Anal. Calcd for $C_{19}H_{20}N_2O_2$: C, 74.00; H, 6.54; N, 9.09. Found: C, 74.16; H, 6.46; N, 9.15.

1-Benzoyl-4-formyl-4-methyl-5-phenyl-1,4-dihydropyridazine (6b).—To 500 mg (1.31 mmol) of the aldehyde **5b** dissolved in 30 ml of CH_2Cl_2 was added 300 mg of *N*-bromosuccinimide in 8.0 ml of pyridine. After the solution had stood for 6 hr at room temperature, 16.5 ml of iced, concentrated HCl was added and the organic phase was washed, dried, and evaporated. Addition of ether and chilling gave 380 mg (76%) of off-white crystals in two crops, mp (first crop) 111–113°. Recrystallization from methylene chloride–ether gave white crystals of **6b**: mp 113–114°; ν^{KBr} 1670, 1720 cm^{-1}; δ^{CDCl_3} 1.48 (s, 3), 6.52 (s, 1), 7.1–7.8 (m, 11), 7.85 ppm (s, 1).

Anal. Calcd for $C_{19}H_{16}N_2O_2$: C, 74.98; H, 5.30; N, 9.21. Found: C, 75.09; H, 5.13; N, 9.12.

1-Benzoyl-4-methyl-5-phenyl-1,4-dihydropyridazine (7b).—To 200 mg (0.658 mmol) of **6b** dissolved in 20 ml of methanol was added 0.4 ml (0.7 mmol) of 10% potassium hydroxide. After the solution had stood for 20 min at 25°, 93 mg of white crystals of **7b** had precipitated from the solution. These crystals were collected and washed with cold methanol, mp 142–143°. The filtrate was neutralized with HCl, concentrated, and extracted with CH_2Cl_2. The organic layer was dried and evaporated to an oil. Addition of ether gave 13 mg of 7b, mp 141–143°, total yield 106 mg (58%). Recrystallization from ether–methylene chloride raised the melting point to 142.5–143°; ν^{KBr} 1650 cm^{-1}; δ^{CDCl_3} 1.26 (d, 3, J = 7.0 Hz), 3.55 (q of d, 1, $J_{4,4\text{-}CH_3}$ = 7.0, $J_{3,4}$ = 3.6 Hz), 6.95 (d, 1, J = 3.6 Hz), 7.15–7.75 (m, 10), 7.90 ppm (s, 1).

Anal. Calcd for $C_{18}H_{15}N_2O$: C, 78.23; H, 5.84; N, 10.14. Found: C, 78.05; H, 5.72; N, 10.18.

Conversion of 6b to 4-Methyl-5-phenylpyridazine (9).—To a solution of 100 mg (0.327 mmol) of the 4-formyl-1,4-dihydropyridazine **6b** in 30 ml of methanol was added 1.5 ml (2.7 mmol) of 10% KOH. After 1 hr at 25° the reaction mixture was neutralized with 1 *N* HCl. The methanol was then removed *in vacuo* under nitrogen, chloroform was added to the remaining oil, and this solution was washed with $NaHCO_3$ and water and dried. The chloroform layer was evaporated under N_2. An nmr spectrum ($CDCl_3$) indicated equal amounts of 4-methyl-5-phenylpyridazine (**9**) [δ^{CDCl_3} 2.28 (s, 3), 7.05–755 (m), 8.95 (s, 1), 9.02 (s, 1)] and 4-methyl-5-phenyl-1,4-dihydropyridazine (**8**) [δ^{CDCl_3} 1.03 (d, 3, J = 6.8 Hz), 3.3–3.6 (m, 1), 6.62 (d, 1, J = 4 Hz)]. Oxygen was then bubbled through the solution for 15 min. An nmr spectrum of the black solution showed mostly 4-methyl-5-phenylpyridazine with some of the dihydro compound **8** remaining. After 45 min of oxygenation the nmr showed only 4-methyl-5-phenylpyridazine and a few impurity peaks. The solution was then evaporated and the residue was distilled in a short-path sublimer at 73°. The distillate crystallized on the cold finger upon the addition of a seed crystal of authentic 4-methyl-5-phenylpyridazine. The sublimation was continued and gave 25 mg (45%) of colorless crystals, mp 80–82° (lit.[9] 82–84°). Resublimation raised the melting point to 82–83°. The infrared spectrum was identical with a spectrum of authentic 4-methyl-5-phenylpyridazine.

Competition of Thermal and Acid-Catalyzed Reactions of 3b.—Alcohol **3b** (31 mg) and 11 or 22 mg of benzoic acid were dissolved in 1 ml of benzene and placed in a test tube with a 6-cm glass rod sealed to the bottom as a stem. The solution was frozen in an ice–salt bath and the tube was sealed and supported on the stem above the liquid level of a refluxing solvent (toluene, benzene, or acetone). After 18 hr (72 hr with acetone bath) the tubes were opened, benzene was evaporated, and nmr spectra were taken in $CDCl_3$. The composition of the mixtures were determined by integration of the methyl region of these spectra, which generally contained three peaks: δ 2.15 (oxide **2b**), 1.20 (aldehyde **5b**), and 1.30 (unknown, usually less than 10% of the total integral).

