Anal. Calcd for $C_{22}H_{24}ClN_3O$: C, 69.19; H, 6.33; N, 11.00. Found: C, 69.30; H, 6.40; N, 10.77.

Alkylation of **39a** and **b** with basic halides in the presence of NaH was less satisfactory.

Registry No.—**1b** amidoxime 2HCl, 36271-17-7; **1c**, 36271-18-8; **1d**, 36271-19-9; **1e**, 36208-00-1; **1e** amidoxime, 36271-20-2; **2a** HCl, 36271-21-3; **2b** HCl, 36271-22-4; **2c** 2HCl, 36271-23-5; **2e** 2HCl, 36271-24-6; **4a**, 36271-25-7; **4b**, 36271-26-8; **4c**, 36271-27-9; **4d**, 36271-28-0; **4e**, 36271-29-1; **5a**, 36271-30-4; **5a** HCl, 36271-31-5; **5b**, 36271-32-6; **5b** HCl, 36271-33-7; **5c** HCl, 36271-34-8; **5e** HCl, 36271-35-9; **6**, 36271-36-0; **6** HCl, 36271-37-1; **8b**, 36258-91-0; **9b**, 36258-92-1; **11**, 36207-97-3; **12a**, 36270-92-5; **12b**, 36270-93-6; **13**, 36270-94-7; **14**, 36270-95-8; **16**, 4015-28-5; **16** dihydro formic acid salt, 36270-97-0; **17**, 36270-98-1; **18a**, 36270-99-2; **18b**, 36271-00-8; **18c**, 10456-63-0; **18d**, 36271-02-0; **19**, 36207-98-4; **21b**, 36271-03-1; **22**, 36271-04-2; **23**, 1022-13-5; **24**, 36271-06-4; **24** amide, 36271-07-5; **25**, 2898-12-6; **25** HCl, 2898-11-5; **26a**, 24139-18-2; **26b** HCl, 36271-11-1; **26c** HCl, 21139-23-1; **26d**, 21139-24-2; **28b**, 3311-40-8; **28c**, 16219-18-4; **28d**, 36271-15-5; **28e**, 36271-16-6; **29a** (R′ = CH_3), 36259-21-9; **29b** (R′ = H), 36259-22-0; **29b** (R′ = H) *N*-chloroacetyl derivative, 36259-23-1; **29b** (R′ = H) HBr, 36259-24-2; **29b** (R′ = CH_3), 36259-25-3; **29c** (R′ = H), 16175-35-2; **29c** (R′ = CH_3), 36259-27-5; **29d** (R′ = H), 36259-28-6; **29e** (R′ = H), 36259-29-7; **29e** (R′ = CH_3), 36259-30-0; **30c**, 36208-04-5; **31**, 36259-31-1; **32a** (R′ = CH_3), 36259-32-2; **32b** (R′ = H), 36259-33-3; **32b** (R′ = CH_3), 36259-34-4; **33b**, 36259-35-5; **34a**, 36259-36-6; **34b**, 36258-42-1; **35a**, 36258-43-2; **35b**, 36258-44-3; **35c**, 36258-45-4; **35d**, 36258-46-5; **36a** (R = H), 36258-47-6; **36a** (R = CH_3), 36258-48-7; **36a** dicarboxylic acid, 36258-49-8; **36b** (R = H), 36258-50-1; **36b** (R = CH_3), 36258-51-2; **37a**, 36258-52-3; **37b**, 36258-53-4; **38a**, 36208-05-6; **38a** HCl, 36258-54-5; **38a** imino acid HCl, 36258-55-6; **38b** HCl, 36258-56-7; **39a**, 36258-57-8; **39b**, 36258-58-9; **39c** (X = H), 36258-59-0; **39c** (X = Cl), 36258-60-3; **39d** (X = Cl, n = 2), 36258-61-4; **39d** (X = Cl, n = 3), 36258-62-5; i, 36258-63-6; *p*-chloroanilinoacetonitrile, 24889-92-7; *p*-chloroanilinoacetamide, 21979-12-4; *N*-acetyl-*p*-chloroanilinoacetonitrile, 36258-66-9; *p*-chloro-*N*-acetylanilinoacetonitrile amidoxime, 36258-67-0; 4-*N*-benzylideneaminoveratrale, 13548-24-8; 2,3-dimethoxy-6,7,9,13b-tetrahydroisoindolo[2,1-*d*][1,4]benzodiazepine HCl, 36258-69-2; 2-(α-hydroxybenzyl)-4-chloroanilinoacetonitrile, 36258-70-5; 6-chloro-1,2-dihydro-2,2-dimethylquinazoline 3-oxide, 4844-66-0; *N*-(2-aminoethyl)-*N*-methyl-2-benzoyl-4-chloroaniline hydrochloride, 36258-72-7; 6,7-dihydro-13b-hydroxyisoindolo[2,1-*d*][1,4]benzodiazepine-6,9-dione, 36258-73-8; 6,7-dihydroisoindolo[2,1-*d*][1,4]benzodiazepine-6,9-dione, 36258-74-9; 5-methyl-6,7-dihydroisoindolo[2,1-*d*][1,4]benzodiazepine-6,9(13b*H*)-dione, 36258-75-0; 2-aminomethyl-3-(2′-carbomethoxyphenyl)-5-chloro-1-methylindole, 36258-76-1; bis[3-(2′-carbomethoxyphenyl)-5-chloro-1-methylindolyl-2-methyl]amine, 36258-77-2; 3-(2′-carbomethoxyphenyl)-1-methylindole-2-carboxaldehyde, 36258-78-3; *N*-methyl-*m*-methoxyacetanilide, 36258-79-4.

