methyl *trans*-2,3-dichlorobicyclo[2.1.1]hexyl-*endo*-5 ketone in 20 ml of methylene chloride. The solution was stirred for 1 hr at 0° and 24 hr at room temperature. It was poured into 100 g of ice water, the mixture was shaken vigorously, and the methylene chloride layer was separated. After the mixture was washed with 100 ml of 5% sodium carbonate solution and 100 ml of saturated salt solution and dried over magnesium sulfate, distillation gave 8.2 g (83%) of *trans*-2,3-dichlorobicyclo[2.1.1]hexyl *endo*-5-acetate, bp 60–65° (0.1 mm). Vpc analysis indicated 80% purity, with 10% of methyl *trans*-2,3-dichlorobicyclo[2.1.1]-hexane-*endo*-5-carboxylate and 10% of unidentified impurities. An analytical sample was collected by vpc.

Anal. Calcd for $C_8H_{10}Cl_2O_2$: C, 46.0; H, 4.8; Cl, 33.9. Found: C, 45.8, 45.7; H, 4.8, 4.8; Cl, 34.0, 34.0.

Attempted Dehalogenation of *trans*-2,3-Dichlorobicyclo[2.1.1]-hexyl *endo*-5-Acetate.—The dehalogenation with magnesium amalgam as described above was carried out for 7 days. The only products formed were methyl bicyclo[2.1.1]hexene-*endo*-5-carboxylate (formed from the 10% dichloro ester impurity) and benzene. The dehalogenation with sodium phenanthrene also was carried out as described above. The product was separated by vpc (10 ft × 0.375 in. 5% Carbowax 20M at 115°) into four components with retention times of 2, 6, 7.5, and 10 min. The first component appeared to be 1,2-di(Δ^3-cyclopentenyl)ethane (10%). The second and third components were identified as *exo*-bicyclo[3.1.0]hex-3-en-2-ol (70%) (identified by hydrogenation to the known *exo*-bicyclo[3.1.0]hexanol-2)[24] and Δ^3-cyclopentenylmethanol (10%). The fourth component (10%) appeared to be a mixture and was not identified.

***trans*-2,3-Dichlorobicyclo[2.1.1]hexan-*endo*-5-ol.**—An ether solution of methyllithium was prepared from 2.0 g of lithium, 150 ml of anhydrous ether, and methyl bromide. A solution of 5.0 g (24 mmol) of *trans*-2,3-dichlorobicyclo[2.1.1]hexyl *endo*-5-acetate (80% pure) in 75 ml of ether was cooled in an ice–salt bath and 72 ml (1.5 equiv) of the methyllithium solution was added over a period of 10 min with stirring. After stirring for an additional 5 min, the solution was added dropwise to a rapidly stirred mixture of 100 ml of saturated ammonium chloride solution and 100 ml of chipped ice. The ether layer was washed twice with 100 ml of water, and twice with saturated salt solution. After the solution was dried over magnesium sulfate, the solvent was removed using a rotary evaporator, giving 4.5 g of a semisolid. The residue was dissolved in 10 ml of carbon tetrachloride. Cooling afforded 1.5 g (37%) of long white needles. The filtrate contained an additional 30% of the alcohol. After recrystallization from hexane–cyclohexane it had mp 88.8–90.6°.

Anal. Calcd for $C_6H_8Cl_2O$: C, 43.1; H, 4.8; Cl, 42.5. Found: C, 43.0, 43.1; H, 5.2, 5.2; Cl, 42.4, 42.5.

(24) E. J. Corey and R. L. Dawson, *J. Amer. Chem. Soc.*, **85**, 1782 (1963).

Reduction of *trans*-2,3-Dichlorobicyclo[2.1.1]hexyl *endo*-5-Acetate with Lithium Aluminum Hydride.—A solution of 0.5 g of *trans*-2,3-dichlorobicyclo[2.1.1]hexyl *endo*-5-acetate (80% pure) in 10 ml of ether was added to 200 mg of lithium aluminum hydride in 30 ml of ether. After the usual work-up, the residue (0.2 g, 50%) was analyzed by vpc (10 ft × 0.375 in. 5% Carbowax 20M at 165°) and found to contain four components with retention times of 14, 16, 30, and 35 min. The first component (45%) was *trans*-2,3-dichlorobicyclo[2.1.1]hexan-*endo*-5-ol. The second (17%) was *trans*-3-chloro-*cis*-2-chloro-*trans*-4-hydroxybicyclo[3.1.0]hexane, and the third (15%) was *trans*-2,3-dichlorobicyclo[2.1.1]hexane-*endo*-5-methanol (from the methyl ester impurity). The fourth component (20%) was not identified.

Hydrolysis of *trans*-2,3-Dichlorobicyclo[2.1.1]hexyl *endo*-5-Acetate.—A mixture of 1.0 g of the acetate, 10 ml of 1 *N* sodium hydroxide solution, and 20 ml of ether was stirred at room temperature for 8 hr. The ether layer was washed with saturated salt solution and dried over magnesium sulfate. Removal of the solvent using a rotary evaporator gave 0.5 g of a yellow oil. It was separated into five components with retention times of 5, 10, 13, 16, and 34 min by vpc. The ratios were 2:5:2:2:1. The major component was unchanged starting material. The first component appeared to be 2-chloro-*trans*-4-hydroxybicyclo-[3.1.0]hex-2-ene. The third component was a 1:1 mixture of two compounds, one of which was methyl *trans*-2,3-dichlorobicyclo[2.1.1]hexane-*endo*-5-carboxylate (present in the reactant). The fourth was *cis*-2-chloro-*trans*-3-chloro-*trans*-4-hydroxybicyclo[3.1.0]hexane. The fifth was identical with the last component from the lithium aluminum hydride reduction.