		% of total methyl	
Temp, °C	Acid, mg	2b	5b
110	11	55	35
80	11	90	5
80	22	90	
56	11	80	

Registry No.—**1,** 5109-67-1; **2b,** 36529-44-9; **3b,** 36529-45-0; **3b** benzoate, 36529-46-1; **3b** acetate, 36529-47-2; **4b**, 36529-55-2; **5a**, 36529-56-3; **5a,** 1,2-diacetyl derivative, 36529-57-4; **5b**, 36529-58-5; **5b,** 36529-58-5; **5b** 1,2-bibenzoyl derivative, 36529-59-6; **6b,** 36529-60-9; **7b,** 36529-61-0; 1-benzoyl-4-methyl-5-phenyl-1,2,3,4-tetrahydropyridazine-4-methanol, 36529-62-1.

Heterocyclic Studies. 38. Rearrangement of a 9-Acyl-1,9-diazabicyclo[4.2.1]nonadienone to a Pyrrolo[1,2-*b*]pyridazinone[1]

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Rearrangement of the diazabicyclo[4.2.0] ketone **1** by the action of heat, acid, or base gives the pyrrolopyridazinone **2** plus formaldehyde. The structure of **2** was determined by X-ray crystallography.

We recently reported the formation of the adducts **1** by 1,3-dipolar cycloaddition of thermally generated 1-acyl-2,3-dihydro-1,2-diazepininium betaines and dimethyl acetylenedicarboxylate.[2] We now describe an unusual reaction of these adducts that occurs under a variety of conditions. The major product, obtained in 90–100% yields in methanolic acid or base, or on heating in acetic acid or in a melt, are the pyrrolopyridazinones **2**. The remainder of the molecule, corresponding to CH_2O, was identified as formaldehyde.

Structure of 2.—The structure of **2a** was determined by X-ray crystal structure analysis. Figure 1 is a perspective view of the molecule from a point about 45° from the normal to the plane of the ring system. Hydrogen atoms are excluded for clarity. Bond distances and angles are given in Table I and II.[3]

The structure of the molecule in the crystal is such that the phenyl ring and nearest methoxy group are nearly perpendicular (89°) to the central ring system plane while the bromophenyl group is about 45° with

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(1) Supported in part by Grant GP-9322 from the National Science Foundation.

(2) O. S. Rothenberger and J. A. Moore, *J. Org. Chem.*, **37**, 2796 (1972).

(3) Tables of fractional coordinates, thermal parameters, and structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JOC-72-3774. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

TABLE I

INTERATOMIC BOND DISTANCES FOR NONHYDROGEN ATOMS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR 2

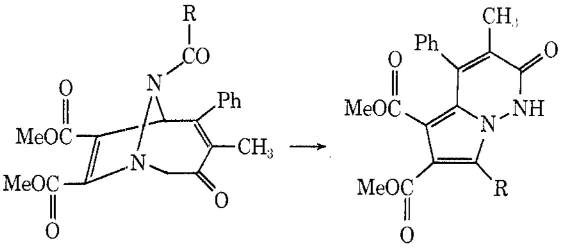
Atom 1	Atom 2	Distance, Å
Br	C74	1.909 (8)
C74	C73	1.358 (10)
C73	C72	1.390 (12)
C72	C71	1.409 (10)
C71	C76	1.361 (9)
C76	C75	1.402 (11)
C75	C74	1.377 (10)
C71	C7	1.467 (11)
C7	C6	1.393 (10)
C6	C61	1.454 (12)
C61	0611	1.182 (11)
C61	0612	1.316 (11)
0612	C62	1.421 (13)
C6	C5	1.405 (11)
C5	C51	1.479 (11)
C51	0511	1.200 (10)
C51	0512	1.335 (11)
0512	C52	1.449 (11)
C5	C4A	1.369 (10)
C4A	C4	1.438 (12)
C4	C41	1.489 (12)
C41	C42	1.360 (16)
C42	C43	1.387 (17)
C43	C44	1.389 (20)
C44	C45	1.317 (20)[a]
C45	C46	1.393 (17)
C46	C41	1.371 (15)
C4	C3	1.348 (11)
C3	C31	1.504 (12)
C3	C2	1.433 (11)
C2	02	1.333 (9)
C2	N1	1.303 (10)
N1	N8	1.378 (8)
N8	C7	1.375 (10)

[a] This is shorter than the normal C–C bond distance in an aromatic ring; the difference is probably not significant.