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Heterocyclic Studies. 37. Rearrangements of a Dihydro-1,2-diazepin-4-ol and 1,2-Diazabicyclo[3.2.0]hepten-6-ol to a Tetrahydropyridazine

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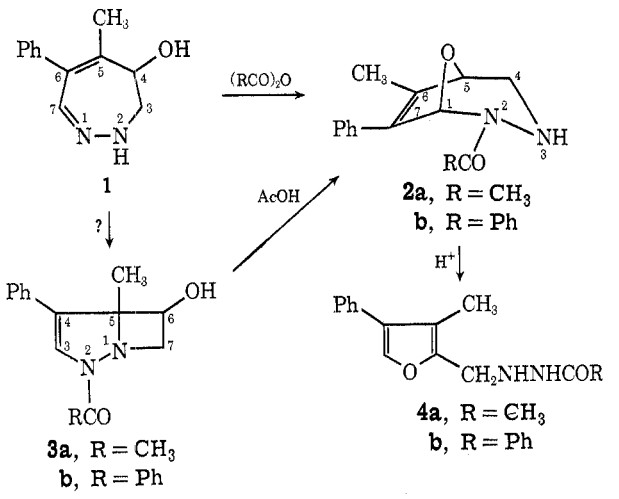
Acylation of diazepinol **1** in the presence of weak organic bases gives the oxides **2**; the bicyclo[3.2.0]alcohols **3** rearrange to **2**, but are not intermediates in the conversion **1** → **2**. With triethylamine, acylation of **1** gives the 4-formyltetrahydropyridazines **5**, which are also obtained by thermal rearrangement of **3**. The tetrahydropyridazines are converted by successive oxidation and deacylation to 4-methyl-5-phenylpyridazine (**9**). The reaction of **1** and **3** are suggested to occur *via* an acyldiazepinium cation–acylbetaine system (**10–12**).

The preparation and interconversion of the diazepinol **1**, bicyclo[3.2.0] alcohol **3a**, and bridged oxide **2a** were reported some time ago.[1] The bicyclic alcohol **3a**, obtained by reduction of the corresponding ketone, is converted by mild acid to the oxide **2a**; the latter is also produced by acetylation of **1**. The noncrystalline acetate ester of **3a** was obtained in impure form by acetylation of **1** in the presence of pyridine, and **3a** was suggested as an intermediate in the conversion of **1** to **2**. A terminal acid-catalyzed elimination leads from **2** or **3** to furfurylhydrazine derivatives **4**. Further work in this series has extended our understanding of these reactions and has revealed an important rearrangement process which was missed in the earlier work.

