by subtracting from the initial concentration the amount of ammonia incorporated into adduct, assuming one ammonia incorporated per adduct methyl group.

The pK_A of Ammonium Ion.—The pK_A of ammonium ion has been found to satisfy the following equation at 25°.[30]

$$pK_A = pK_A^\circ + 0.132[NH_4Cl] + 0.198[KCl] \quad (22)$$

The value of pK_A° is obtained from the data of Bates and Pinching,[31] who determined pK_A as a function of temperature and extrapolated to zero ionic strength.

$$pK_A^\circ = 2835.75/T - 0.6322 + 0.001225T \quad (23)$$

The variation of mean activity coefficients with temperature over the range of 10–35° has been found to be at most 4% at 2 *m* concentration.[32] Therefore, we have used eq 22 over this temperature range with the appropriate pK_A° determined by eq 23. Any specific effect of the phosphate buffer was not considered.

Appendix

The interpretation of the nmr line broadening results for acetaldehyde in the presence of ammonia depends upon the relationship between chemical exchange and nmr line shapes. From the arguments presented in the text, the system involves exchange among three chemically distinguishable sites.

$$A \underset{1/\tau_{ba}}{\overset{1/\tau_{ab}}{\rightleftharpoons}} B \underset{1/\tau_{cb}}{\overset{1/\tau_{bc}}{\rightleftharpoons}} C \quad (A1)$$

The dependence of nmr line shape on chemical exchange can be analyzed with the standard classical Bloch equations. This treatment is valid in the present system, in which intact methyl groups and methine protons are exchanging among different chemical species.[33] Below are presented the general equations describing the behavior of the chemical shift and line width of the A resonance in the presence of chemical exchange when [A] ≫ [B], [C]. These equations are expressed in the form most useful for the analysis of the system under study.

$$\pi\Delta\nu_A = \frac{1}{T_{2a}} + \frac{1}{\tau_{ab}}\left[1 - \frac{\tau_B/\tau_{ba}}{1 + \tau_B^2\Delta\omega_{BC}^2}\right] \quad (A2)$$

$$\omega_{obsd} - \omega_A = -\frac{[B]}{[A]}\left[\frac{\tau_B^2/\tau_{ba}^2}{1 + \tau_B^2\Delta\omega_{BC}^2}\right]\Delta\omega_{BC} \quad (A3)$$

$$\frac{1}{\tau_B} \equiv \frac{1}{T_{2b}} + \frac{1}{\tau_{ba}} + \frac{\epsilon}{\tau_{bc}} \quad (A4)$$

$$\Delta\omega_{BC} \equiv \Delta\omega_b + \gamma\frac{[C]}{[B]}\Delta\omega_c \quad (A5)$$

$$\epsilon = \frac{1/T_{2c}^2 + 1/T_{2c}\tau_{cb} + \Delta\omega_c^2}{(1/T_{2c} + 1/\tau_{cb})^2 + \Delta\omega_c^2} \leq 1 \quad (A6)$$

$$\gamma = \frac{1}{\left(1 + \frac{\tau_{cb}}{T_{2c}}\right)^2 + \tau_{cb}^2\Delta\omega_c^2} \leq 1 \quad (A7)$$

The line width $\Delta\nu_A$ as usually defined is the full width at half height; ω_i and T_{2i} are the chemical shift (in rad/sec) and the spin–spin relaxation time (in seconds) for the site i in the absence of exchange; ω_{obsd} is the observed chemical shift for site A in the presence of exchange; $\Delta\omega_i = \omega_{RF} - \omega_i \approx \omega_{obsd} - \omega_i$, where ω_{RF} is the frequency of the swept RF field. The terms τ_B, which can be considered a generalized lifetime for site B, and $\Delta\omega_{BC}$, a generalized chemical shift, have been defined to reduce the complexity of the expressions A2 and A3, resulting a in pseudo-two-site formalism.

Registry No.—Acetaldehyde, 75-07-0; ammonia, 7664-41-7; 2,4,6-trimethylhexahydro-*s*-triazine, 638-14-2; acetaldehyde hydrate, 4433-56-1.

(30) M. T. Emerson, E. Grunwald, and R. A. Kromhout, *J. Chem. Phys.*, **33**, 547 (1960).
(31) R. G. Bates and G. D. Pinching, *J. Amer. Chem. Soc.*, **72**, 1393 (1950).
(32) H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold, New York, N. Y., 1958, p 727.
(33) H. M. McConnell, *J. Chem. Phys.*, **28**, 430 (1958).

Heterocyclic Studies. 39. Enolic and Bicyclic Isomers of 2,3- and 1,5-Dihydro-1,2-diazepin-4-ones[1]

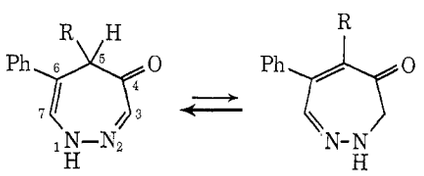
JAMES A. MOORE,* WALTER J. FREEMAN, KEISUKE KURITA, AND MELVIN G. PLEISS

Department of Chemistry, University of Delaware, Newark, Delaware 19711

Received December 12, 1972

Conditions are described for conversion of the 1,5- and 2,3-dihydrodiazepinones **1** and **2** to *N*-acyl ketones and to *N*-acylenol esters. Enol acylation is much more rapid in the 1,5-dihydro series. Acylation of the 1,5-dihydrodiazepinones under conditions favoring N-2 substitution leads to 2-acyl-2,3-diazabicyclo[3.2.0]-3-heptenones. These bicyclic ketones lose the elements of methylketene or phenylketene on heating, giving 1-acyl-4-phenylpyrazoles.

In an earlier note we reported the formation of the 1,5-dihydrodiazepinone **1a** by base-catalyzed isomerization of the 2,3-dihydro tautomer **2a**.[2] Interconversion of these ketones involves an equilibrium of the respective enolates in which the 1,5-dihydro isomer predominates (**1a**:**2a** ~8). This approach has been applied also to the 2,3-dihydro-5,6-diphenyldiazepinone **2b**,[3] and provided the 1,5-dihydro tautomer **1b** in about 50% yield. The position of the equilibrium could not be measured as was done in the 5-methyl series because of the lack of a distinctive nmr signal, but it clearly favors the 1,5-dihydro tautomer.