TABLE II

INTERATOMIC BOND ANGLES AND THEIR ESTIMATED STANDARD DEVIATIONS FOR NONHYDROGEN ATOMS OF 2

Atom 1	Central atom	Atom 3	Angle, deg
Br	C74	C75	117.0 (5)
Br	C74	C73	118.4 (6)
C73	C74	C75	124.6 (7)
C74	C75	C76	116.3 (6)
C75	C76	C71	122.4 (7)
C76	C71	C72	118.1 (7)
C71	C72	C73	121.3 (6)
C72	C73	C74	117.2 (7)
C7	C71	C76	121.7 (7)
C7	C71	C72	120.2 (6)
N8	C7	C71	123.7 (6)
N8	C7	C6	104.4 (7)
C71	C7	C6	131.7 (7)
C7	C6	C61	129.7 (7)
C6	C61	0611	124.5 (8)
C6	C61	0612	116.4 (7)
0611	C61	0612	118.6 (9)
C61	0612	C62	118.9 (7)
C7	C6	C5	109.7 (6)
C61	C6	C5	120.1 (7)
C6	C5	C51	126.1 (6)
C6	C5	C4A	107.4 (7)
C51	C5	C4A	126.5 (7)
C5	C51	0511	127.1 (8)
C5	C51	0512	111.1 (7)
0511	C51	0512	121.8 (7)
C51	0512	C52	116.0 (6)
C5	C4A	C4	136.8 (7)
C5	C4A	N8	106.8 (7)
N8	C4A	C4	116.4 (6)
C4A	C4	C41	117.3 (7)
C41	C42	C43	122.4 (10)
C42	C43	C44	116.9 (11)
C43	C44	C45	121.7 (12)
C44	C45	C46	120.8 (11)
C45	C46	C41	119.6 (10)
C41	C4	C3	123.5 (8)
C4A	C4	C3	119.2 (7)
C4	C3	C31	123.2 (7)
C4	C3	C2	118.4 (7)
C31	C3	C2	118.5 (7)
C3	C2	02	118.7 (7)
C3	C2	N1	125.6 (7)
02	C2	N1	115.7 (6)
C2	N1	N8	114.6 (6)
N1	N8	C4A	125.8 (6)
N1	N8	C7	122.4 (6)
C4A	N8	C7	111.7 (6)



1a, R = p-BrC$_6$H$_4$
b, R = C$_6$H$_5$
c, R = CH$_3$

2
+
CH$_2$=O

respect to the same plane. The central ring system is quite flat, the plane being defined by a least-squares fitting process using atoms C41, C4, C3, C31, C2, O2, N1, N8, C7, C71, C6, C61, C5, C51, and C4A; none of these defining atoms are more than 0.22 Å from the least-squares plane and all but three are within 0.1 Å of the defined plane. The molecules are tightly packed in parallel sheets with the plane of the central ring system roughly parallel with the 011 plane of the unit cells. The bond distances of the molecule agree favorably compared to those listed as typical bond lengths.[4] The bond lengths in the central ring system can be seen to have intermediate values consistent with a 10-π aromatic system.

On the Formation of 2.—When the reaction of 1 (R = BrC$_6$H$_4$) was carried out in acetic acid-d_4, two singlet peaks of equal intensity (δ 4.8 and 5.2, total integral 2 with respect to the CH$_3$ singlet) were present in the nmr spectrum of the total reaction mixture in addition to the peaks due to 2. Similar peaks were present in the spectrum of a solution prepared from gaseous CH$_2$O and glacial acetic acid. When the amount of CH$_2$O was increased substantially, the intensity of the singlet at δ 4.8 increased relative to that at δ 5.2, and the δ 4.9 peak became a doublet (J = 2 Hz). The species giving rise to these nmr signals are not known with certainty. No stable compounds such as methylene glycol diacetate are known to be

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(4) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1968.