To provide more complete characterization of the [3.2.0] bicyclic alcohols, the *N*-benzoyl alcohol **3b** was prepared and converted to the crystalline acetate and benzoate esters. As in the acetyl series, a single epimeric alcohol was produced in the reduction of the benzoyl[3.2.0] ketone; the hydroxyl configuration is assumed to be endo from the expected exo attack of

(1) J. A. Moore, R. W. Medeiros, and R. L. Williams, *J. Org. Chem.*, **31**, 52 (1966).

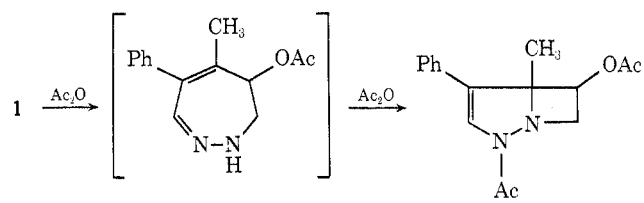


hydride. The bridged oxide **2b** and the corresponding furan **4b** were obtained under conditions similar to those used in the acetyl series.

Acylation of Diazepinol 1.—To clarify the formation of [3.2.0] bicyclic alcohols **3** from **1**, and possibly find a route to the exo isomers of **3**, benzoylation of the diazepinol **1** was carried out under a variety of conditions. With benzoyl or acetyl chloride and pyridine or dimethylaniline, only the bridged oxides **2** were isolated; the nmr spectrum of the total product from benzoyl chloride indicated traces of **3b** and the benzoate ester. Reinvestigation of the reaction of **1** with acetic anhydride–pyridine revealed a very complex mixture which was analyzed by nmr. The relative areas of methyl peaks showed nearly equal amounts of **3a** (as its acetate), **2a** (as such and as the N-3 acetyl derivative), and a third component (**5a**, discussed below, plus its N-2 acetyl derivative).

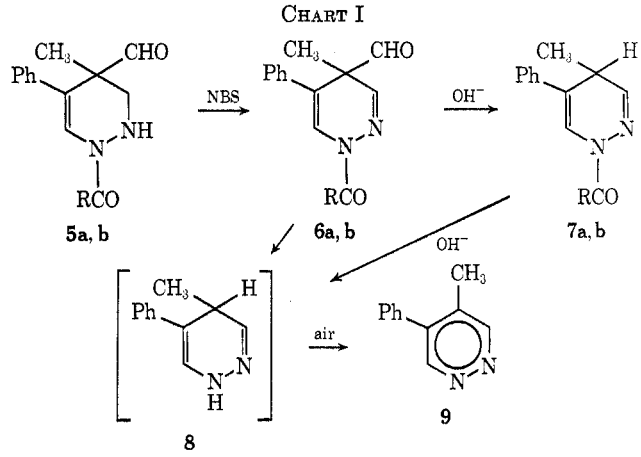
Although the [3.2.0] alcohols **3** are readily transformed to the oxides **2** with acetic acid or with the hydrochlorides of pyridine or dimethylaniline, it was found that this isomerization is *not* the major pathway to the oxides in these acylations. A reaction of **1** and benzoyl chloride which was quenched with ammonia after a few minutes gave only **2b** and unreacted **1**, and in an experiment with equimolar amounts of the diazepinol **1** and [3.2.0] alcohol **3b** with 1 equiv of benzoyl chloride **1** was completely converted to **2b** without significant isomerization of the bicyclic alcohol.

These results establish that attack of acid chlorides on the diazepinol **1**, paralleling the corresponding diazepinone,[2] occurs predominantly at N-1, with the oxides **2** arising by direct internal nucleophilic attack at C-7 by the hydroxyl group, without intermediacy of the [3.2.0] alcohol. The minor formation of **3a** acetate observed with acetic anhydride seems best accounted for by initial acetylation of the hydroxyl group of **1** followed by attack at N-1; in this case, bridging to the [3.2.0] system is the only path avail-



(2) J. A. Moore, F. J. Marascia, R. W. Medeiros, and R. L. Wineholt, *J. Org. Chem.*, **31**, 35 (1966).

CHART I



able. An attempt to isolate the diazepinol *O*-acetate by using insufficient acetic anhydride was unsuccessful.