1,5-dihydro 2,3-dihydro

1a, R = CH_3 **2a**, R = CH_3
b, R = C_6H_5 **b**, R = C_6H_5

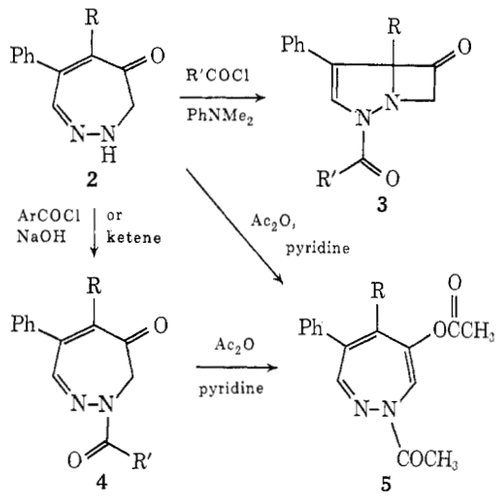
Both of these diazepinone systems contain a multiplicity of nucleophilic centers. In the 2,3-dihydro series, substitutions at N-1, N-2, and C-3 have been observed. Highly reactive electrophiles such as acid chlorides and oxonium reagents attack **2a** at the N-1 position, leading in the former case to the bicyclo-

(1) Supported in part by grants from the National Science Foundation and the Unidel Foundation.
(2) M. G. Pleiss and J. A. Moore, *J. Amer. Chem. Soc.*, **90**, 1369 (1968). Complete details of these base-catalyzed reactions will be found in the Ph.D. Dissertation of M. G. Pleiss, University of Delaware, 1969.
(3) A. Nabeya, F. B. Culp, and J. A. Moore, *J. Org. Chem.*, **35**, 2015 (1970).

[3.2.0] ketones **3** (Chart I).[4] The latter compounds have now been obtained also from **2b**. Alkylation

CHART I

ACYLATION OF 2,3-DIHYDRODIAZEPINONES

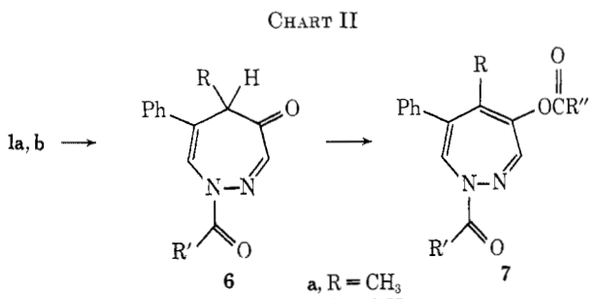


a, R = CH_3
b, R = C_6H_5

of **2a** under basic conditions occurs, presumably *via* the N anion, at N-2.[5]

We have now extended the study of acylation reactions in both diazepinone series. 2-Aroyl derivatives **4** of the 2,3-dihydrodiazepinones are best obtained under Schotten–Baumann conditions, and parallel reactions in the 1,5-dihydro series give the 1-aroyldiazepinones **6** (Chart II). The preferred reagent for the acetyl ketones is ketene.

CHART II



a, R = CH_3
b, R = C_6H_5

Enol Acylation.—Prolonged treatment of the NH or *N*-acetyl-2,3-dihydrodiazepinones **2** or **4** with acetic anhydride–pyridine at 80° has been found to give crystalline yellow-orange *diacetyl* products. These compounds have ν_{CO} 1755 and 1680 cm^{-1} and are readily hydrolyzed to the parent NH ketones **2**. These properties permit assignment of the acetoxydiazepine structures **5**. Although enolization was clearly implicated by the base-catalyzed deuterium exchange of the C-3 protons of **2**[2] and the equilibration of **2** and **1**, the diazepines **5** are the first enol derivatives to be isolated in this system. Attempts to obtain enol ethers or enamines of **2** have been unsuccessful.

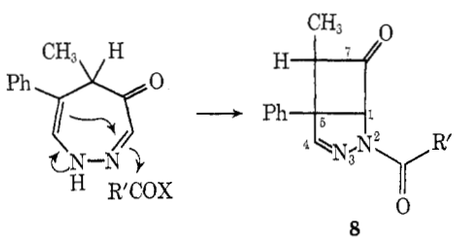
(4) J. A. Moore, F. J. Marascia, R. W. Medeiros, and R. L. Wineholt, *J. Org. Chem.*, **31**, 34 (1966).
(5) W. J. Theuer and J. A. Moore, *ibid.*, **32**, 1602 (1967).

The 1-acyl-1,5-dihydro ketones **6** were also converted to enol esters **7** by further acylation. These reactions were very much more rapid than those in the 2,3-dihydro series. Solutions of the *N*-acetyl ketones **4a** and **6** (R' = CH_3) containing 1.6 equiv of Ac_2O and 1.6 equiv of Et_3N were kept at 25° for 36 hr; the formation of enol acetates **5** and **7** was 6 and 90%, respectively (by nmr). The facility of enol acylation in the 1,5-dihydro series permitted the preparation of enol benzoates **7a** (R'' = Bz) as well; the corresponding benzoate esters could not be isolated from the 2,3-dihydrodiazepinones.

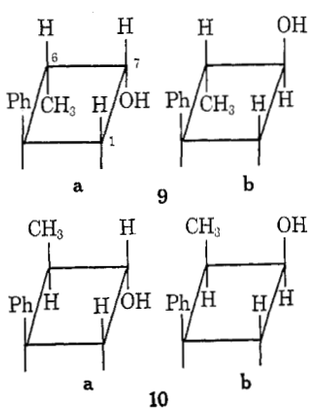
The ease of enol acylation was particularly marked in the 5,6-diphenyl-1,5-dihydro series. Reaction of the NH ketone **1b** with excess acetic anhydride gave the enol acetate **7b** (R' = R'' = CH_3) plus a colorless isomer (**12**) discussed below. The 1-acetyl ketone **6b** (R' = CH_3), available by ketene acylation of **1b**, was not detected.

The enol acetates in the two series had very similar spectra, and their structures would not be distinguished except by formation from and hydrolysis to the respective ketones. Studies on the thermal reactions of these diazepines will be reported in a later paper.

