, 1b,** and **1e** was described in a publication from these laboratories.[8] Additional compounds obtained by this route are listed in Table I.

Preparation of Benzotriazepinones 2a–o and 3a–h. The requisite benzoic acid hydrazide (**1a–g**) was suspended in a 25% excess of an orthoester and stirred at reflux until solution resulted. Heating and stirring were continued for an additional 4 h unless precipitation of solid terminated the agitation. After chilling of the reaction mixture the crystals were filtered, washed quickly with cold ether, and recrystallized from ethanol (properties and exceptions are noted in Table II). The nitrobenzoic acid hydrazide (**1g**) required modified reaction conditions and cyclization was considerably less facile.

7-Nitro-1,2,4-trimethyl-1,4-dihydro-5*H*-1,3,4-benzotriazepin-5-one (3f) and 2-Methylamino-5-nitrobenzoic Acid 2-*N*-(1-Ethoxyethylidene)-1-*N*-methylhydrazide (4). 2-Methylamino-5-nitrobenzoic acid 1-methylhydrazide (**1g,** 11.22 g, 0.050 mol) was added to 40 ml of 2-methoxyethyl ether. The mixture was heated to reflux, whereupon solution occurred. To the refluxing solution was then dropwise added, over a period of 30 min, 8.50 g (0.050 mol) of triethyl orthoacetate. After 20 h, refluxing was terminated, and while still warm, the solution was concentrated in vacuo. The viscous liquid which resulted was stirred vigorously in ether, to induce crystallization. The solid was lixiviated with ether. Evaporation of the ether gave **4** as a yellow solid. Recrystallization of the product from ether afforded 1.85 g (15%) of **4** as fine needles: mp 127.0–127.5 °C; ir (KBr) 3380 (N–H), 1660 (shoulder C=O), 1610 (C=N), 1320 cm^{-1} (C–NO_2); NMR ($CDCl_3$) δ 1.21 (t, 3, CH_2CH_3), 1.87 [s, 3, N=C(CH_3)OEt], 2.93 (d, 3, NHCH_3), 3.30 (s, 3, hydrazide CH_3), 4.14 (q, 2, CH_2CH$_3$), 6.67 (d, J = 9 Hz, 1, ArH_3), 7.07 (q, 1, NH), 8.10 (d, J = 9 Hz, 1, ArH_4), 8.30 (s, 1, ArH_6).

Anal. Calcd for $C_{13}H_{18}N_4O_4$: C, 53.10; H, 6.16; N, 19.06. Found: C, 52.88; H, 6.27; N, 18.85.

The solid which remained after lixiviation was recrystallized from ethanol, affording 5.40 g (44%) of **3f** as fine yellow needles: mp 185.5–186.0 °C; ir (KBr) 1660 (shoulder C=O), 1635 (C=N), 1600 (Ar, C=C), 1520 and 1340 cm^{-1} (C–NO_2); NMR ($CDCl_3$) δ 2.18 (s, 3, C_2CH_3), 3.20 (s, 3, N_1CH_3), 3.34 (s, 3, N_4CH_3), 7.04 (d, J = 9 Hz, 1, H_9), 8.21 (d, J = 9 Hz, 1, H_8), 8.70 (s, 1, H_6).

2-Methylamino-5-nitrobenzoic Acid 2-*N*-(1-Methoxy)benzylidene-1-*N*-methylhydrazide (5). 2-Methylamino-5-nitrobenzoic acid 1-methylhydrazide (**1g,** 6.72 g, 0.030 mol) and 2-methoxyethyl ether (40 ml) were heated to reflux and treated, by dropwise addition, with 6.35 g (0.03 mol) of trimethyl orthobenzoate. After 20 h of refluxing, the solvent and other volatile products were removed in vacuo. Crystallization of the brown liquid was effected by vigorous stirring in ether followed by addition of petroleum ether. The solid which slowly precipitated was washed with ether and was dried in vacuo; 6.30 g (68%) of **5** was obtained. Recrystallizations from ethanol afforded **28** as analytically pure needles: mp 155.0–155.5 °C; ir (KBr) 3380 (N–H), 1655 (shoulder C=O), 1625 (C=N), 1580 (Ar, C=C), 1540 and 1320 cm^{-1} (C–NO_2); NMR ($CDCl_3$) δ 2.64 (d, 3, NHCH_3), 3.30 (s, 3, hydrazide CH_3), 3.98 (s, 3, OCH_3), 6.22 (q, 1, NH), 6.41 (d, J = 9 Hz, 1, ArH_6), 7.00–7.50 (m, 5, C_6H_5), 7.94–8.32 (m, 2, ArH_3 and -H_4).

Anal. Calcd for $C_{17}H_{18}N_4O_4$: C, 59.66; H, 5.30; N, 16.38. Found: C, 59.72; H, 5.47; N, 16.28.

Methyl 2-Ethoxymethyleneiminobenzoate (6). A mixture of 75.5 g (0.50 mol) of methyl anthranilate and 111.0 g (0.75 mol) of triethyl orthoformate was heated to reflux. The ethanol which was given off was collected in a Barrett receiver and was removed as it accumulated. Refluxing was terminated after 75 ml (58 g) of ethanol had accumulated. The excess ortho ester was evaporated in vacuo giving a dark red liquid. The product was purified by distillation under reduced pressure with the product fraction distilling at 92–97 °C under 0.1–0.03 mm. The ester (46.0 g) was obtained in 45% yield. An additional distillation afforded analytically pure ester: bp 91 °C (0.1 mm); ir (neat) 1735 (C=O), 1655 (C=N), 1185 and 1075 cm^{-1} (C–O); NMR (neat) δ 1.25 (t, 3, CH_2CH_3), 3.70 (s, 3, OCH_3), 4.24 (q, 2, CH_2CH$_3$), 6.60–7.45 (m, 3, ArH_3, -H_4, -H_5), 7.51 (s, 1, N=CHOEt), 7.75 (d, J = 8 Hz, 1, ArH_6).

Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32; N, 6.76. Found: C, 63.75; H, 6.33; N, 6.54.

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Registry No.—**4,** 59169-99-2; **5,** 59170-00-2; **6,** 59204-51-2; triethyl orthoformate, 122-51-0; triethyl orthoacetate, 78-39-7; triethyl orthopropionate, 115-80-8; trimethyl orthobenzoate, 707-07-3; methyl anthranilate, 134-20-3.

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Preparation of New Nitrogen-Bridged Heterocycles. Reaction of Pyridinium *N*-Imines with Azirine Derivatives

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Monocyclic and bicyclic pyridinium *N*-imine salts **2–5, 10–12,** and **16–19** reacted smoothly with 2-phenylazirine (**1**) in the presence of alkali at room temperature to give the corresponding 3-phenyl-1,9a-dihydro-2*H*-pyrido[1,2-*b*]-*as*-triazine derivatives **6–9, 13–15,** and **20–24** in fairly good yields, and quinolinium **26** and isoquinolinium *N*-imine dimer **27** reacted with 2,3-diphenylazirine **25** in refluxing benzene to afford 2,3-diphenyldihydropyridotriazines **28** and **29** in 90 and 93% yields, respectively. Utility of pyridinium *N*-imine as a trapping agent for transient azirine was proven in Neber reaction of acetophenone oxime *O*-tosylate **30** in the presence of pyridinium *N*-imines. Structural elucidation of these products was accomplished by physical and spectral means and by comparison with similar pyridotriazines prepared earlier by us. Possible mechanisms of this reaction are also discussed.

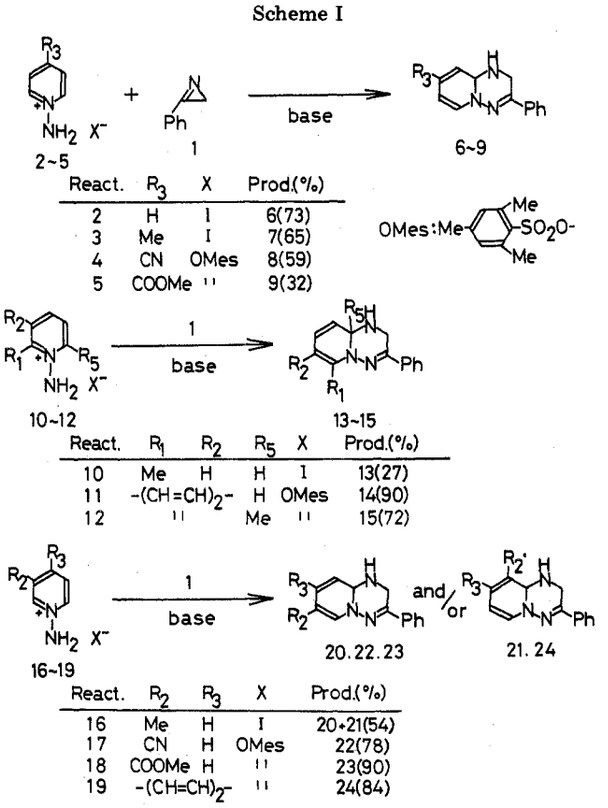
The unexpected formation of several 1,9a-dihydro-2*H*-pyrido[1,2-*b*]-*as*-triazine derivatives from the reactions of pyridinium *N*-imines with α-haloacrylates[1] prompted us to examine the possible intermediates involved in this reaction and to find a new synthetic route for this class of compound using such intermediates. Mechanistic consideration suggested intervention of a haloaziridine or azirine derivative, and support for the latter intermediate was obtained from the reaction of pyridinium *N*-imine with 2-phenylazirine.[2] The reaction with azirines is superior to that with α-haloacrylates for preparation of dihydropyridotriazines, since extension to a wide variety of pyridinium *N*-imines is possible and the yields are generally high. This paper describes preparation of 1,9a-dihydro-2*H*-pyrido[1,2-*b*]-*as*-triazines from the reactions of various pyridinium *N*-imines with azirines and the trapping of transient azirine using pyridinium *N*-imine.

Results and Discussion

Reactions of Pyridinium *N*-Imines with Azirine Derivatives. The reactions of pyridinium *N*-imine salts **2–5, 10–12,** and **16–19** with 2-phenylazirine **1** were carried out in methylene chloride or chloroform in the presence of potassium carbonate or basic ion-exchange resin (Amberlite IRA 410) at room temperature. These results are summarized in Scheme I.

The reactions of the parent **2** and 4-substituted pyridinium *N*-imine salts **3–5** with azirine **1** gave the corresponding adducts **6–9** in 73, 65, 59, and 32% yields, and those of 2-substituted *N*-imine salts **10–12** afforded also adducts **13–15** in 27 (crude), 90, and 72% yields, respectively. In the latter cases, decreased yields of the adduct due to steric hindrance of the 2-substituent on the pyridine ring were observed with the monocyclic *N*-imine salt **10,** but not in the bicyclic compounds **11** and **12.** Similar reactions of unsymmetrically substituted

Scheme I



pyridinium *N*-imine salts **16–19** gave regioselectively or regiospecifically the corresponding products **20** and **21, 22, 23,** and **24** in 54 (total yield), 78, 90, and 84% yields. The ratio of