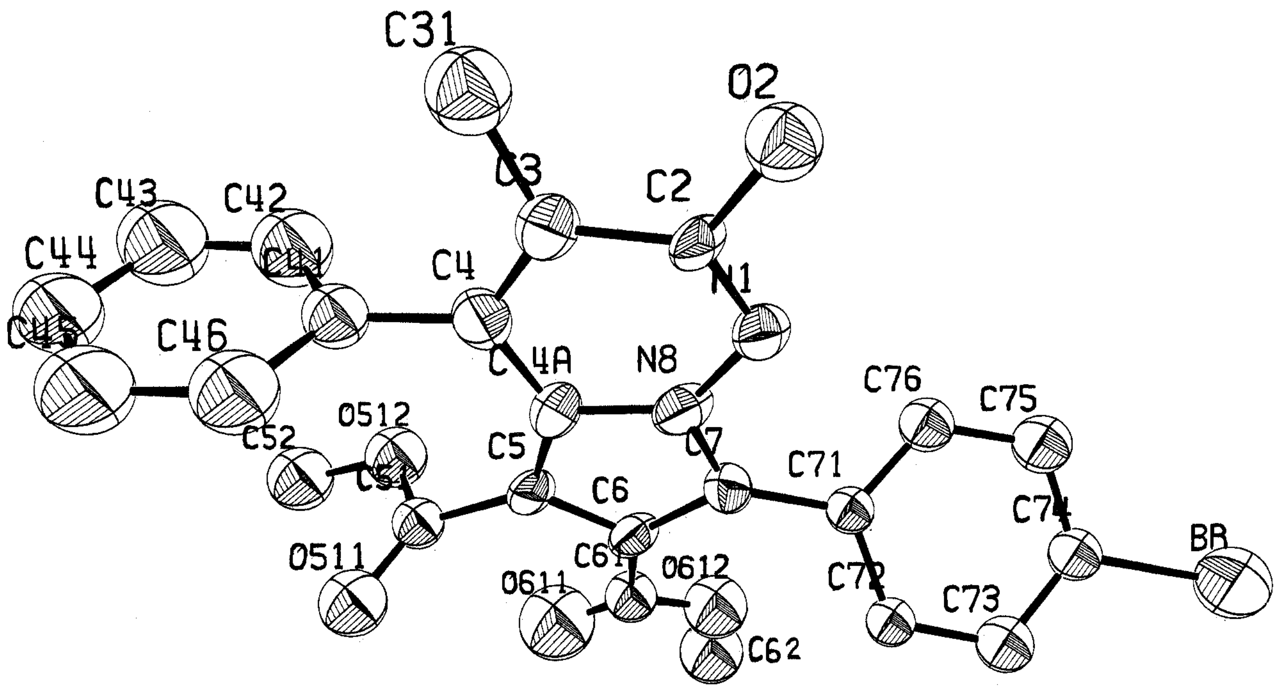
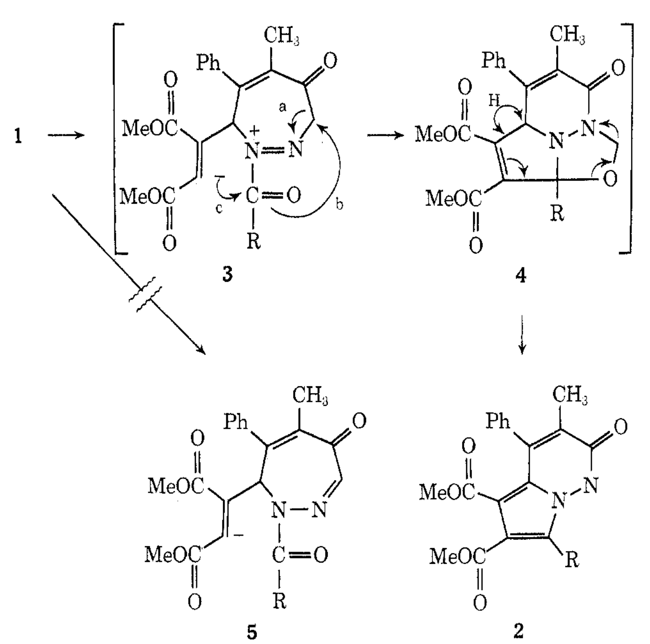


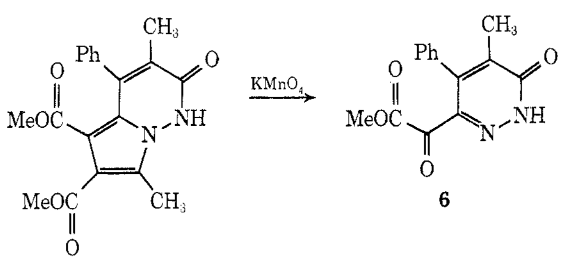
Figure 1.—ORTEP drawing of 2 in perspective with 50% probability thermal ellipsoids (hydrogens are not shown).

formed in HCHO–CH$_3$CO$_2$H solutions.[5] We presume that at low HCHO concentration, the nmr spectrum is due to CH$_3$CO$_2$CH$_2$OCH$_2$OH; at higher concentrations the spectrum may arise from a mixture of this dimethylene glycol monoacetate plus paraldehyde, or from CH$_3$CO$_2$CH$_2$(OCH$_2$)$_n$OH.

The presence of CH$_2$O in the reaction mixture of 1 in acetic acid-d_4 is significant, since it reveals that no deuterium exchange occurs in the CH$_2$ group. The conversion of 1 to 2 must involve breaking the N1–C8 bond at some point; the fact that the CH$_2$ unit remains intact means that at least in acetic acid, this step does not occur by β elimination to 5. Overall, the reaction appears to include the bond changes a, b, and c depicted in 3. The timing of these steps cannot be specified, and the intermediates 3 and 4 represent an arbitrary formalism at this point.