2,3-Diazabicycloheptenones.—Reaction of the NH 1,5-dihydrodiazepinone **1a** with acid chlorides and dimethylaniline leads to the bicyclo[3.2.0] ketones **8**. The benzoyl ketone **8** (R' = C_6H_5, 60% yield) was crystalline; the ir spectrum contained the expected ν_{CO} at 1790 cm^{-1} for a four-membered cyclic C=O group. The nmr spectrum [δ 1.38 (d, 3, J = 7.4 Hz), 4.16 (dq, 1, J = 7.4 and 3.2 Hz), 6.06 (d, 1, J = 3.2 Hz), 6.93 (s, 1), 7.1–7.5 (m, 10)] was consistent with **8**, but did not permit assignment of the steric configuration of the methyl group.



To establish this point, the ketone was reduced with $NaBH_4$. A major carbinol isomer was crystallized in 35% yield; the nmr spectrum of the mother liquor showed peaks due to both isomers. The four possible carbinols are the two pairs **9a** and **9b** and **10a** and **10b**.



The parameters of importance for the stereochemical assignment are the coupling constants $J_{6,7}$ and $J_{1,7}$ for the three methine protons at 1, 6, and 7 in the carbinols. The dd signals for H-1 and H-7 of both isomers were well separated in the spectrum of the mixture, permitting direct measurement of the values given in Table I.

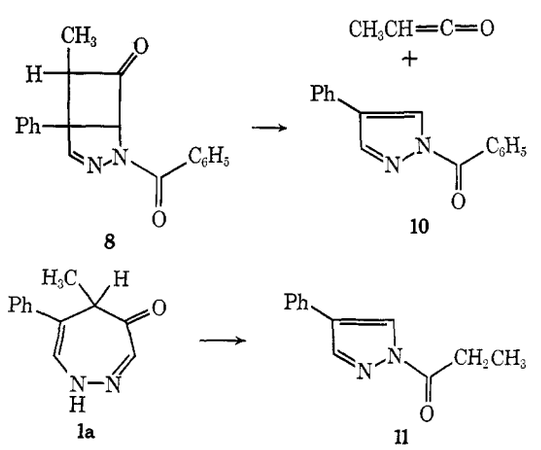
TABLE I
NMR DATA FOR BICYCLIC CARBINOLS 9[a]

	δ, ppm	
	Major isomer	Minor isomer
H-1	5.08	4.86
H-6	3.08	~3.0[b]
H-7	4.48	3.66[c]
6-CH_3	1.17	~1.2[b]
	J, Hz[d]	
1,6	1.2	1.2
1,7	5.3	3.5
6,7	8.6	6.3
CH_3-6	7.2	7

[a] In CCl_4; Perkin-Elmer Model R-12B spectrometer. [b] Obscured by peak of major isomer. [c] Small additional splitting of the dd. [d] Estimated error ±0.3 Hz.

The two isomeric alcohols are **9a** and **9b** or **10a** and **10b**. In **9a** and **9b**, one isomer (**9a**) has the methine protons 1,7 and 6,7 *both* cis, and the other isomer (**9b**) has *both* trans. In the isomeric pair **10**, the isomers have 1,7 cis, 6,7 trans, or vice versa. On the basis that $J_{cis} > J_{trans}$ for vicinal methine protons in cyclobutanes,[6] the data in Table I show that the pair of isomers obtained in the $NaBH_4$ reduction are **9a** and **9b**, since *both* $J_{6,7}$ and $J_{1,7}$ are larger (cis) in one isomer than the corresponding $J_{6,7}$ and $J_{1,7}$ in the other. Thus the ketone **8** must have the endo methyl configuration. It follows that the major crystalline alcohol is the endo alcohol **9a** with the two cis coupling constants. This is clearly predictable, since both the five-membered ring and the endo methyl group act to direct hydride attack from the outer face of the four-membered ring.

In contrast to the complex thermal isomerization of the 1,2-diazabicyclic ketones **3a**,[7] the *N*-benzoyl-2,3-diaza[3.2.0] ketone **8** undergoes cleavage at 100° to methylketene and 1-benzoyl-4-phenylpyrazole (**10**).

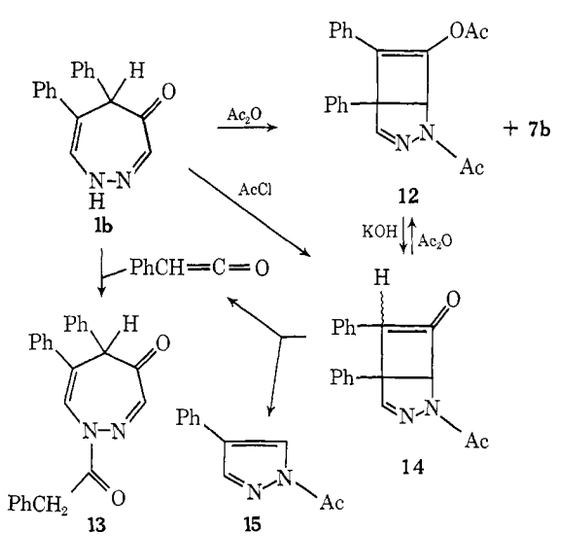


When the pyrolysis was carried out in a heated column with an aniline trap at the exit, propionanilide was isolated in very low yield. In these reactions, a very characteristic sweet odor accompanied the decomposition. The same odor had been noted earlier on heating the parent diazepinone **1a** to its melting point (dec), and we were thus prompted to examine the pyrolysis products of **1a**. Entrainment of the diazepinone in a nitrogen stream through a 300° packed column led to much tar, but 4-phenylpyrazole and 1-propionyl-4-phenylpyrazole (**11**) were isolated in a combined yield of 30%. The latter compound is responsible for the odor, which was also observed with a sample prepared by propionylation of 4-phenylpyrazole.

Pyrolysis of 2,3-dihydrodiazepinone **2a** in the same apparatus gave 4-phenylpyrazole in 10% yield, presumably by prior isomerization to **1**. In view of the severe conditions and the greater stability of **1**, no mechanistic significance can be attached to this result.