Attempted Dehalogenation of *trans*-2,3-Dichlorobicyclo[2.1.1]-hexan-*endo*-5-ol.—The reaction of 1.0 g of the alcohol with magnesium amalgam formed from 1.5 g of magnesium and 150 g of mercury was carried out as described above. Vpc analysis of the product (10 ft × 0.375 in. 5% Carbowax 20M at 120°) showed four components with retention times of 5, 6, 7.5, and 8.5 min. The major component (8.5 min, 85%) was identified as Δ^3-cyclopentenylmethanol, and the third component was found to be Δ^2-cyclopentenylmethanol. The remaining components were not identified because of their low concentration.

The reaction of 0.5 g of the alcohol with sodium phenanthrene in dimethyl ether was carried out using the procedure described above. The residue was analyzed by nmr and none of the desired olefinic alcohol was found. Vpc analysis was not successful because of the apparent thermal instability of the product.

Registry No.—*exo*-**7**, 35672-74-3; **8**, 35672-75-4; **9**, 823-71-2; **10**, 35672-77-6; **10** monotosylhydrazone, 35655-59-5; **11**, 35672-78-7; **20**, 35672-79-8.

The Structures and Syntheses of Two Dihydropyrindines Isolated from California Petroleum[1]

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The structures of two nitrogen bases isolated from California petroleum have been assigned as *trans*-5,7-dimethyl-6,7-dihydro-5*H*-1-pyrindine and 5,7,7-trimethyl-6,7-dihydro-5*H*-1-pyrindine on the basis of spectral and synthetic studies. The *cis*-5,7-dimethyl and the 5,5,7-trimethyl analogs were prepared also. An improved synthesis of the 1-pyrindone nucleus is described. The nmr spectra of various 6,7-dihydro-5*H*-1-pyrindines are presented.

The occurrence of nitrogen bases as minor constituents of petroleum has led to numerous studies on the nature of these substances.[2] In general these bases are simple alkyl derivatives of pyridine, quinoline, and related benzo analogs, although a few more complex compounds have been identified.[2,3]

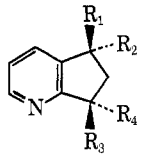
We wish to report the structure elucidations and syntheses of two new bases isolated from California

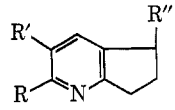
(1) Financial support of this research by the Robert A. Welch Foundation is gratefully acknowledged.

(2) (a) H. L. Lochte and E. R. Littman, "The Petroleum Acids and Bases," Chemical Publishing Co., New York, N. Y., 1955; (b) L. R. Snyder, *Accounts Chem. Res.*, **3**, 290 (1970).

(3) (a) L. R. Snyder, *Anal. Chem.*, **41**, 1084 (1960); (b) L. R. Snyder and B. E. Buell, *ibid.*, **40**, 1295 (1968); (c) E. J. Buell, *ibid.*, **39**, 756 (1967); (d) D. K. Albert, *ibid.*, **39**, 1113 (1967); (e) H. V. Drushel and A. J. Sommers, *ibid.*, **38**, 19 (1966); D. R. Latham and W. E. Haines, *ibid.*, **37**, 54 (1965).

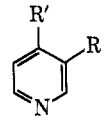
petroleum: *trans*-5,7-dimethyl-6,7-dihydro-5*H*-1-pyrindine (**1**) and 5,7,7-trimethyl-6,7-dihydro-5*H*-1-pyrindine (**2**). The parent base **5**[4a] and the three monomethyl analogs **6a–c**[4b–e] have been isolated previously from petroleum sources.





1, $R_1 = R_4 = CH_3$; $R_2 = R_3 = H$
2, $R_1 = R_3 = R_4 = CH_3$; $R_2 = H$
3, $R_1 = R_3 = CH_3$; $R_2 = R_4 = H$
4, $R_1 = R_2 = R_3 = CH_3$; $R_4 = H$

5, $R = R' = R'' = H$
6a, $R = CH_3$; $R' = R'' = H$
b, $R' = CH_3$; $R = R'' = H$
c, $R'' = CH_3$; $R = R' = H$



7, R = cyclopentyl; R′ = H
8, R = H; R′ = cyclopentyl

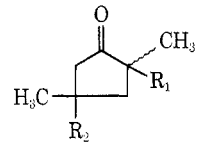
Results and Discussion

A preliminary structural assignment[5] of the two bases under consideration, originally characterized as picrates A and B, as the isomeric 3- and 4-cyclopentylpyridines (**7**, **8**) ($C_{10}H_{13}N$) was retracted upon synthesis of authentic **7** and **8**.[6] Reexamination of these substances by high-resolution mass spectroscopy[7] revealed that the base derived from picrate A has the expected composition $C_{10}H_{13}N$, while the base from picrate B corresponds to the empirical formula $C_{11}H_{15}N$. The nmr spectra for picrates A and B indicated that both materials were *ca.* 80–90% pure; the chemical shift data for the predominant isomer in each case are given in the Experimental Section.