When triethylamine rather than pyridine or dimethylaniline was used as the acid acceptor in the reaction of diazepinol **1** with benzoyl chloride, an entirely different reaction occurred, and the tetrahydropyridazine aldehyde **5b** (Chart I) was the only product isolated. With acetyl chloride and triethylamine, a mixture of the oxide **2a** and aldehyde **5a** was obtained. The aldehyde **5a** and its N-2 acetyl derivative were also present in the mixtures obtained with acetic anhydride. The aldehydes were found to be much more readily obtained by thermal rearrangement of the bicyclic alcohols, and this was the source of material used for characterization.

Thermal Rearrangement of Bicyclic Alcohols.—The *N*-benzoyl and *N*-acetyl [3.2.0] alcohols **3a** and **3b** undergo isomerization in refluxing toluene to give the respective pyridazinealdehydes **5a** and **5b** in high yields. The nmr spectra of these products contained peaks for $CH_3C<$, $-CH_2-$(AB), $-CH{=}N$, and CHO groups; the ir spectra showed ν_{NH} 3300 and ν_{CO} 1630 and 1710 cm^{-1}. Reduction of **5b** with $NaBH_4$ gave a carbinol with δ_{CH_3} shifted 0.4 ppm upfield, indicating the CH_3CCHO grouping.

Structure **5b** was proven by stepwise degradation to the pyridazine **9**. This conversion requires two deacylations and two oxidations (Chart I).

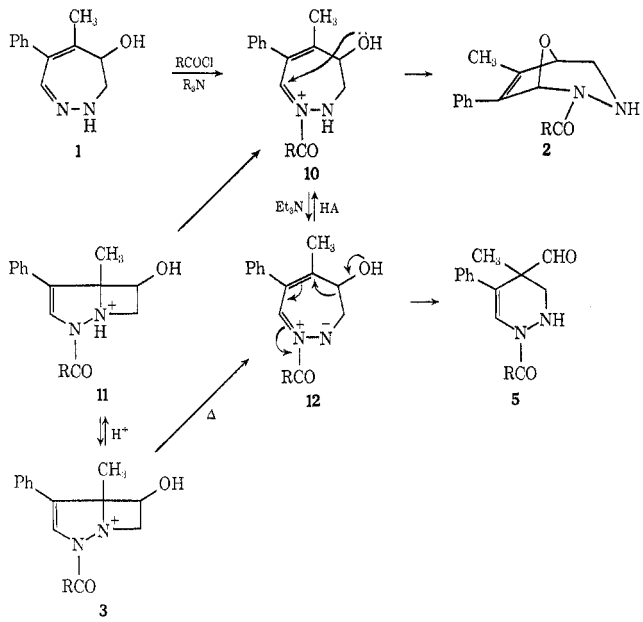
An initial oxidation with NBS proceeded very smoothly to the dihydropyridazine **6b**. Mild treatment of **6b** with base unexpectedly caused preferential loss of the *C*-formyl group with formation of **7b** [δ_{CH_3} 1.25 (d, J = 7 Hz), $\delta_{H\text{-}4}$ 3.55 (q of d, J = 7.0, 3.6 Hz)]. Longer treatment of **6b** or **7b** with base gave **8** admixed with the pyridazine **9**; the nmr spectrum corresponded very closely to that of a similar preparation of **8** + **9** from a different source.[3] Air oxidation of the crude dihydropyridazine led to the crystalline pyridazine **9**, identical with an authentic sample.

Discussion

The formation of the aldehydes by these two reactions suggests a common pathway from **1** and **2**, and the betaine **12** appears to be a logical intermediate

(3) J. A. Moore, E. J. Volker, and C. M. Kopay, *ibid.*, **36**, 2676 (1971).