In the diphenyl series, acylation under conditions favoring substitution at N-2 was more complex, and exclusive attack at N-2 was not achieved. Treatment of **1b** with AcCl–pyridine at 20° gave three products which were separated by SiO_2 chromatography and identified as the 1-acetyldiazepinone **6b** (R′ = CH_3), 1-acetyl-4-phenylpyrazole (**15**), and 1-phenylacetyldiazepinone **6b** (R′ = $PhCH_2$). This odd collection of products suggests that the diphenylbicyclic ketone **14** is significantly less stable than **8**, with phenylketene being lost under the reaction conditions and trapped by unreacted diazepinone.

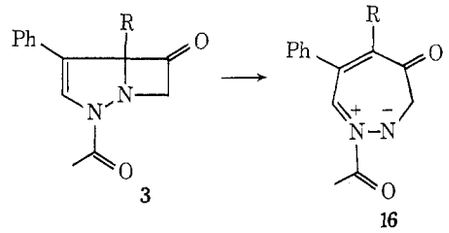
Definite information on this point was gained from the minor diacetyl product of **1b** and acetic anhydride, obtained together with the enol acetate **7b** as mentioned above. This compound had ν_{CO} 1770 and 1680 cm^{-1} and an nmr peak at δ 5.5 ppm. These properties and the source of the compound suggested the bicyclic enol acetate **12**, and this was confirmed by very mild hydrolysis to the ketone **14** (ν 1800 cm^{-1}) which crystallized in slightly impure form. A solution of **14** in $CDCl_3$ decomposed at 25° ($t_{1/2}$ = 24 hr) to **15** and presumably phenylketene.



The difference in the course of the thermal reactions of the bicyclic ketones **3** and **8** is noteworthy. The

(6) H. Weitkamp and F. Korte, *Tetrahedron, Suppl.*, **7**, 75 (1966).
(7) O. S. Rothenberger and J. A. Moore, *J. Org. Chem.*, **37**, 2796 (1972).

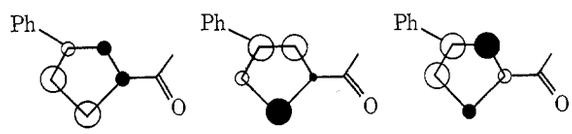
ketones **3** at 80° undergo ring opening to the acyldiazepinium betaines **16**;[7] no scission to pyrazole



3 **16**

and ketene is detected. The reaction **3** → **16** is much slower (for **3**, R = Ph, $t_{1/2}^{80°}$ = 2 hr) than the cleavage of **8** or **14** to pyrazole plus ketene, suggesting that the divergent course of the reactions lies in a lower energy path for the ketene scission with ketones **8** and **14**.

Orbital symmetry considerations for the cycloaddition reactions of ketene with the C-4–C-5 and N-2—C-3 bonds of 1-acyl-4-phenylpyrazole predict an allowed and forbidden $_{\pi}2_a + _{\pi}2_s$ path, respectively, if only the highest occupied (HOMO) and lowest unoccupied (LUMO) orbitals of the pyrazole are considered. The pertinent MOs calculated by the HMO method[8] are shown. However, MO ψ_6, separated only by 0.36β from the HOMO and having local



ψ_6 (0.9837β) ψ_7 (0.6243β) HOMO ψ_8 (−0.5346β) LUMO

symmetry opposite to that in the HOMO, may also contribute significantly, making the prediction ambiguous. In fact perturbation treatment[9] including all the MOs indicates no essential difference between the two cycloaddition reactions either for the totally synchronous or for the nonsynchronous path. Moreover, little difference is predicted for the π-complex formation between the carbonyl carbon atom of ketene and the respective π bond of the pyrazole. Thus, the difference observed in the thermal behavior between **3** and **8** cannot be attributed to orbital symmetry control.

Experimental Section

Infrared spectra in KBr pellets were recorded on a Perkin-Elmer Model 137. Ir spectra in $CHCl_3$ were recorded on a Perkin-Elmer Model 180 instrument. Nmr spectra were obtained on a Varian Model A-60A spectrometer.

5,6-Diphenyl-2,3-dihydro-4*H*-1,2-diazepin-4-one (2b).—The following procedure is an improvement over the earlier one,[3] which required evaporation of a relatively large volume of acetic acid; this step causes darkening and formation of oily by-products.

A solution of 10 g of 3-diazoacetyl-*cis*-3,4-diphenyl-1-pyrazoline in 50 ml of tetrahydrofuran plus 200 ml of MeOH was treated at 0° with 3 ml of 1 *N* methanolic KOH and allowed to stand for 4 hr. Tlc showed nearly complete conversion to the 5-pyrazoline. The solution was then brought to pH 7 by the addition of concentrated HCl and was stirred at 0° for 1 hr (end of gas evolution). The dark orange solution was evaporated *in vacuo* to a thick syrup. On heating this syrup with 200 ml of ether some solid separated and the remainder of the oil dissolved. The solid was filtered and extracted further with ether, and the combined ether solution was evaporated to give a total of 7.1 g (79%) of **2b**, mp 192–196°.

5,6-Diphenyl-1,5-dihydro-1,2-diazepin-4-one (1b).—A solution of 3.8 g of the 2,3-dihydrodiazepinone **2b** in 18 ml of dimethyl sulfoxide was treated with 1.8 ml of 1 *N* NaOH and stirred at 60° under nitrogen for 2 days. The mixture was then poured into 250 ml of water and extracted with ether. The ether solution was washed thoroughly with water to remove DMSO and was then dried and evaporated to give 3.2 g of tan solid. After silicic acid chromatography (twice) and charcoal treatment, recrystallization from benzene–cyclohexane gave 1.7 g of **1b**: mp 133–134°; ν^{KBr} 3400, 1650 cm^{-1}; δ^{CDCl_3} 5.10 (br singlet, actually unresolved m, 1, H-5), 6.94 (dd, J = 4.3, 1.7 Hz, H-3 or H-7), 7.05–7.35 (m, 11, 2Ph + H-3 or H-7).

Anal. Calcd for $C_{17}H_{14}N_2O$: C, 77.84; H, 5.38; N, 10.68. Found: C, 77.85; H, 5.25; N, 10.56.