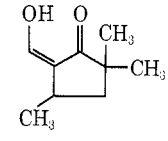
Consideration of the nmr data suggests that both bases possess a 6,7-dihydro-5*H*-1-pyrindine (**5**) nucleus. The presence of two doublet methyl groups and a methylene group (δ 2.20 ppm) remote from the pyridine nucleus[8] in the base corresponding to picrate A is consistent with the tentative assignment of this material as either *cis*- or *trans*-5,7-dimethyl-6,7-dihydro-5*H*-1-pyrindine (**3** or **1**). In an analogous fashion, the base derived from B is in accord with either the 5,5,7-trimethyl- or 5,7,7-trimethyldihydropyrindine structure (**4** or **2**). In order to confirm these tentative skeleton assignments and to resolve the geometric isomer uncertainty in the dimethyl base and the position isomer ambiguity in the trimethyl base, the synthesis of these four substances was undertaken.

The trimethyl-2-pyridones **13** and **14** were prepared from the trimethylcyclopentanones **10**[10] and **11**[11] *via* Michael addition of cyanoacetamide[12] to the corresponding hydroxymethylene derivatives (*e.g.*, **12**). The resulting adducts (part structure **15**) furnished **13** and **14** upon treatment with hydrochloric acid.

From a synthetic point of view the key cyanoacetamide addition step proceeded in only a modest yield (*ca.* 25%). Accordingly the behavior of the *n*-butylthiomethylene derivative (**16**) of 2,4-dimethylcyclopentanone (**9**)[13] was examined in this Michael reaction. Although no reaction was observed when **16** was treated with cyanoacetamide under the normal conditions,[12] *e.g.*, piperidine–ethanol at 40°, smooth conversion did occur when the substrates were heated at reflux with sodium ethoxide in ethanol. Spectral data indicated that the resulting adduct, obtained in 68% yield, was the 3-cyano-2-pyridone **17**. Hydrochloric acid treatment of **17** yielded a cis–trans mixture of the dimethyl-2-pyridone **18**.



9, $R_1 = R_2 = H$
10, $R_1 = H$; $R_2 = CH_3$
11, $R_1 = CH_3$; $R_2 = H$



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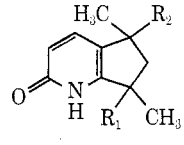
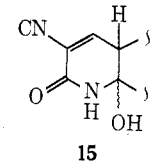
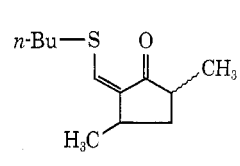


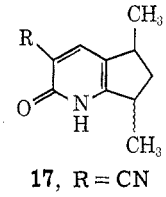
13, $R_1 = H$; $R_2 = CH_3$
14, $R_1 = CH_3$; $R_2 = H$



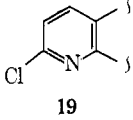
15



16



17, R = CN
18, R = H



19

Conversion of the 2-pyridones **13**, **14**, and **18** to the corresponding dihydro-5*H*-1-pyrindines **4**, **2**, and **1** and **3**, respectively, was unexceptional; treatment with dichlorophenylphosphene oxide furnished the 2-chloro-derivatives **19**, then either chemical or catalytic (preferred) reduction of **19** yielded the desired pyrindines. The nmr data for the free bases and for their picrates are summarized in Table I. In addition, data for some other dihydro-5*H*-1-pyrindine derivatives are included in Table I.

These data unambiguously identify the naturally occurring trimethyl compound, B, as the 5,7,7 isomer **2**. The mixture melting point of picrate B and the

(4) (a) J. Eguchi, *Bull. Chem. Soc. Jap.*, **8**, 235 (1928); (b) P. Arnall, *J. Chem. Soc.*, 1702 (1958); (c) H. L. Lochte and A. G. Pittman, *J. Amer. Chem. Soc.*, **82**, 469 (1960); (d) H. Suzumura, *Bull. Chem. Soc. Jap.*, **34**, 1097 (1959); (e) H. L. Lochte and A. G. Pittman, *J. Org. Chem.*, **25**, 1462 (1960).

(5) H. L. Lochte, E. D. Thomas, and P. Truitt, *J. Amer. Chem. Soc.*, **66**, 550 (1944).

(6) H. L. Lochte and E. N. Wheeler, *ibid.*, **76**, 5548 (1954).

(7) We wish to thank Professor C. Cone for his assistance in obtaining the high-resolution mass spectra data.

(8) Typical chemical shifts for methylene groups bonded to pyridine rings: C_2–CH_2–, δ 2.78;[9a] C_3–CH_2–, 2.61;[9b] C_4–CH_2–, 2.59[9c] ppm.

(9) Sadtler Standard Spectra, NMR Spectra, Sadtler Research Laboratories, Philadelphia, Pa: (a) spectrum no. 7556; (b) spectrum no. 6074; (c) spectrum no. 7557.

(10) (a) R. L. Wasson and H. O. House, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 552; (b) G. D. Ryerson, R. L. Wasson, and H. O. House, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 957.

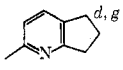
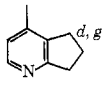
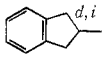
(11) Prepared by a modification of S. F. Birch and E. A. Johnson, *J. Chem. Soc.*, 1493 (1951). The resulting mixture of ketones (**10**, **11**) was separated efficiently by selective formation of the hydroxymethylene derivative **12** of the *less* hindered ketone **11**.

(12) W. C. Thompson, *J. Amer. Chem. Soc.*, **53**, 3160 (1931).

(13) D. Klamann and W. Lache, *Brennst.-Chem.*, **45**, 33 (1964).