The 10-π aromatic pyrrolo[1,2-*b*]pyridazine system of 2 has been encountered before in a cycloaddition of dimethyl acetylenedicarboxylate and pyridazine.[6] The tautomeric structure 2 is consistent with the properties of the compound; it is a somewhat stronger acid [pK_a (50% aqueous DMF) = 7.8] than the parent 3-pyridazinone [pK_a (H$_2$O) = 10.4[7]]. The chemical properties of 2 were not extensively explored. The compounds are readily oxidized by KMnO$_4$. Very mild oxidation of 2c (R = CH$_3$) gave a product, C$_{14}$H$_{12}$N$_2$O$_4$, in 40% yield. The composition and spectral properties [δ 2.07 (s, 3), 3.85 (s, 3), 12.9 (s, 1); ν 1760, 1720, 1660 cm^{-1}] indicate the glyoxylate structure 6, apparently formed by fortuitously incomplete oxidation under the conditions used. Comparable KMnO$_4$ oxidation to an oxalate product has been reported in other systems.[8]



Experimental Section

7,8-Bis(methoxycarbonyl)-9-*p*-bromobenzoyl-4-methyl-5-phenyl-1,9-diazabicyclo[4.2.1]nona-4,7-dien-3-one (1a).—A suspension of 2.0 g (5.2 mmol) of 2-*p*-bromobenzoyl-5-methyl-4-phenyl-1,2-diazabicyclo[3.2.0]-3-hepten-6-one[9] in 20 ml of

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(5) J. F. Walker, "Formaldehyde," 3rd ed, Reinhold, New York, N. Y., 1964, p 345.

(6) R. L. Letsinger and R. Lasco, *J. Org. Chem.*, **21**, 764 (1956).

(7) A. Albert and J. N. Phillips, *J. Chem. Soc.*, 1294 (1956).

(8) E. Huisgen, M. Morikawa, K. Herbig, and E. Brunn, *Chem. Ber.*, **100**, 1094 (1967).

(9) J. A. Moore, F. J. Marascia, R. W. Medeiros, and R. L. Wineholt, *J. Org. Chem.*, **31**, 34 (1966).

freshly distilled dimethyl acetylenedicarboxylate was heated at 80° for 8 hr. A homogeneous solution resulted after 15 min. After 8 hr the total reaction mixture was chromatographed (silicic acid, $CNCl_3$) to give a pale yellow oil. Crystallization from ether gave 966 mg (32%) of white, crystalline **1a**: mp 181°; ν^{KBr} 1750, 1720, 1650, 1620 cm^{-1}; δ^{CDCl_3} 1.92 (d, J = 1 Hz, 3), 3.43 (s, 3), 3.72 (s, 3), 5.00 (q, J = 1 Hz, H-6), 5.39 (d, J = 4.5 Hz), 5.63 (d, J = 4.5 Hz), 7.13–7.68 (m, 9).

Anal. Calcd for $C_{25}H_{21}N_2O_6Br$: C, 57.15; H, 4.03. Found: C, 56.85; H, 3.84.

5,6-Bis(methoxycarbonyl)-7-*p*-bromophenyl-3-methyl-4-phenylpyrrolo[1,2-*b*]pyridazin-2-one (2a). A. Methanolic Sodium Methoxide.—A 570-mg (1.1 mmol) sample of **1a** was added to a solution of 25 ml of anhydrous methanol containing 0.2 g of sodium methoxide. After slight warming to dissolve **1a** the solution was kept at 25° for 30 min and was then neutralized by the dropwise addition of concentrated HCl. Removal of methanol under vacuum left a solid white residue, which was taken up in CH_2Cl_2. After washing (H_2O), drying ($MgSO_4$), and removal of solvent, there remained a pale yellow solid which was recrystallized from methanol to give 525 mg (97%) of **2a** as fine white needles: mp 262°; ν^{KBr} 1700, 1610 cm^{-1}; δ^{CDCl_3} 1.87 (s, 3), 3.22 (s, 3), 3.63 (s, 3), 7.2–7.7 (m, 10). Slow crystallization from ethanol gave the alcoholate.

Anal. Calcd for $C_{24}H_{19}N_2O_5Br$: C, 57.77; H, 4.63; N, 5.19. Found: C, 57.79; H, 4.30; N, 5.11.

Crystallization from 2-propanol also produced an alcoholate.

Crystals suitable for X-ray analysis were obtained by slowly cooling a hot, saturated solution of **2a** in benzene to 40° during 6 hr and maintaining this temperature for 2 days. This procedure gave very pale yellow cubes whose melting point and ir spectrum were identical with those of a sample crystallized from methanol.