2-Benzoyl-4,5-diphenyl-1,2-diazabicyclo[3.2.0]-3-hepten-6-one (3b, R′ = C_6H_5).—A solution of 260 mg (1 mmol) of **2b** and 0.5 ml of *N*,*N*-dimethylaniline in 10 ml of CH_2Cl_2 was treated with 0.12 ml (141 mg, 1 mmol) of benzoyl chloride. After 4 hr at 20° the solution was washed with ice water and then dilute HCl and $NaHCO_3$ solution. The solution was dried and evaporated to a solid. Crystallization from ether gave 270 mg of light brown crystals of bicyclic ketone. Further crystallization from benzene–cyclohexane gave nearly colorless crystals: mp 133° dec; ν^{KBr} 1800, 1650 cm^{-1}; δ^{CDCl_3} AB part of ABX (H-7 exo, H-7 endo, and H-3) δ_A 4.57 (dd, 1, J_{AX} = 0.9, J_{AB} = 17 Hz), δ_B 4.77 (dd, 1, J_{AX} = 0.9, J_{AB} = 17 Hz), 7.1–7.6, 7.7–8.0 (m, 11).

Anal. Calcd for $C_{24}H_{18}N_2O_2$: C, 78.67; H, 4.95. Found: C, 78.92; H, 4.85.

The 2-acetyl bicyclic ketone (**3b**, R′ = CH_3) was similarly obtained from 260 mg of **2b** and 0.15 ml of acetyl chloride. The bicyclic ketone crystallized from ether: 151 mg (50%); mp 158–160°; ν^{KBr} 1795, 1665 cm^{-1}; δ^{CDCl_3} 2.26 (s, 3), 4.55 (d, 1, J = 16.8 Hz), 4.90 (d, 1, J = 16.8 Hz), 7.1–7.6 (m, 10), 7.80 (s, 1).

Anal. Calcd for $C_{19}H_{16}N_2O_2$: C, 74.98; H, 5.30; N, 9.21. Found: C, 74.81; H, 5.29; N, 8.94.

2-Acetyl-5-methyl-6-phenyl-2,3-dihydro-1,2-diazepin-4-one (4a, R′ = CH_3).—A solution of 600 mg (3 mmol) of **2a** in 10 ml of CH_2Cl_2 was treated with 12 mmol of ketene. After 4 days the solution was evaporated and the oil was crystallized on seeding with an earlier sample. Sublimation at 90° (0.3 mm) gave 560 mg (77%) of the acetyl ketone **4a**, R′ = CH_3: mp 90–91° (lit.[10] mp 89–90°); ν^{CHCl_3} 1696, 1677 cm^{-1}; δ^{CDCl_3} 1.89 (s, 3), 2.22 (s, 3), 4.55 (s, 2), 7.1–7.5 (m, 5).

1-Acetyl-5,6-diphenyl-1,5-dihydro-4*H*-1,2-diazepin-4-one (6b, R′ = CH_3).—A solution of 262 mg (1 mmol) of **1b** in CH_2Cl_2 was treated with 6 mequiv of ketene. After standing for 12 hr the solution was chromatographed on silicic acid and the resulting yellow oil (280 mg) was dissolved in cyclohexane. After 1 week at 0°, the solution deposited 200 mg of light yellow crystals: mp 105–106°; ν^{KBr} 1725, 1670 cm^{-1}; δ^{CDCl_3} 2.32 (s, 3), 5.16 (m, 1, H-5), 7.1–7.4 (m, 11), 7.85 (d, 1, J = 1.7 Hz, H-3 or H-7).

Anal. Calcd for $C_{19}H_{16}N_2O_2$: C, 74.98; H, 5.30; N, 9.21. Found: C, 75.08; H, 5.29; N, 9.03.

1-Acetyl-5-methyl-6-phenyl-1,5-dihydro-1,2-diazepin-4-one (6a, R′ = CH_3).—A solution of 1.5 g (7.5 mmol) of **1a** in CH_2Cl_2 was treated with 22 mmol of ketene. After 1 day the solution was concentrated and the yellow solid was sublimed at 90–100° (0.2 mm) to give 1.6 g (90%) of **6** (R′ = CH_3) as yellow needles: mp 110–111°; ν^{KBr} 1720, 1655 cm^{-1}; δ^{CDCl_3} 1.18 (d, 3, J = 7 Hz), 2.56 (s, 3), 3.73 (q, 1, J = 7 Hz), 7.19 (s, 6), 7.48 (d, 1, J = 1.5 Hz).

Anal. Calcd for $C_{14}H_{14}N_2O_2$: C, 69.40; H, 5.83; N, 11.56. Found: C, 69.25; H, 5.80; N, 10.94.

(8) We are indebted to Dr. Tadamichi Fukunaga, Central Research Department, E. I. du Pont de Nemours and Co., for these calculations and the perturbation analysis.

(9) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, Chapter 6; F. F. Hudson, *Angew. Chem., Int. Ed. Engl.*, **12**, 36 (1973).

(10) J. A. Moore and J. Binkert, *J. Amer. Chem. Soc.*, **81**, 6029 (1959).

1-Benzoyl-5-methyl-6-phenyl-1,5-dihydro-1,2-diazepin-4-one (6a, R′ = C_6H_5).—A solution of 600 mg (3 mmol) of **1a** in 10 ml of CH_2Cl_2 containing 0.35 ml of benzoyl chloride and 15 ml of 10% aqueous KOH was agitated vigorously on a "Super-Mixer" for 15 min. Mixing was repeated with three further 0.35-ml portions of benzoyl chloride. The CH_2Cl_2 layer was washed, dried, and evaporated and the yellow oil was chromatographed on 20 g of silicic acid. Evaporation of the yellow eluent fraction gave 850 mg of yellow solid, mp 123–125°. Crystallization from CH_2Cl_2–ether gave **6** (R′ = C_6H_5) as yellow prisms: mp 127–129°; ν^{KBr} 1720, 1670 cm^{-1}; δ^{CDCl_3} 1.28 (d, 3, J = 7.2 Hz), 3.97 (ddq, 1, J = 7.2, 1.2, and 1.2 Hz), 7.50 (m, 12).

Anal. Calcd for $C_{19}H_{16}N_2O_2$: C, 74.98; H, 5.30; N, 9.21. Found: C, 74.88; H, 5.48; N, 8.95.