TABLE I

NMR DATA FOR SOME 6,7-DIHYDRO-5*H*-1-PYRINDINES[a]

Compd	C-5 H	C-6 H_2	C-7 H	Methyl groups
2[b,c]	2.9–3.4 (m)	1.47 (dd, 9, 12) 2.15 (dd, 7, 12)		1.17 (s), 1.27 (d, 7), 1.34 (s)
2[d]	3.3–3.9 (m)	1.83 (dd, 9, 13) 2.45 (dd, 8, 13)		1.47 (d, 7), 1.49 (s), 1.60 (s)
4[b]		1.46 (dd, 10, 13) 2.16 (dd, 7, 13)	3.0–3.4 (m)	1.18 (s), 1.32 (s), 1.35 (d, 7)
4[d]		1.84 (dd, 7, 13) 2.46 (dd, 8, 13)	3.6–4.1 (m)	1.36 (s), 1.48 (s), 1.51 (d, 7)
1[b,c,e]	2.9–3.5 (m)	1.93 (2 H, t, 6)	2.9–3.5 (m)	[f]
1[c,d]	3.1–4.1 (m)	2.20 (2 H, m)	3.1–4.1 (m)	1.42 (d, 7), 1.42 (d, 7)
3[b,c,e]	2.9–3.5 (m)	1.2–1.5 (m) 2.3–2.9 (m)	2.9–3.5 (m)	[f]
3[d]	3.1–4.1 (m)	1.4–1.8 (m) 2.6–3.1 (m)	3.1–4.1 (m)	1.46 (d, 7), 1.52 (d, 7)
 [d,g]	3.13 (t, 7)[h]	2.33 (qn, 7)	3.31 (t, 7)[h]	2.78 (s)
 [d,g]	3.08 (t, 7)[h]	2.36 (q, 7)	3.49 (t, 7)[h]	2.54 (s)
 [d,i]	3.2–3.8 (m)	1.7–2.1 (m) 2.4–2.8 (m)	3.2–3.8 (m)	1.44 (d, 7)
 [d,i]	[j]	[j]	[j]	1.38 (d, 6.5)

[a] Chemical shifts are reported in parts per million downfield from internal TMS, 100-MHz spectra, $CDCl_3$ solvent unless specified otherwise; coupling constants (hertz) in parentheses; q = quartet, qn = quintet. [b] Solvent CCl_4. [c] 60-MHz spectrum. [d] Spectrum of picrate salt. [e] Data were obtained on the cis–trans mixture. [f] Overlapping methyl group signals, δ 1.17–1.44 ppm. [g] Reference 4c. [h] Based on data available; these assignments could be reversed. [i] Reference 4e. [j] Complex envelope, δ 2.6–3.9 ppm.

picrate of **2** showed no depression, thus confirming this assignment.

Although separation of the cis and trans isomers in the synthetic dimethyl series could be effected at the 2-pyridone (**18**) stage, considerable equilibration occurred during conversion to the 2-chloro derivative **19**. Thus isomer separation was carried out on the dihydropyrindines by fractional recrystallization of the mixture of picrates. The trans structure **1** was assigned to the picrate which showed a two-proton multiplet at δ 2.20 ppm for the C-6 methylene group. Since *both* C-6 methylene protons in the trans isomer **1** have identically disposed adjacent groups, the common chemical shift for these protons is in accord with the proposed structure. In contrast, the picrate of the other isomer revealed two nonequivalent one-proton signals for the C-6 methylene moiety, multiplets at δ 2.85 and *ca.* 1.5 ppm (partially obscured by the methyl group adsorptions). This is in accord with the nonequivalent nature of the two C-6 protons in the cis structure **3**. Analogous nmr data were observed in the 2-pyridone series and the cis- and trans-isomer assignments were made accordingly.

The nmr data for the naturally occurring base A are in complete agreement with those for the trans isomer **1**, thus establishing both the gross carbon skeleton and the stereochemistry of this material.

Experimental Section

Melting points were determined on a Mel-Temp apparatus and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 237B grating infrared spectrometer; nmr spectra were measured on a Varian Associates Model A-60 or HA-100 spectrometer. High-resolution mass spectra were obtained using a CEC Model 21-100 mass spectrometer. The microanalytical determinations were done by the Chemalytics, Inc., Tempe, Ariz.

100-MHz Nmr Data for Picrates A and B.—Picrate A[5] had mp 117–119°; nmr ($CDCl_3$) δ 8.60 (d, 1, J = 6 Hz, C-2 H), 7.70 (dd, 1, J = 6, 8 Hz, C-3 H), 8.15 (d, 1, J = 8 Hz, C-4 H), 3.1–4.1 (m, 1, C-5 H), 2.20 (m, 2, C-6 CH_2), 3.1–4.1 (1, m, C-7 H), and 1.42 ppm (6, d, J = 7 Hz, C-5 and C-7 CH_3 groups).

Picrate B[5] had mp 140–146°; nmr ($CDCl_3$) δ 8.56 (d, 1, J = 6 Hz, C-2 H), 7.74 (dd, 1, J = 6, 8 Hz, C-3 H), 7.17 (d, 1, J = 8 Hz, C-4 H), 3.3–4.0 (1, m, C-5 H), 1.83 (1, dd, J = 9, 13 Hz, C-6 H), 2.45 (1, dd, J = 7, 13 Hz, C-6 H), 1.47 (3, d, J = 7 Hz, C-5 CH_3), 1.49 (3, s, C-7 CH_3), and 1.60 ppm (3, s, C-7 CH_3).

***cis*- and *trans*-2,4-dimethylcyclopentanone** (9) was prepared from 3,5-dimethylphenol by the procedure of Klamann and Lache[13] in an overall yield of 54%, bp 92–96° (60 mm).

2,4,4-Trimethylcyclopentanone (11) was prepared by the method of House[10] from isophorone oxide in 48% yield, bp 69–70° (32 mm).