Anal. Calcd for $C_{24}H_{19}N_2O_5Br$: C, 58.19; H, 3.87; *m/e* 494.0478. Found: C, 58.28; H, 3.80; *m/e* 494.0489.

B. Pyrolysis in Melt.—A 105-mg (0.2 mmol) sample of **1a** was heated at 195° in a test tube for 15 min. The smell of formaldehyde was readily apparent. Crystals of **2a** began to form in the liquid melt after 5 min of heating. When the odor of formaldehyde was no longer detectable, the sample was cooled and weighed (98 mg, 99%). Recrystallization from methanol gave **2a**, mp 260–261°; the melting point was unchanged on admixture with **2a** prepared in part A above. In another experiment, the gaseous formaldehyde was led into an ethanol solution of dimedone. Colorless crystals of the methylene bisdione crystallized, mp 189–190° (lit.[10] mp 191–191.5).

C. Acetic Acid.—A solution of 20 mg (0.05 mmol) of **1a** in 0.5 ml of acetic acid-d_4 was heated in an nmr tube at 100°. After 10 min the nmr spectrum indicated a 1:1 mixture of unreacted **1a** and product **2a**. In addition to the signals assignable to **1a** and **2a**, the spectrum contained two singlets of equal intensity at δ 4.8 and 5.2. The nmr spectrum after 30 min at 100° showed complete conversion of **1a** to **2a**. The two singlets at δ 4.8 and 5.2 had a total integral of 2 with respect to the CH_3 singlet of **2a**. Upon cooling, pale yellow crystals formed; the mp and ir spectrum were identical with those of **2a** obtained previously. The conversion of **1a** to **2a** in hot acetic acid proceeded in 90% yield on a preparative scale (200 mg of **1a**).

The nmr spectrum of gaseous formaldehyde (generated thermally from paraformaldehyde) in CD_3CO_2D also exhibits two singlets of nearly equal intensity at δ 4.8 and 5.2. Incremental additions of gaseous formaldehyde increased the intensity of the upfield signal.

D. Methanolic HCl.—A solution of 50 mg (0.1 mmol) of **1a** in 10 ml of methanol and 1 ml of concentrated HCl was heated at 65° for 30 min. Removal of the solvents under reduced pressure and trituration of the oily residue with ether gave 45 mg of crystalline solid. The nmr spectrum of this material showed approximately 15% conversion of **1a** to **2a**. This mixture was redissolved in methanolic HCl and heated to reflux for 18 hr. Work-up as before gave pure **2a** (ir and nmr).

5,6-Bis(methoxycarbonyl)-4,7-diphenyl-3-methylpyrrolo[1,2-*b*]pyridazin-2-one (2b).—A solution of 250 mg (0.56 mmol) of **1b**[2] in 8 ml of methanol was treated with 2 ml of 50% sodium methoxide in methanol. After standing for 20 min at room temperature, the solution was acidified with concentrated HCl and reduced to an oil under reduced pressure. Addition of CH_2Cl_2 followed by washing (H_2O), drying ($MgSO_4$), and concentration gave a solid residue which was recrystallized from methanol to obtain 200 mg (86%) of **2b** as white needles: mp 230–231°; λ_{max}^{MeOH} 238 nm (ϵ 26,900); pK_a = 7.8 (67% DMF–H_2O); ν^{KBr} 3400, 1730, 1680, 1610 cm^{-1}; δ^{CDCl_3} 1.87 (s, 3), 3.24 (s, 3), 3.62 (s, 3), 7.43 (m, 10), 7.6–7.9 (b, 1).

Anal. Calcd for $C_{24}H_{20}N_2O_5$: C, 69.22; H, 4.84; N, 6.73. Found: C, 69.50; H, 4.72; N, 6.66.

The conversion of **1b** to **2b** was also effected in 84% yield (after recrystallization) by heating **1b** as a melt for 20 min at 170°.

5,6-Bis(methoxycarbonyl)-3,7-dimethyl-4-phenylpyrrolo[1,2-*b*]pyridazin-2-one (2c).—To a solution of 100 mg (0.26 mmol) of **1c**[2] in 3 ml of methanol was added 0.8 ml of 5% sodium methoxide in methanol. After standing for 5 min at room temperature, the solution was acidified and the product was isolated as described for **2b**; the oil crystallized from ether, giving 80 mg (87%) of **2c** as white crystals: mp 201–202°; λ_{max}^{MeOH} 232 nm (ϵ 29,900); pK_a = 7.7 (67% DMF–H_2O); ν^{KBr} 3240, 1710, 1680, 1620 cm^{-1}; δ^{CDCl_3} 1.97 (s, 3), 2.68 (s, 3), 3.23 (s, 3), 3.84 (s, 3), 7.42 (m, 5), 7.5–9.0 (b, 1).

Anal. Calcd for $C_{19}H_{18}N_2O_5$: C, 64.40; H, 5.12; N, 7.91. Found: C, 64.16; H, 5.05; N, 7.73.