The **p-methoxybenzoyl-1,5-dihydrodiazepinone** (**6a**, R′ = p-$CH_3OC_6H_4$) was obtained by essentially the same procedure from 500 mg of **1** and 850 mg of anisoyl chloride: 591 mg (71%); mp 130–132°; ν^{KBr} 1705, 1670 cm^{-1}; δ^{CDCl_3} 1.29 (d, 3, J = 7.5 Hz), 3.5–4.1 (m, 4 including OCH_3), 6.95 (d, 2, J_{AB} = 8.5 Hz, B of aryl A_2B_2), 7.38 (s, 6), 7.75 (s, 1), 7.82 (d, 2, J_{AB} = 8.5 Hz, A of aryl A_2B_2).

Anal. Calcd for $C_{20}H_{18}N_2O_3$: C, 71.84; H, 5.43; N, 8.38. Found: C, 71.57; H, 5.33; N, 8.16.

The **p-nitrobenzoyl-1,5-dihydrodiazepinone** (**6a**, R′ = p-$NO_2C_6H_4$) was similarly prepared in 78% yield: mp 136–137°; ν 1700, 1655 cm^{-1}; δ^{CDCl_3} 1.32 (d, 3), 3.83 (ddq, 1), 7.26 (s, 1), 7.38 (s, 5), 7.65 (d, 1, J = 1.1 Hz), 8.00 (d, 2, J = 9 Hz, B of aryl A_2B_2), 8.23 (d, 2, J = 9 Hz, A of A_2B_2).

Anal. Calcd for $C_{19}H_{15}N_3O_4$: C, 65.32; H, 4.33; N, 12.03. Found: C, 65.30; H, 4.38; N, 11.84.

2-Acetyl-4-acetoxy-5-methyl-6-phenyl-2*H*-1,2-diazepine (5a).[11]—One gram of the 2-acetyl ketone **4a** (R′ = CH_3) was dissolved in 4 ml of pyridine and 2 ml of acetic anhydride. After heating 1 hr at 80°, tlc showed the presence of starting **4a** plus a slower moving yellow compound. After heating for 2 hr the two yellow zones were of approximately equal size and a third slower moving colorless compound appeared. After 4 hr the reaction mixture was concentrated at reduced pressure and ether was added. The yellow solid which separated was collected and washed with ether–pentane to give 440 mg of yellow crystals, mp 130°. Recrystallization from ether–pentane gave 370 mg of the enol acetate **5**: mp 135–136°; λ_{max}^{MeOH} 352 nm (ϵ 500), 260 (sh); ν^{CHCl_3} 1760, 1675 cm^{-1}; δ^{CDCl_3} 1.70 (s, 3), 2.22 (s, 3), 2.28 (s, 3), 6.45 (s, 1), 7–7.5 (m, 6).

Anal. Calcd for $C_{16}H_{16}N_2O_3$: C, 67.59; H, 5.67; N, 9.85. Found: C, 67.76; H, 5.60; N, 9.94.

2-Acetyl-4-acetoxy-5,6-diphenyl-2*H*-1,2-diazepine (5b).—Two grams of **4b** (R′ = CH_3)[3] was acetylated for 4 hr as described above. After concentration of the reaction mixture, addition of ether gave a mixture of **4b** and the enol acetate. After further acetylation for 1 hr, evaporation gave a yellow solid which was washed with ether to give 1.1 g of the enol acetate **5b**, mp 152–154°. The ir and nmr spectra were identical with those of a sample from another source.[12]

1-Acetyl-4-acetoxy-5-methyl-6-phenyl-1*H*-1,2-diazepine (7a, R′ = R″ = CH_3).—A solution of 500 mg of 1-acetyl-5-methyl-1,5-dihydrodiazepinone (**6a**) (R′ = CH_3), 0.6 ml of Ac_2O, and 0.9 ml of Et_3N in 5 ml of CH_2Cl_2 was allowed to stand for 60 hr at 25° and was then washed with HCl, $NaHCO_3$, and H_2O. The dried solution was concentrated. The yellow residue crystallized from ether to give 400 mg (56%) of **7a** as yellow prisms, mp 100–102°. The analytical sample was crystallized from ether: mp 102–103; ν^{CHCl_3} 1762 and 1675 cm^{-1}; δ^{CDCl_3} 1.66 (s, 3), 2.27 (s, 6), 6.45 (s, 1), 7.23 (s, 1), 7.22 (s, 5).

Anal. Calcd for $C_{16}H_{16}N_2O_3$: C, 67.59; H, 5.67; N, 9.85. Found: C, 67.58; H, 5.70; N, 9.78.

1-Benzoyl-4-benzoyloxy-5-methyl-6-phenyl-1*H*-1,2-diazepine (7a, R′ = R″ = C_6H_5).—A solution of 380 mg of **6a** (R′ = C_6H_5), 0.43 ml of benzoyl chloride, and 0.5 ml of Et_3N in 3 ml of CH_2Cl_2 stood for 27 hr at 25°. The green solution was washed as above, dried, and evaporated. The residue crystallized from ether to give 249 mg (56%) of enol benzoate **7a** (R′ = R″ = C_6H_5) as yellow crystals: mp 141–143°; ν^{CHCl_3} 1739, 1663 cm^{-1}; δ^{CDCl_3} 1.86 (s, 3), 6.70) (s, 1), 7.49 (m, 12), 7.94 (m, 2).

5,6-Diphenyl-1,5-dihydro-1,2-diazepin-4-one (1b) plus Acetic Anhydride.—A solution of 400 mg of **1b** in 2 ml of pyridine and 2 ml of Ac_2O stood for 16 hr and was then poured into water. The oily precipitate solidified after 20 hr at 0° and was collected and dried (450 mg). Recrystallization from benzene–hexane gave 300 mg of yellow crystals, mp 149–150°. Further recrystallization gave the enol acetate **7b** (R′ = R″ = CH_3): mp 150–151°; ν^{KBr} 1750, 1680 cm^{-1}; δ^{CDCl_3} 2.03 (s, 3), 2.33 (s, 3), 6.07 (s, 1, H-7), 7.1–7.2 (m, 10), 7.40 (s, 1, H-3).

Anal. Calcd for $C_{26}H_{20}N_2O_3$: C, 76.45; H, 4.94; N, 6.86. Found: C, 76.44; H, 4.87; N, 6.86.

Anal. Calcd for $C_{21}H_{18}N_2O_3$: C, 72.82; H, 5.24; N, 8.09. Found: C, 72.83; H, 5.10; N, 7.90.