2,2,4- and 2,4,4-Trimethylcyclopentanone (10 and 11).—The procedure of Birch and Johnson[11] was followed using dihydroisophorone as a substrate to yield a mixture of ketones **10** and **11** in a yield of 80%, bp 66.5–68° (41 mm). Vpc analysis[14] showed an isomer composition of 59% **11** and 41% **10**.

3,5,5-Trimethyl-2-hydroxymethylenecyclopentanone (12).—Sodium hydride (57% mineral oil suspension, 6.45 g, 0.155 mol), under nitrogen was washed with hexane and then stirred for 30 min with a mixture of **10** and **11** (33 g, 0.26 mol, 0.15 mol of **11**) in benzene (300 ml). Ethyl formate (24 g, 0.31 mol) and 3 drops of methanol were added and the mixture was stirred for 16 hr at room temperature. The reaction mixture was diluted with ether (200 ml) and extracted with 5% NaOH solution. The combined aqueous extracts were acidified with concentrated HCl, saturated with NaCl, and extracted with ether. The ether extracts were dried ($MgSO_4$), the ether was evaporated,

(14) Vpc column: 10% FFAP, Chromosorb W, 10 ft × 0.125 in., 120°.

and the residue was distilled to yield 15.3 g of **12** (65% based on sodium hydride): bp 75–80° (9 mm); ir (CCl_4) 1680 (C=O) and 1610 cm^{-1} (enol double bond); nmr (CCl_4) δ 1.05 (s, 3, C-5 Me), 1.1 (s, 3, C-5 Me), 1.15 (d, 3, J = 7 Hz, C-3 Me), 1.3 (dd, 1, J = 12, 10 Hz, C-4 H), 1.95 (dd, 1, J = 12, 7 Hz, C-4 H), 2.5–3.1 (m, 1, C-3 H), 7.1 (d, 1, J = 1.5 Hz, vinyl H), and 12.2 ppm (s, 1, enol OH).

Ketone **11** could be regenerated by heating **12** with aqueous 15% NaOH at reflux for 4 hr. Vpc analysis[14] of the resulting product showed >99% **11**.

3,3,5-Trimethyl-2-hydroxymethylenecyclopentanone.—Sodium hydride (57% mineral oil suspension, 12.6 g, 0.311 mol), 2,4,4-trimethylcyclopentanone[10] (12.6 g, 0.10 mol), and ethyl formate (22.2 g, 0.31 mol) were allowed to react as described above to yield 10.9 g (71%) of product: bp 57–58° (2.3 mm); ir (thin layer) 1659 (C=O), 1607 cm^{-1} (enol double bond); nmr (CCl_4) δ 1.09 (d, 3, J = 7 Hz, C-5 Me), 1.16 (s, 3, C-3 Me), 1.21 (s, 3, C-3 Me), 1.45 (d, 1, J = 11.5 Hz, C-4 H), 1.99 (dd, 1, J = 11.5, 8 Hz, C-4 H), 2.1–2.9 (m, 1, C-5 H), 7.10 (s, 1, vinyl H), and 11.73 ppm (s, 1, enol OH).

3,5-Dimethyl-2-hydroxymethylenecyclopentanone.—Sodium hydride (57% mineral oil suspension, 21.5 g, 0.50 mol), 2,4-dimethylcyclopentanone[13] (19 g, 0.17 mol), and ethyl formate (37.8 g, 0.51 mol) in benzene with 3 drops of methanol were allowed to react as described above. Work-up yielded 15 g (63%) of product: bp 100–105° (35 mm); ir (CCl_4) 1680 (C=O) and 1612 cm^{-1} (enol double bond); nmr (CCl_4) δ 1.10 (d, 3, J = 7 Hz, C-3 or C-5 Me), 1.16 (d, 3, J = 6.5 Hz, C-3 or C-5 Me), 1.4–1.0 (0.5, C-4 H of cis isomer), 1.77 (dd, 1, J = 7, 8 Hz, C-4 H of trans isomer), 2.1–3.1 (m, 2.5, C-3 and C-5 H of cis and trans isomer, C-4 H of cis isomer), 7.04 (d, 0.5, J = 2 Hz, vinyl H), 7.20 (d, 0.5, J = 1.5 Hz, vinyl H of other isomer), and 11.13 ppm (s, 1, enol OH).

5,7,7-Trimethyl-6,7-dihydro-5*H*-1-pyrindin-2-ol (14).—Hydroxymethylene ketone (**12**) (14 g, 91 mmol), cyanoacetamide (10.5 g, 0.12 mol), piperidine (2.8 ml), H_2O (50 ml), and enough ethanol to effect solution were heated together at 40°. Filtration of the reaction mixture after 2.5 and 5 days yielded a white solid, which was recrystallized from ethanol to yield 4.3 g of solid A (22% based on part structure **15**): mp 250–265° dec; ir ($CHCl_3$) 3460 (C=O) and 1575 cm^{-1} (double bond); mass spectrum m/e 220 (M^+).

Solid A (2.5 g, 13 mmol) and concentrated HCl (10 ml) were heated in a bomb at 185–195° for 5.5 hr. The reaction mixture was diluted with water and neutralized with solid $NaHCO_3$. The resulting solid was collected and recrystallized from ethanol to yield 1.9 g (95%) of **14**: mp 188–189°; ir ($CHCl_3$) 1655 (C=O) and 1610 cm^{-1} (C=C); nmr ($CDCl_3$) δ 1.19 (d, 3, J = 7 Hz, C-5 Me), 1.29 (s, 3, C-7 Me), 1.45 (s, 3, C-7 Me), 1.52 (m, 1, C-6 H), 2.17 (dd, 1, J = 7.5, 12.5 Hz, C-6 H), 2.75–3.35 (m, 1, C-5 H), 6.38 (d, 1, J = 9 Hz, C-3 H), and 7.28 ppm (d, 1, J = 9 Hz, C-4 H).