Oxidation of 2 (R = CH_3).—To a solution of 170 mg (0.48 mmol) of **2c** (R = CH_3) in 9 ml of water containing 6 drops of 6 *N* sodium hydroxide was added 500 mg of potassium permanganate. The resulting solution was stirred for 5 min and then acidified. Solid sodium bisulfite was added to reduce the excess manganese dioxide. The clear aqueous solution was extracted with CH_2Cl_2. Evaporation of the dried organic layer gave an oil which crystallized from ether to yield 60 mg (46%) of **methyl [(4-methyl-3-oxo-5-phenylpyridazinyl)-6]glyoxylate (6)** as white crystals: mp 194–195°; ν^{KBr} 3000–2700, 1760, 1720, 1660 cm^{-1}; δ^{CDCl_3} 2.07 (s, 3), 3.85 (s, 3), 7.42 (m, 5), 12.9 (s, 1).

Anal. Calcd for $C_{14}H_{12}N_2O_4$: C, 61.76; H, 4.44; O, 23.51. Found- C, 61.68; H, 4.70; O, 23.9.

X-Ray Analysis.—Crystals were received as prismatic needles; a sample showing good crystal quality under microscopic examination with and without polarized light was chosen from the batch. The sample was approximately 0.34 × 0.21 × 0.50 mm and was mounted with the 0.50-mm length parallel with the rotation axis of the goniometer head.

By preliminary precession camera investigation, the unit cell was found to be monoclinic. Data were taken on the sample in space group $P2_1/n$ because of the near-cubic form of the resulting cell. This space group has the general positions, $\pm(x, y, z; x + {}^1/_2, y - {}^1/_2, z + {}^1/_2)$; the sample was thus mounted with its 101 axis parallel with the rotation axis of the goniometer.[11]

Precision lattice constants were obtained by least-squares refinement[11] of 2θ diffractometer angular settings on 19 reflections in the range $5° < |2\theta| < 35°$ (λ = 0.7107, for Mo K_α radiation). These calculations gave a = 12.593 (2), b = 14.429 (3), c = 12.441 (3), β = 101.69° [cos β = −0.2026 (4)] (numbers in parentheses are the estimated standard deviation). Assuming four formula units per cell, the calculated density was found to be 1.486 (3) g/cm³, which agrees favorably with the experimental density found by immersion in a liquid of equal density of 1.4 g/cm³ at 21 ± 1°, the ambient laboratory temperature.

For Mo K_α radiation, the linear absorption coefficient, μ, was calculated to be 19.4 cm^{-1}, which would cause no more than a 6% error in any structure factor calculation. Approximately 1600 independent reflections ($|\sin \theta/\lambda| \leq 0.649$ Å^{-1}) were measured by the θ–2θ scanning technique using a card-controlled Picker diffractometer. With approximately 290 parameters to be set in the final anisotropic model (excluding hydrogens), this gives about five reflections per parameter to be set.

Diffracted intensities were measured at a take-off angle of approximately 2°. The range of each scan, at a rate of 2°/min, consisted of a reflection base width of 2° and an increment, $\Delta(2\theta) = (0.285 \tan \theta)°$, to allow for spectral dispersion; background counts, for 30-sec duration, were taken at limits of the scan. The intensities of three standard reflections were monitored at intervals of 50 data points as alignment checks while these three plus three others were used at roughly 12-hr intervals as decomposition checks. Through the data collection period, these monitored reflections showed no noticable trend. The criteria for distinguishing observed reflections from unobserved

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(10) E. C. Horning, *J. Org. Chem.*, **11**, 95 (1946).

(11) All structure refinements were done using "X-ray '70" programs from Dr. James Stewart, University of Maryland. The Burroughs B-6700 computer at the University of Delaware was employed.

was set such that, to be observed, $F_{\text{obsd}} < 3.0\sigma_F$, where σ_F is the standard deviation on F_{obsd} computed from scan and background counts corrected for instrumental instability (estimated as 0.5%).

The structure was resolved through an initial three-dimensional Patterson synthesis, which gave the position of the bromine atom. Successive three-dimensional Fourier and difference-Fourier syntheses quickly lead to the placement of all other nonhydrogen atoms.

All nonhydrogen atoms were then treated with converging cycles of full-matrix least-squares refinement. In the final cycles, hydrogen positions were calculated,[12] nonunit weights were introduced, and anisotropic temperature factors were introduced for all nonhydrogen atoms. Hydrogen positional and thermal parameters were not refined but positional parameters were recalculated at the close of each least squares cycle to reposition them according to shifts in the nonhydrogen ring and methyl carbon atoms. Hydrogens were placed at 1.08 Å from the nearest phenyl-ring atoms and in the plane of the rings, at 0.99 Å from the nitrogen, N1, at approximately 109° from the two next nearest ring atoms (C2 and N8), and at 1.10 Å from the three terminal methyl carbons, C52, C62, and C31, at the proper tetrahedral angles (bonding distances are from ref 4). The phenyl-ring and nitrogen hydrogen positions checked satisfactorily against their respective positions on difference Fourier maps. It was not possible to locate hydrogens about the three methyl carbons on difference maps, possibly owing to relatively free rotation of these methyl groups.