The mother liquor from crystallization of the enol acetate was concentrated. Slow crystallization from benzene–hexane gave 50 mg of colorless solid. Recrystallization from hexane gave white crystals of the bicyclic enol acetate **12**: mp 156–157°; ν^{KBr} 1770, 1680, 1660 cm^{-1}; δ^{CDCl_3} 2.38 (s, 3), 2.33 (s, 3), 5.33 (s, 1), 7.2–7.4 (m, 11).

Anal. Calcd for $C_{21}H_{18}N_2O_3$: C, 72.82; H, 5.24; N, 8.09. Found: C, 72.84; H, 5.06; N, 8.06.

2-Benzoyl-6-*endo*-methyl-5-phenyl-2,3-diazabicyclo[3.2.0]-3-hepten-7-one (8).—To a solution of 1.0 g of the 1,5-dihydrodiazepinone **1a** in 40 ml of CH_2Cl_2 was added 0.66 ml of *N*,*N*-dimethylaniline and 0.63 ml of benzoyl chloride. After standing for 4 days the solution was washed with aqueous HCl, $NaHCO_3$, and water, dried, and concentrated. The oil was diluted with ether. Crystallization gave 920 mg (60%) of **8** as a pale, cream-colored solid, mp 102–110°. Recrystallization from ether–pentane gave white crystals, mp 107–108°; for spectra, see text.

Anal. Calcd for $C_{19}H_{16}N_2O_2$: C, 74.98; H, 5.30; N, 9.21. Found: C, 74.96; H, 5.13.

The 2-acetyl ketone was prepared similarly and obtained as an oil: ν 1790, 1665 cm^{-1}; δ^{CDCl_3} 1.36 (d, 3, J = 8 Hz), 2.30 (s, 3), 4.16 (dq, 1, J = 8 and 3.5 Hz), 5.91 (d, 1, J = 3.5 Hz), 6.95 (s, 1), 7.34 (m, 5).

2-Benzoyl-6-*endo*-methyl-5-phenyl-2,3-diazabicyclo[3.2.0]-3-hepten-7-*endo*-ol (9).—A solution of 304 mg (1 mmol) of ketone **8** in 10 ml of ethanol–water was treated with 200 mg of $NaBH_4$. After 1.5 hr at 26° the solution was acidified with acetic acid, concentrated, and extracted with ether. The oil from the ether solution crystallized to give white prisms of **9**, 106 mg, mp 125–127°; for nmr, see text.

Anal. Calcd for $C_{19}H_{18}N_2O_2$: C, 74.49; H, 5.92. Found: C, 74.39; H, 6.11.

Pyrolysis of 8.—A solution of 305 mg of **8** in toluene was dropped into a vertical helix-filled tube heated to 250° while a stream of nitrogen was passed through the apparatus. The vapors from the column passed first into an empty trap at room temperature and then into a solution of aniline (6 ml) in 50 ml of ether. The toluene solution collected in the first trap was evaporated to yield 107 mg of yellow solid, mp 115–117°. Recrystallization from ether gave white plates of 1-benzoyl-4-phenylpyrazole: mp 128–129°; ν^{KBr} 1690 cm^{-1}; δ^{CDCl_3} 7.18–7.63 (m, 8), 7.92–8.22 (m, 3), 8.61 (s, 1).

Anal. Calcd for $C_{16}H_{12}N_2O$: C, 77.40; H, 4.87; N, 11.28. Found: C, 76.94; H, 4.82; N, 11.25.

A comparison sample prepared by benzoylation of 4-phenylpyrazole[13] (C_6H_5COCl, pyridine, 25°) had mp 124–127°; a mixture of the two samples showed no melting point depression.

The ether–aniline solution from the second trap was washed with four portions of 2 *N* HCl and then with Na_2CO_3 and water. The ether solution was evaporated to give 18 mg of brownish solid. Recrystallization from ether gave 6 mg of colorless crystals, mp 106–107°. The infrared spectrum had the same peaks and approximately the same relative intensities as that of an authentic sample of propionanilide (lit. mp 104–105°).

Pyrolysis of 1a.—A 200-mg sample of the diazepinone **1a** was placed in a cool top section of the helix-packed column. The column temperature was set at 300° and a nitrogen flow was begun. The top section was then rapidly heated to melt the diazepinone. A total of 120 mg of yellowish solid was collected in the empty exit trap; tlc of this solid indicated the presence of three compounds. After the column was cooled, 76 mg of dark

(11) This compound was originally prepared by Dr. J.-L. Derocque.

(12) A. Nabeya, K. Kurita, and J. A. Moore, *J. Org. Chem.*, **37**, 2954 (1972).

(13) E. Klingsberg, *J. Amer. Chem. Soc.*, **83**, 2934 (1961). We are indebted to Dr. Klingsberg for a generous gift of 4-phenyl-1,2-dithiolium hydrogen sulfate.

oil was recovered by washing; this material showed eight spots on tlc.

The solid from the trap was triturated with CCl_4 and 32 mg of white solid, mp 232–233°, was collected. The infrared spectrum was identical with that of 4-phenylpyrazole (lit. mp 236–237°). Chromatography of the CCl_4 solution on silicic acid gave 19 mg of solid in the first fractions. Recrystallization gave 9 mg of 1-propionyl-4-phenylpyrazole: mp 101–103°: ν_{CO} 1735 cm^{-1}; mixture melting point with material prepared by propionylation of 4-phenylpyrazole (C_6H_5COCl, Et_3N, 10 min, 80°), 102–103°.

Pyrolysis of 2a.—Treatment of **2a** (310 mg) as described above gave a yellow oil in the first trap. Dilution with ether and seeding gave 24 mg (11%) of 4-phenylpyrazole, mp 230–233°.

5,6-Diphenyl-1,5-dihydro-1,2-diazepin-4-one (1b) plus Acetyl Chloride.—To a solution of 262 mg of diazepinone **1b** in 5 ml of CH_2Cl_2 at 0° was added 0.08 ml (1 equiv) of pyridine followed by 0.07 ml (1 equiv) of acetyl chloride. After 25 min, the solution was poured into ice water and the organic layer was washed twice with water, dried, and evaporated to a yellow oil which was chromatographed in $CHCl_3$ on silicic acid. Three bands separated and were collected in individual cuts which were evaporated to give (1) 100 mg of yellow oil, (2) 40 mg of white solid, (3) 90 mg of yellow oil.