CHART II



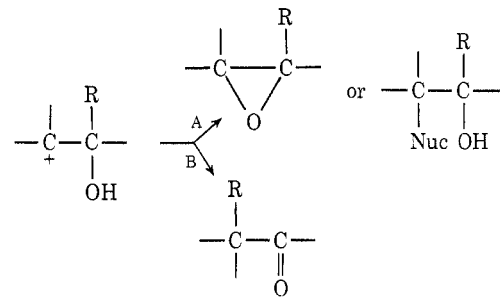
R=CH_3 or C_6H_5

available from both starting points (Chart II). The corresponding diazabicyclo[3.2.0] ketones have been shown to give on heating analogous acyl betaines which can be trapped by dipolarophiles.[4] Similar attempts to trap **12** by heating the alcohol **3b** in dimethyl acetylenedicarboxylate resulted in a complex mixture in which only the tetramer[5] of the acetylenic ester was identified; Michael addition of the alcohol may be a complicating factor in this case.

As depicted in Chart II, the acyl betaine **12** is presumed to arise, *via* the acyl cation **10**, from diazepinol **1** when the acylation is carried out with a sufficiently strong base, *e.g.*, triethylamine. With the much weaker bases pyridine or dimethylaniline, bridging of **10** to the bicyclic oxide occurs. In this view the presence of acid in the thermal rearrangement of **3** should lead to protonation of the betaine **12** and thence to the oxide, and this was observed. Isomerization of the [3.2.0] alcohol **3b** at 110° in the presence of 1 equiv of benzoic acid produced a mixture of aldehyde and oxide (*ca.* 3:5); at 80° with 1 equiv of acid the product was almost entirely oxide.

In the isomerization of the bicyclic alcohol **3** to **2** with pyridine or dimethylaniline hydrochloride at room temperature, the diazepinium cation **10** is probably formed *via* the protonated bicyclic alcohol **11**. This process again finds a parallel in the bicyclo[3.2.0]-ketone series, in which acidic methanol brings about ring opening and coordination of alcohol at C-7.[2]

The proposed pathways to **2** and **5** from cation **10** and betaine **12**, respectively, are lacking in a number of details, but this scheme provides a rationale for the main findings. The reactions leading to **2** and **5** are formally analogous to the product-forming steps in processes such as pinacol and Tiffenau–Demjanow rearrangements, or the reactions of carbonyl compounds with diazoalkanes, *viz.*



The distribution of products between paths A and B depends upon, among several factors, the extent of electron deficiency in the system. In diazoalkane–carbonyl reactions, for example, negative substituents in the carbonyl compound increase the amount of oxide (path A), whereas alkyl substitution in the diazo compound favors path B.[6] These and related effects reflect the need for stabilization of positive charge in the transition state for migration of R (path B). This requirement should be much better met in the neutral betaine than in the acyl cation, and the product distribution in the reactions of **1** and **3** is thus consistent with the general pattern observed in this type of rearrangement.

Experimental Section

2-Benzoyl-5-methyl-4-phenyl-1,2-diazabicyclo[3.2.0]-3-hepten-6-ol (3b).—To a solution of 2.00 g of 2-benzoyl-5-methyl-4-phenyl-1,2-diazabicyclo[3.2.0]-3-hepten-6-one[2] in 250 ml of ethanol was added 300 mg of $NaBH_4$ dissolved in 20 ml of ethanol. After standing at 25° for 2.5 hr, the reaction mixture was neutralized with acetic acid, concentrated, diluted with water, and extracted with CH_2Cl_2. The organic layer was washed with water, dried, and evaporated to an oil. On addition of ether (containing a small amount of methanol) and chilling, 1.41 g (71%) of slightly yellow prisms were obtained in two crops, mp 145–147° (first crop). Recrystallization from methanol–ether gave colorless prisms of **2b**: mp 148–149°; ν^{KBr} 3300, 1620 cm^{-1}; δ^{CDCl_3} 1.57 (s, 3), AMX (δ_A 4.45, δ_M 4.07, δ_X 3.28, J_{MX} = 9, J_{AX} = J_{AM} = 6.5 Hz), 3.42 (s, 1 D_2O exchange), 7.2–7.9 ppm (m, 11).

Anal. Calcd for $C_{19}H_{18}N_2O_2$: C, 74.49; H, 5.92; N, 9.15. Found: C, 74.63; H, 5.99; N, 9.04.