Anal. Calcd for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.50; H, 8.65; N, 7.65.

5,5,7-Trimethyl-6,7-dihydro-5*H*-1-pyrindin-2-ol (13).—3,3,5-Trimethyl-2-hydroxymethylenecyclopentanone (10 g, 65 mmol), cyanoacetamide (7.1 g, 85 mmol), H_2O (35 ml), and piperidine (2 ml) in ethanol were allowed to react as described above. Filtration of the reaction mixture after 7–14 days yielded a white solid which was recrystallized from ethanol to yield 4.6 g of solid B (31% based on part structure **15**): mp 280–283° dec; (Nujol mull) 1661 cm^{-1} (broad); mass spectrum m/e 220.

Solid B (1.0 g, 4.60 mmol) and concentrated HCl (4 ml) were treated as described above to yield after recrystallization from ethanol 710 mg (88%) of **13**: mp 163–166°; ir ($CHCl_3$) 3470–2400 (br, NH), 1665 (C=O), 1605 cm^{-1} (C=C); nmr ($CDCl_3$) δ 1.12 (s, 3, C-5 Me), 1.25 (s, 3, C-5 Me), 1.39 (d, 3, J = 6.5 Hz, C-7 Me), 1.53 (m, 1, C-6 H), 2.2 (dd, J = 8, 12.5 Hz, C-6 H), 2.95–3.55 (m, 1, C-7 H), 6.42 (d, 1, J = 9 Hz, C-3 H), and 7.28 ppm (d, 1, J = 9 Hz, C-4 H).

Anal. Calcd for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.40; H, 8.48; N, 7.71.

5,7,7-Trimethyl-6,7-dihydro-5*H*-1-pyrindine (2).—Dihydropyrindol (**14**) (1.4 g, 7.9 mmol) and dichlorophenylphosphine oxide were heated for 4 hr at 160–190°. The mixture was diluted with H_2O (50 ml), neutralized with solid $NaHCO_3$, and extracted with ether. After drying ($MgSO_4$), the ether was evaporated to yield 1.25 g of 5,7,7-trimethyl-2-chloro-6,7-dihydro-5*H*-1-pyrindine (part structure **19**) (81%): nmr (CCl_4) 1.18 (s, 3, C-7 Me), 1.28 (d, 3, J = 7 Hz, C-5 Me), 1.34 (s, 3, C-7 Me), 1.52 (dd, 1, J = 9, 12.5 Hz, C-6 H), 2.19 (dd, J = 7, 12.5 Hz, C-6 H), 3.1 (m, 1, C-6 H), 6.97 (d, 1, J = 8 Hz, C-3 H), and 7.32 ppm (d, 1, J = 8 Hz, C-4 H).

A mixture of the crude 2-chlorodihydropyrindine (1.2 g, 6.15 mmol), sodium methoxide (440 mg, 6.45 mmol), and Raney nickel (0.2 g) in ethanol (33 ml) was hydrogenated (atmospheric pressure, room temperature). After hydrogen absorption ceased, the catalyst was removed by filtration through Celite, the solvent was evaporated, and the residue was distilled to give 810 mg (82%) of **2**: bp 58–59° (1.8 mm); nmr (CCl_4) δ 6.91 (dd, 1, J = 5, 7.5 Hz, C-3 H), 7.29 (m, 1, C-4 H), 8.25 ppm (m, 1, C-2 H), and Table I. The picrate of **2**, mp 153–155°, showed nmr ($CDCl_3$) δ 7.76 (dd, 1, J = 6, 8 Hz, C-3 H), 8.20 (br d, 1, J = 8 Hz, C-4 H), 8.58 ppm (br d, 1, J = 6 Hz, C-2 H), and Table I. The mixture melting point of picrate **2** and picrate B was 136–146°.

Anal. Calcd for $C_{17}H_{18}N_4O_7$: C, 52.30; H, 4.65; N, 14.35. Found: C, 52.52; H, 4.54; N, 14.28.

5,5,7-Trimethyl-6,7-dihydro-5*H*-1-pyrindine (4).—Dihydropyrindol (**13**) (1.4 g, 7.9 mmol) and dichlorophenylphosphine oxide (3.5 g, 18 mmol) were treated as described above to yield 1.18 g of 5,5,7-trimethyl-2-chloro-6,7-dihydro-5*H*-1-pyrindine (part structure **19**) (77%): ir (CCl_4) 1125 and 1170 cm^{-1} (aryl Cl); nmr (CCl_4) δ 1.18 (s, 3, C-5 Me), 1.30 (s, 3, C-5 Me), 1.31 (d, 3, J = 7 Hz, C-7 Me), 1.5 (dd, 1, J = 9.5, 12.5 Hz, C-6 H), 2.2 (dd, 1, J = 7.5, 12.5 Hz, C-6 H), 2.85–3.70 (m, 1, C-7 H), 6.99 (d, 1, J = 8 Hz, C-3 H), and 7.32 ppm (d, 1, J = 8 Hz, C-4 H).