The first fraction was a mixture and was rechromatographed. No bands separated and the eluate was collected in three equal fractions. The first cut was a yellow oil (30 mg) whose nmr spectrum showed one major component and trace impurities. The peaks due to the major component agreed precisely with those in the spectrum of 1-phenylacetyl-1,5-dihydrodiazepinone described below.

The third fraction of the second chromatogram was a yellow oil (20 mg) whose nmr spectrum matched that of the 1-acetyl-1,5-dihydrodiazepinone (**6b**, R′ = CH_3).

The solid from the second fraction of the first chromatogram (of the total product) was recrystallized from petroleum ether (bp 30–60°) to give 30 mg of colorless crystals, mp 80–81°; the ir spectrum (22 peaks) matched that of 1-acetyl-4-phenylpyrazole described below.

1-Phenylacetyl-5,6-diphenyl-1,5-dihydro-1,2-diazepin-4-one (13).—A solution of 130 mg of the diphenyl-1,5-dihydroketone **1b** in 5 ml of CH_2Cl_2 and 2 ml of 10% aqueous NaOH was vigorously stirred in a vibrating mixer and 0.13 ml of phenylacetyl chloride was added. After 10 min the organic layer was separated, washed with acid and water, dried, and evaporated. The resulting yellow oil was chromatographed on silicic acid. The oil obtained was homogeneous by spectral criteria but did not crystallize: ν_{CO} 1730, 1675 cm^{-1}; δ^{CDCl_3} 3.98, 4.06 (calcd δ_A and δ_B of AB dd, J_{AB} = 14.5 Hz, $PhCH_2$), 5.10 (m, H-5), 6.9–7.5 (m, 16), 7.82 (d, 1, J = 1.8 Hz, H-3 or H-7).

1-Acetyl-4-phenylpyrazole (15).—A solution of 50 mg of 4-phenylpyrazole in 0.5 ml of Ac_2O and 0.2 ml of pyridine stood for 2 hr and was then evaporated *in vacuo*. Benzene was added and the solution was again evaporated; this treatment was repeated twice and a trace of anhydride was then removed in a nitrogen stream. The crystalline residue was recrystallized from ether–pentane to give colorless needles of **15**: mp 79–80°; ν_{CO}^{KBr} 1730 cm^{-1}; δ^{CDCl_3} 2.72 (s, 3), 7.2–7.6 (m, 5), 7.95 (s, 1), 8.44 (s, 1).

Anal. Calcd for $C_{11}H_{10}N_2O$: C, 70.95; H, 5.41. Found: C, 70.95; H, 5.23.

2-Acetyl-5,6-diphenyl-2,3-diazabicyclo[3.2.0]-3-hepten-6-one (14).—A suspension of 50 mg of the enol acetate **12** in 1 ml of methanol was treated with 0.3 ml of 1 *N* methanolic KOH at 0°. After the resulting light yellow solution was stirred for 30 min the solution was neutralized with acetic acid, concentrated at 0°, and extracted with $CHCl_3$. The extract was washed, dried, and evaporated to give a solid residue. Recrystallization from $CHCl_3$–methanol gave 33 mg of colorless crystals, mp 105–107°. Recrystallization gave **14**: mp 108–109°; ν^{KBr} 1790, 1675 cm^{-1}; δ^{CDCl_3} 2.39 (s, 3), 5.32 (d, 1, J = 3 Hz), 5.98 (d, 1, J = 3 Hz), 6.73 (s, 1), 7.1–7.5 (m, 10).

Anal. Calcd for $C_{19}H_{16}N_2O_2$: C, 74.98; H, 5.30. Found: C, 74.25; H, 5.30.

Reacetylation of **14** (30 mg) with Ac_2O–pyridine gave enol acetate **12** (30 mg), mp 153–156°, ir same as sample from **1b**.

Thermal Decomposition of 14.—The nmr spectrum of a solution of **14** in $CDCl_3$ was recorded at intervals over several days. After a few minutes a peak at δ 2.72 due to **15** was apparent. At 17 hr the ratio of this peak to the CH_3 peak of **14** was 3.5:6.5, and peaks appeared at δ 7.95 and 8.45 due to **15**. In addition, a peak $^2/_3$ of the intensity of the CH_3 peak of **15** was present at δ 3.70. This is attributed to the CH_2 of phenylacetic acid or some other derivative of phenylketene. The reaction was followed to 90% completion. A first-order plot of log [**15**] *vs.* time gave a straight line; $k_1 = 8 \times 10^{-5}$ sec^{-1}.

Registry No.—**1a,** 19971-06-3; **1b,** 40635-76-5; **2a,** 1706-26-9; **2b,** 24301-66-4; **3b** (R′ = C_6H_5), 40711-72-6; **3b** (R′ = CH_3), 5109-45-5; **4a** (R′ = CH_3), 4134-95-6; **4b** (R′ = CH_3), 24301-69-7; **5a,** 40711-76-0; **5b,** 40635-77-6; **6a** (R′ = CH_3), 40711-78-2; **6a** (R′ = C_6H_5), 40711-79-3; **6a** (R′ = *p*-$CH_3OC_6H_4$), 40711-80-6; **6a** (R′ = *p*-$NO_2C_6H_4$), 40711-81-7; **6b** (R′ = CH_3), 40711-82-8; **7a** (R′ = R″ = CH_3), 40711-83-9; **7a** (R′ = R″ = C_6H_5), 40711-84-0; **7b** (R′ = R″ = CH_3), 40711-85-1; **8,** 40704-70-9; **8** 2-acetyl derivative, 40704-71-0; **9a,** 40704-72-1; **9b,** 40704-73-2; **12,** 40711-86-2; **13,** 40711-87-3; **14,** 40711-88-4; **15,** 40711-89-5; 3-diazoacetyl-*cis*-3,4-diphenyl-1-pyrazoline, 40711-90-8; 1-benzoyl-4-phenylpyrazole, 40711-91-9; propionanilide, 620-71-3; 4-phenylpyrazole, 10199-68-5; 1-propionyl-4-phenylpyrazole, 40711-92-0.