The benzoate ester of **3b** was obtained in 70% yield with benzoyl chloride–pyridine (CH_2Cl_2, 25°, 30 min): mp 155–156°; δ^{CDCl_3} 1.82 (s, 3), AMX (δ_A 5.44, δ_M 4.33, δ_X 3.57, J_{MX} = 10, J_{AX} = J_{AM} = 6.5 Hz), 7.1–7.9 (m, 16).

The acetate was obtained with Ac_2O–pyridine, mp 152–153°, δ_A 5.27, δ_M 4.15, δ_X 3.50.

Anal. Calcd for $C_{21}H_{20}N_2O_3$: C, 72.39; H, 5.79. Found: C, 72.16; H, 5.81.

2-Benzoyl-6-methyl-7-phenyl-8-oxa-2,3-diazabicyclo[3.2.1]-oct-6-ene (2b).—Bicyclic alcohol **3b** (300 mg) was added to 10 ml of CH_2Cl_2 containing anhydrous pyridine hydrochloride prepared from 0.1 ml of pyridine. After standing for 2 hr at 25° the solution was washed with 1 *N* HCl, 5% $NaHCO_3$, and water, and was then dried and evaporated to an oil which crystallized from ether to give 208 mg (70%) of **2b** as white plates, mp 195–197°. After recrystallization from CH_2Cl_2–ether the melting point was 201–202°; ν^{KBr} 3300, 1630 cm^{-1}; δ^{CDCl_3} 2.20 (s, 3), AB pattern (δ_A 3.56, δ_B 2.65, J_{AB} = 14 Hz, the A doublet was broad and flat but sharpened on addition of D_2O and was split further, J = 3 Hz), 4.65 (br, s, 1), 4.85 (br s, D_2O exchange), 6.97 (s, 1), 7.3–7.8 ppm (m, 11).

Anal. Calcd for $C_{19}H_{18}N_2O_2$: C, 74.49; H, 5.92; N, 9.15. Found: C, 74.39; H, 5.76; N, 9.27.

When *N,N*-dimethylaniline hydrochloride was used instead of pyridine hydrochloride, **2b** was obtained in 42% yield.

1-Benzoyl-2-(3-methyl-4-phenylfurfuryl)hydrazine (4b).—Hydrogen chloride gas was bubbled through a solution of 170 mg of

(4) O. S. Rothenberger and J. A. Moore, *J. Org. Chem.*, **37**, 2796 (1972).
(5) J. C. Kauer and H. E. Simmons, *ibid.*, **33**, 2720 (1968).
(6) C. D. Gutsche, *Org. React.*, **8**, 369 (1954).

oxide **2b** in 10 ml of CH_2Cl_2 for 7 min. After washing with water and $NaHCO_3$ and drying, the solution was evaporated to an oil which crystallized from ether to give 112 mg (66%) of **4b** as colorless crystals, mp 128–130°. After recrystallization from CH_2Cl_2–ether the melting point was 130–131°; ν^{KBr} 3250, 3300, 1650 cm^{-1}; δ^{CDCl_3} 2.08 (s, 3), 4.13 (s, 2), 4.65 (s, 1 D_2O exchange), 7.2–7.9 (m, 11), 8.4 ppm (br s, 1 D_2O exchange).

Anal. Calcd for $C_{19}H_{18}N_2O_2$: C, 74.49; H, 5.92; N, 9.15. Found: C, 74.40; H, 5.81; N, 9.13.

Reaction of 1 with Benzoyl Chloride in Triethylamine.—Diazepinol **1** (70 mg, 0.35 mmol) was dissolved in 1 ml of CH_2Cl_2 containing 0.049 ml (0.35 mmol) of triethylamine, and 0.040 ml (0.35 mmol) of benzoyl chloride in 1.0 ml of CH_2Cl_2 was added. After standing at 0° for 30 min the reaction mixture was extracted with 1 *N* HCl, 5% sodium bicarbonate, and water. The methylene chloride layer was dried and evaporated to an oil. Addition of ether and chilling gave 26 mg (24% of off-white crystals, mp 121–125°, ir identical with that of **5b** described below.

The nmr spectrum of the crude oil obtained before the isolation of **5b** contained peaks for **5b** and also starting diazepinol **1**, alcohol **3b**, oxide **2b**, and the benzoate of **3b**. A tlc of the crude oil showed zones corresponding in R_f value with each of these compounds. The relative amounts were estimated from the contribution of the respective methyl peaks for each compound to the total integral of the methyl region of the nmr (Table I).