The crude 2-chlorodihydropyrindine (1.18 g, 6.05 mmol) was refluxed for 6 hr with Zn dust (7.75 g, 0.12 mol) and concentrated HCl (29 ml). The mixture was then diluted with H_2O, filtered, and made basic. The white, gummy precipitate was removed by filtration and washed several times with ether. The aqueous solution was extracted with ether, the ether extracts were dried ($MgSO_4$), and the ether was evaporated. The residue was distilled to yield 0.42 g of **4**: bp 89–91° (4.3 mm); nmr (CCl_4) δ 6.90 (dd, 1, J = 5, 8 Hz, C-3 H), 7.27 (br d, 1, J = 8 Hz, C-4 H), 8.24 ppm (br d, 1, J = 5 Hz, C-2 H), and Table I. The picrate of **4**, mp 168.5–170.5°, showed nmr ($CDCl_3$) δ 7.71 (dd, 1, J = 6, 8 Hz, C-3 H), 8.08 (dd, 1, J = 2, 8 Hz, C-4 H), 8.61 ppm (dd, 1, J = 2, 6 Hz, C-2 H), and Table I. The mixture melting point of picrate **4** and picrate B was 118–151°.

Anal. Calcd for $C_{17}H_{18}N_4O_7$: C, 52.30; H, 4.65; N, 14.35. Found: C, 52.58; H, 4.72; N, 13.69.

3,5-Dimethyl-2-*n*-butylthiomethylenecyclopentanone (16).—3,5-Dimethyl-2-hydroxymethylenecyclopentanone (7.0 g, 50 mmol), *n*-butylthiol (5.55 g, 61.5 mmol), and *p*-toluenesulfonic acid (16 mg) were refluxed for 4.5 hr in benzene with a water separator. After washing with 10% $NaHCO_3$ and H_2O and drying ($MgSO_4$), the solvent was evaporated and the residue was distilled to yield 9.75 g (92%) of **16**: bp 91–93° (0.1 mm); ir ($CHCl_3$) 1690 (C=O), 1580 cm^{-1} (double bond); nmr ($CDCl_3$) δ 0.9–1.3 (6, CMe), 1.3–3.1 (m, 13), and 7.26 ppm (br s, 1, vinyl H).

Anal. Calcd for $C_{12}H_{20}OS$: C, 67.89; H, 9.50. Found: C, 68.19; H, 9.21.

***cis*- and *trans*-5,7-Dimethyl-3-cyano-6,7-dihydro-5*H*-1-pyrindin-2-ol (17).**—Thiobutylmethylene ketone **16** (6.5 g, 29 mmol), cyanoacetamide (4.1 g, 49 mmol), and sodium methoxide (2.6 g, 49 mmol) were heated in ethanol at reflux for 3.5 days. The solvent was evaporated and the residue was dissolved in water and acidified with concentrated hydrochloric acid. The solid formed was collected by filtration and recrystallized from ethanol to yield 3.75 g (68%) of **17**: mp 256–260° dec; ir ($CHCl_3$) 1655 (C=O), 1587 (double bond), and 2215 cm^{-1} (C≡N); nmr ($CDCl_3$) δ 1.22, 1.28, 1.38, 1.5 (all d, 6 H, J = 7 Hz, C-5 and C-7 Me), 1.15–1.55 (0.6 H, cis C_6H), 2.04 (t, 0.8 H, J = 7 Hz, trans C_6H_2), 2.4–3.7 (m, 2.6 H), 7.74 (s, 1, C-4 H), 13.0–14.2 ppm (broad, 1, NH).

Anal. Calcd for $C_{11}H_{12}N_2O$: C, 70.18; H, 6.43; N, 14.88. Found: C, 70.08; H, 6.56; N, 14.75.

***cis*- and *trans*-5,7-Dimethyl-5*H*-1-pyrindin-2-ol (18).**—Compound **17** (0.6 g, 3 mmol) and concentrated HCl (2.25 ml) were heated as above in a sealed tube at 140–150° for 4 hr. The reaction mixture was diluted with H_2O (20 ml) and neutralized with solid $NaHCO_3$. The resulting solid was collected and crystallized from ethanol to yield 0.45 g (87%) of **18**. The isomers could be separated by fractional recrystallization from ethanol: mp (mixture) 195–199°; ir ($CHCl_3$) 1650 (C=O), 1601 cm^{-1} (double bond). The trans isomer showed nmr ($CDCl_3$)

δ 1.17 (d, 3, J = 7 Hz, C-5 or C-7 Me), 1.34 (d, 3, J = 7 Hz, C-5 or C-7 Me), 1.94 (t, 2, J = 7 Hz, C-6 H), 6.40 (d, 1, J = 9.5 Hz, C-4 H), 7.34 (d, 1, J = 9.5 Hz, C-3 H), and 2.9–3.5 ppm (m, 2, C-5 and C-7 H). The cis isomer showed nmr ($CDCl_3$) δ 1.22 (d, 3, J = 7 Hz, C-5 or C-7 Me), 1.42 (d, 3, J = 7 Hz, C-5 or C-7 Me), 1.1–1.55 (1, C-6 H), 2.3–2.9 (m, 1, C-6 H), 2.7–3.4 ppm (m, 2, C-5 and C-6 H).

Anal. Calcd for $C_{10}H_{13}NO$: C, 73.59; H, 8.03; N, 8.58. Found: C, 73.71; H, 8.03; N, 8.61.

cis- and *trans*-5,7-Dimethyl-6,7-dihydro-5*H*-1-pyrindine (3 and 1).—The mixture of **18** (310 mg, 1.9 mmol) and dichlorophenylphosphine oxide (3 g, 15.4 mmol) was treated as described above. The crude product was filtered through silica gel with chloroform to yield 320 mg (93%) of 5,7-dimethyl-2-chloro-6,7-dihydro-5*H*-1-pyrindine: nmr ($CDCl_3$) δ 1.00–1.40 (6, C-5 and C-7 CH_3), 1.2–1.5 (0.6, cis C_6 H), 1.78 (t, 0.8, J = 7 Hz, trans C_6 H_2), 2.17–2.77 (m, 0.6, cis C_6 H_2), 2.7–3.5 (m, 2, C_5 and C_7 H), 6.88 (d, 1, J = 8 Hz, C_4 H), 7.25 (d, 2, J = 8 Hz, C_3 H); mass spectrum m/e 181 (molecular ion).