The weighting function used in the final least-squares cycles was $w = 1/|\Delta\bar{F}|^2$, where $|\Delta\bar{F}| = A + B|\bar{F}_{\text{obsd}}|$, and A and B are obtained from a plot of $\Delta\bar{F}$ *vs.* $|\bar{F}_{\text{obsd}}|$ for 20 groups of reflections, each group containing about the same number of reflections. The plot was linear and gave values of 2.80 and 0.0492 for A and B, respectively.

The last cycle yielded a conventional R value of 0.052 and a weighted residual, $wR = 0.068$. Because the primary interest of this study was in the overall architecture of the molecule rather than in the structural details of bond lengths, angles, and thermal parameters, costly additional refinement computations were not made. A final difference Fourier synthesis having a maximum electron density of 1 e/Å^3 was judged to be free of significant features.

Registry No.—**1a**, 36434-07-8; **1b**, 36004-93-0; **1c**, 36004-92-9; **2a**, 36411-13-9; **2b**, 36411-14-0; **2c**, 36411-15-1; **6**, 36411-16-2.

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[12] Hydrogen positional parameters were calculated with ATMCAL, adapted from a general hydrogen position calculating program supplied by Dr. Lloyd Guggenberger, The Du Pont Co., Wilmington, Del.

The Synthesis of 2-Aza-6-oxaadamantane

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A new synthesis of 2-aza-6-oxaadamantane from suitably substituted 9-azabicyclo[3.3.1]nonane (prepared by a double Michael addition of a primary amine to 2,7-cyclooctadienone), has been achieved. The nmr of the various azabicyclic compounds were investigated; J values of the ketones and T_c values of the N-acetyl compounds are discussed.

The 2-aza-6-oxaadamantanic skeleton has already been synthesized by another method.[1] In this paper we report a new approach which should enable the introduction of other functional groups. This method is analogous to that used in the preparation of 2-oxa-[2] and 2-phospha-6-oxaadamantanes.[3]

2-Acetyl-2-aza-6-oxaadamantane was prepared by the steps shown in Scheme I. The parent material in the synthesis, 9-benzyl-9-azabicyclo[3.3.1]nonan-3-one (**1**),[4] was prepared by the exothermic addition of benzylamine to cyclooctadienone, as was also found by Bottini;[5] consecutive reduction of **1** by LiAlH$_4$ yielded the expected endo alcohol **2**,[6] from which the benzyl group could be cleaved by hydrogenolysis under acidic conditions to yield *endo*-9-azabicyclo[3.3.1]nonan-3-ol (**3**) (milder hydrogenation conditions; *e.g.*, hydrogenation in ethanol, at room temperature and 60 psi did not affect the benzyl group). Compound **3** which is a hygroscopic material was identical in all respects with the one described in the literature.[7] Attempts to produce the 9-azabicyclo[3.3.1]nonan-3-one directly by addition of ammonia to cyclooctadienone failed; the only product which was isolated, in ~50% from the reaction mixture, seems to be 3,7-bis[9-(9-azabicyclo[3.3.1]-nonan-3-one)]cyclooctanone (**4**).

Treatment of compound **3** with acetic anhydride–pyridine acetylated the amine as well as the hydroxy group to yield *endo*-9-azabicyclo[3.3.1]nonan-3-ol (**5**) which, on mild basic hydrolysis gave the corresponding alcohol (**6**).[7] (Schotten–Baumann acetylation of **2** which should result in **6** in one step, gave much lower yields due to side reactions.)

Treatment of the endo alcohol **6** with lead tetraacetate in boiling benzene,[2,3] or better in the presence of Pb(OAc)$_4$ and iodine,[8] gave two compounds. Chromatographic separation gave the desired 2-acetyl-2-aza-6-oxaadamantane (**7**) and the parent ketone, 9-acetyl-9-azabicyclo[3.3.1]nonan-3-one (**8**). The formation of **7** from **6** confirms the endo configuration of the latter, since epimerization is not expected to occur in these radical oxidation procedures.[2] Of interest was the nmr spectrum of **7** recorded at 100° (in hexachlorobutadiene), above its coalescence temperature (*vide infra*), which indicated the higher symmetry of the compound in comparison to the spectrum at room temperature. A double irradiation experiment, carried out under these conditions, enabled the measurement of various J values of the system.

Although oxidation of tertiary amines by Pb(OAc)$_4$

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