TABLE I

Compd	δ^{CDCl_3}	Integral, mm	% of total methyl peaks
Aldehyde **5b**	1.20	23	59
Unknown	1.28	2	5
Alcohol **3b**	1.55	1	3
Diazepinol **1** + benzoate of **3b**	1.78	5	13
Unknown	2.03	4	10
Oxide **2b**	2.13	4	10

In another run under similar conditions, aldehyde **3b** represented 58% of the total methyl integral. The percentages of other peaks varied by a few per cent when compared to the original experiment.

Reaction of Diazepinol 1 with Acetic Anhydride.—Acetylations were carried out by a standard procedure using (a) 1 equiv of Ac_2O and 1 equiv of pyridine, (b) 2 equiv of Ac_2O and 2 equiv of pyridine, and (c) 1 equiv of Ac_2O and 1 equiv of triethylamine. Diazepinol **1**, 140 mg (0.7 mmol), was treated with a solution of the Ac_2O (0.066 ml in a and c, 0.13 ml in b) in 1 ml of CH_2Cl_2 and a solution of the appropriate amount of amine in 1 ml of CH_2Cl_2. After 90 min at 25° the solution was washed thoroughly with aqueous $NaHCO_3$, dilute acid, and water, dried, and evaporated to an oil. The nmr spectrum of the total product mixture was scanned (A-60) at 250 Hz and the C–Me and N– or O–COMe peaks in the products were identified by addition of compounds **2**, **3**, and **5** and their acetyl derivatives to portions of the total product mixture and noting enhancement of peaks in the spectra. The peaks corresponding to the various Me signals were then cut from copies of the spectra and weighed. The product ratios were derived by the relative weights of the sharpest Me peak (or average of two or three sharp peaks when present) for each compound. The results are summarized in Table II.

The product composition for run b (excess Ac_2O) was calculated as follows (Table III).

Competition of Diazepinol 1 and Alcohol 3b for Benzoyl Chloride and Pyridine.—To 70 ml (0.35 mmol) of diazepinol **1** and 106 ml (0.35 mmol) of bicyclic alcohol **3b** was added 1.0 ml of a CH_2Cl_2 solution containing 0.030 ml (0.37 mmol) of pyridine and 1.0 ml of a solution of 0.040 ml (0.35 mmol) of benzoyl chloride in CH_2Cl_2. After standing at 0° for 20 min the reaction mixture was extracted with water, 5% $NaNCO_3$, and water, dried, and evaporated to an oil. The nmr spectrum ($CDCl_3$) revealed a large amount of alcohol **3b** (δ 1.57 ppm, integration 50), oxide **2b** (δ 2.15 ppm, integration 34), a small amount of diazepinol **1** (δ 1.80 ppm, integration 6), and an unidentified peak at δ 1.77 (integration 3).

TABLE II

ACETYLATION OF DIAZEPINOL 1

Compd	Peak position, Hz	Peak weights, mg — Condition: 1 Ac_2O–1 Pyr	2 Ac_2O–2 Pyr	1 Ac_2O–1 Et_3N
N-2-Acetyl **5a**	68	8	8	
5a	72	13	5	20
Unknown	75	9	10	
O-Acetyl **3a**	102	6	17	10
O-Acetyl **3a**	104	6	16	10
Diazepinol **1**	108	16		
N-3-Acetyl **2a**	120		3	
N-3-Acetyl **2a**	124		3	
N-2-Acetyl **5a**	125	5	6	
Mixture[a]	129	26	31	11[b]
2a	131	17	16	
N-2-Acetyl **5a**	132	9		
5a	136	19	6	23
Unknown	142	18	16	

[a] Overlapping peaks from two or three compounds. [b] *N*-Acetyl of **3a** acetate.