A mixture of the 2-chlorodihydropyrindine (300 mg, 1.66 mmol), NaOAc (136 mg, 1.66 mmol), and 5% Pd/C (125 mg) in HOAc was hydrogenated in a Parr apparatus (30 lb, 65°, 3 hr). The mixture was filtered through Celite, concentrated *in vacuo*, diluted with H_2O (30 ml), neutralized with solid $NaHCO_3$, and extracted with ether. The ether was dried ($MgSO_4$) and evaporated to yield 200 mg (76%) of 1 and **3**: nmr (CCl_4) δ 7.0 (dd, 1, J = 8, 6 Hz, C_3 H), 7.4 (br d, 1, J = 8 Hz, C_4 H), 8.37 ppm (br d, 1, J = 6 Hz, C_2 H), and Table I. The picrate mixture showed mp 113–124°. The picrate mixture could be separated by fractional recrystallization (EtOH) into the enriched trans and pure cis isomers. The picrate of the cis isomer, mp 125–127°, showed nmr ($CDCl_3$) δ 7.79 (dd, 1, J = 6, 8 Hz, C_3 H), 8.13 (d, 1, J = 8 Hz, C_4 H), 8.58 ppm (d, 1, J = 6 Hz, C_2 H), and Table I. The mixture melting point of picrate **3** and picrate A was 102–120°.

The picrate of the trans isomer (*ca.* 67% pure) showed nmr ($CDCl_3$) δ 7.76 (dd, 1, J = 6, 8 Hz, C_3 H), 8.21 (d, 1, J = 8 Hz, C_4 H), 8.65 ppm (d, 1, J = 6 Hz, C_2 H), and Table I.

Anal. Calcd for $C_{16}H_{16}N_4O_7$: C, 51.06; H, 4.29; N, 14.89. Found: C, 51.18; H, 4.38; N, 15.06.

Registry No.—**1,** 36358-24-4; **1** picrate, 36358-25-5; **2,** 36358-26-6; **2** picrate, 36358-27-7; **3,** 36358-28-8; **3** picrate, 36358-29-9; **4,** 36411-21-9; **4** picrate, 36358-30-2; **12,** 36358-31-3; **13,** 36358-54-0; **14,** 36358-55-1; **16,** 36358-56-2; *cis*-**17,** 36358-57-3; *trans*-**17,** 36411-24-2; *cis*-**18,** 36358-58-4; *trans*-**18,** 36358-59-5; 5,7-dimethyl-2-chloro-6,7-dihydro-5*H*-1-pyridine (cis), 36358-60-8; 3,3,5-trimethyl-2-hydroxymethylene cyclopentanone, 36358-61-9; *cis*-3,5-dimethyl-2-hydroxymethylenecyclopentanone, 36434-06-7; *trans*-3,5-dimethyl-2-hydroxymethylenecyclopentanone, 36357-91-2; 5,7,7-trimethyl-2-chloro-6,7-dihydro-5*H*-1-pyrindine, 36357-92-3; 5,5,7-trimethyl-2-chloro-6,7-dihydro-5*H*-1-pyrindine, 36357-93-4; 5,7-dimethyl-2-chloro-6,7-dihydro-5*H*-1-pyrindine (trans), 36357-94-5.

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Mesoionic Compounds. XX. Cycloaddition Reactions of Pyrylium Betaines[1]

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anhydro-3-Hydroxy-2,4,6-triphenylpyrylium hydroxide underwent 1,3-dipolar cycloaddition reactions with a variety of acetylenic and olefinic dipolarophiles, as well as heterocumulenes, forming 1:1 adducts by reaction at the 2,6 positions. Thermolysis of these adducts either resulted in rearrangement to substituted cyclohexadienones or in dissociation to the initial reactants. The adduct from diphenylacetylene was also converted into cycloheptadiene and cycloheptatriene derivatives.

Reports of 1,3-dipolar cycloaddition reactions[2] utilizing carbonyl ylides were, until quite recently, noticeably absent from the literature. The cycloaddition reactions of tetracyanoethylene oxides to olefins, acetylenes, and aromatic compounds,[3] and the thermal condensations of oxiranes in the presence of dipolarophiles,[4] may be interpreted in terms of an intermediate carbonyl ylide **1**. Recently, *cis*- and *trans*-dicyanostilbene oxides were also shown[5] to undergo cycloadditions at temperatures >100° with a variety of acetylenic and olefinic dipolarophiles and, similarly, *cis*- and *trans*-cyanostilbene oxides also underwent cycloadditions. The reactive intermediates in these reactions were carbonyl ylides formed in a conrotatory, electrocyclic ring opening of the oxirane by fission of the C–C bond.[6] The thermal decomposition of Δ^3-1,3,4-oxadiazolines in the presence of dipolarophiles also appears to involve a carbonyl ylide intermediate.[7]

Our interest in cycloaddition reactions in which mesoionic compounds[8a] are utilized as the source of the 1,3 dipole[8b] led us to study whether a suitable mesoionic-type ring system containing a 1,3 dipole of the

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