TABLE III

Compd	Peaks used	Av weight	Rel amount
N-2-Acetyl **5a**	68, 125	7	2
5a	72, 136	6	2
2a	131	16	5
N-3-Acetyl **2a**	120, 124	3	1
O-Acetyl **3a**	102, 104	16	5

1-Acetyl-4-formyl-4-methyl-5-phenyl-1,2,3,4-tetrahydropyridazine (5a).—A solution of 300 mg of bicyclic alcohol **3a** in 350 ml of toluene was refluxed for 4 hr. The toluene was then removed *in vacuo* and a small amount of ether was added. Chilling gave 2.52 mg (84%) of colorless crystals of **5a**, mp 98–99°. Recrystallization from ether raised the melting point to 99–99.5°; ν^{KBr} 3300, 1710, 1630 cm^{-1}; δ^{CDCl_3} 1.21 (s, 3), 2.25 (s, 3), 2.7–3.6 (m, 2 D_2O AB, δ_A 3.42 δ_B 2.82, J_{AB} = 14 Hz), 4.63 (q, 1 D_2O exchange), 7.67 (s, 1), 7.1–7.4 (m, 5), 9.90 ppm (s, 1).

Anal. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: 68.71; H, 6.48; N, 11.35.

The 1,2-diacetyl derivative was prepared (for authentication of nmr peaks in mixtures) with CH_3COCl and dimethylaniline: mp 127–128°; δ^{CDCl_3} 1.15 (s, 3), 2.12 (s, 3), 2.25 (s, 3), 2.78 (d, 1, J = 14 Hz), 4.97 (d, 1, J = 14 Hz), 7.0–7.6 (m, 6), 9.58 (s, 1).

1-Benzoyl-4-formyl-4-methyl-5-phenyl-1,2,3,4-tetrahydropyridazine (5b).—A solution of 650 ml of **3b** in 250 ml of toluene was refluxed for 4 hr. Evaporation and addition of ether gave 584 mg (90%) of colorless crystals in two crops, mp (combined first and second crops) 129–130°. Recrystallization from ether–methanol gave white prisms of **5b**: mp 132–132.5°; ν^{KBr} 1630, 1710 cm^{-1}; δ^{CDCl_3} 1.15 (s, 3), 2.67–3.67 (m, 2, D_2O AB, δ_A 3.39, δ_B 2.87, J_{AB} = 13.2 Hz), 7.1–7.75 (m, 12), 9.92 ppm (s, 1).

Anal. Calcd for $C_{19}H_{18}N_2O_2$: C, 74.49; H, 5.92; N, 9.15. Found: C, 74.35; H, 5.86; N, 9.09.

The 1,2-dibenzoyl derivative was prepared (65%) from 300 mg of **5b**, 0.7 ml of benzoyl chloride, and 2.7 ml of *N*,*N*-dimethylaniline in 30 ml of CH_2Cl_2 (30°, 6 hr): mp 173–175°; ν 1670, 1720 cm^{-1}; δ^{CDCl_3} 1.20 (s, 3), AB dd (calcd δ_A 3.36, δ_B 3.58, J_{AB} = 6.8 Hz), 6.9–7.6 (m, 16), 9.75 (s, 1).

Anal. Calcd for $C_{26}H_{22}N_2O_3$: C, 76.08; H, 5.40. Found: C, 76.03; H, 5.39

1-Benzoyl-4-methyl-5-phenyl-1,2,3,4-tetrahydropyridazine-4-methanol.—To a solution of 368 mg (1.20 mmol) of **5b** in 60 ml of ethanol was added 56 mg of $NaBH_4$ in 20 ml of ethanol. After standing at 25° overnight, the reaction mixture was neutralized with acetic acid and evaporated. Water was then added and the mixture was extracted with ether. The ether layer was dried, concentrated, and chilled to give 272 mg (74%) of white crystals, mp 154–155°. Recrystallization from ether–acetone raised the melting point to 155.5–156°; ν^{KBr} 3200, 1610 cm^{-1}; δ^{CDCl_3} 0.83 (s, 3), 3.0–3.9 (m, 4), 4.5–5.1 (br s, 1), 7.1–7.9 ppm (m, 12).

Anal. Calcd for $C_{16}H_{20}N_2O_2$: 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 $C_{18}H_{16}N_2O$: 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), 7.05–7.55 (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).

Temp, °C	Acid, mg	% of total methyl	
		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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(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.