(51.8 mmol), and 100 mL of 1-propanol was heated at reflux for 1 h. The mixture was cooled in an ice bath and the precipitate was collected by filtration. After recrystallization from ethanol, there was obtained 8.76 g (63%) of **7** as yellow crystals: mp 115–116 °C; IR (KBr) 1740 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 0.96 (t, 3 H, CH_3, J = 7 Hz), 4.1 (q, 2 H, CH_2, J = 7 Hz), 7.54 (s, 5 H, C_6H_5), 7.8–8.6 (m, 4 H).

Anal. Calcd for $C_{17}H_{14}N_2O_3$: C, 69.37; H, 4.80; N, 9.52. Found: C, 69.03; H, 4.76; N, 9.73.

2-Phenylquinoxaline 1-Oxide (8a). A mixture of 8 g of **7** (27.2 mmol) and 60 mL of 0.5 N NaOH was stirred at room temperature for 1 h. The mixture was filtered from a small amount of suspended solid and the filtrate was neutralized with 65 mL of 0.5 N HCl. The precipitated solid was collected by filtration to give 4.5 g of crude 2-phenylquinoxaline-3-carboxylic acid 1-oxide, mp 142–144 °C dec. The crude acid was suspended in 60 mL of toluene and the mixture was heated at reflux for 2 h. The hot mixture was filtered and the filtrate was evaporated to give a residue. Trituration of this residue with diethyl ether gave 3.1 g of **8a** (51% from **7**) as light yellow crystals: mp 155–156.5 °C (lit.[8] mp 154 °C); ^1H NMR (Me_2SO-d_6) δ 7.5–7.66 (m, 3 H), 7.83–8.2 (m, 5 H), 8.5–8.62 (m, 1 H), 9.07 (s, 1 H).

Anal. Calcd for $C_{14}H_{10}N_2O$: C, 75.65; H, 4.45; N, 12.61. Found: C, 75.70; H, 4.52; N, 12.65.

Syntheses of 1,3-Bis(1′-alkylpyridinium)cyclopentadienides and the X-ray Crystal Structures of 1,3-Bis(1′-methyl-2′-pyridinium)indenide Bromide and 1-(1′-Methyl-2′-pyridinium)-3-(1″-methyl-4″-pyridinium)cyclopentadienide Bromide

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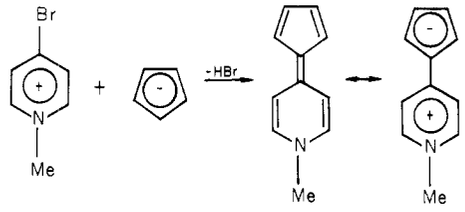
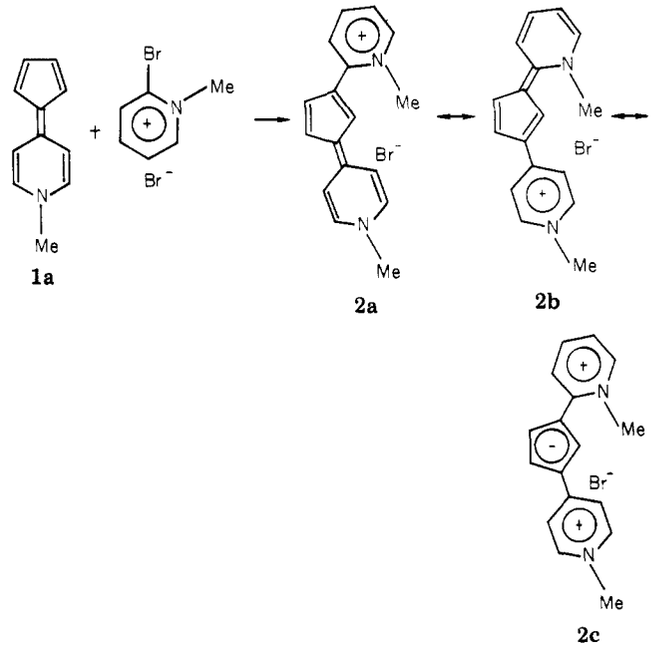
The reaction of cyclopentadienide with excess 2- or 4-bromo-1-alkypyridinium salts is described. The products may be thought of as alkylpyridinium-substituted fulvalenes or as 1,3-bis(alkylpyridinium)cyclopentadienides. The reaction probably proceeds via a fulvalene intermediate since the product can be obtained by starting with the appropriate fulvalene and 2- or 4-bromo-1-alkylpyridinium salt. Unsymmetrical products can be prepared from the fulvalene–pyridinium salt reaction. A similar kind of reaction occurs with indenides and their fulvalene analogues. X-ray crystallographic studies of a symmetrically substituted "indenide" and unsymmetrically substituted "cyclopentadienide" have been carried out. Bond lengths in the central five-membered ring suggest that the products are resonance hybirds of the two possible pyridinium–fulvalene structures that can be written for each compound. There is no evidence to support a tripolar structure, i.e., that of a bis(pyridinium)cyclopentadienide or indenide.

Cyclopentadienide reacts with 2- or 4-halo-1-alkylpyridinium salts to yield cyclopentadienylidene-1,2- or -1,4-dihydropyridines,[2] exemplied by the formation of 1-methyl-4-cyclopentadienylidene-1,4-dihydropyridine (**1**).



1a **1b**

Canonical structures **1a** and **1b** presumably are the major contributors to the resonance hybrid. We reported[3] previously that these cyclopentadienylidenedihydropyridines and their indenylidene analogues can react with 2- or 4-halo-1-alkylpyridinium salts to form cationic products, which can be envisaged as either 1-alkylpyridinium-substituted fulvalenes (e.g., **2a** and **2b**) or 1,3-bis(alkylpyridinium)cyclopentadienides (e.g., **2c**). By analogy to the structures of compounds similar to **2** but with pyridinium replaced by cyclopropenium, reported by Yoshida and co-workers,[4] structure **2c** can be termed a "tripolar mesomeric form". In this paper, we report the syntheses of **3a–g** and the results of X-ray crystallographic investigations of **3b** and **3e**.



1a **2a** **2b** **2c**

(1) From the Ph.D. dissertation of W.D.E., University of Maryland, 1977.

(2) J. A. Berson, E. M. Evleth, and Z. Hamlet, *J. Am. Chem. Soc.*, 87, 2887 (1965).

(3) W. D. Erhardt and H. L. Ammon, *Tetrahedron Lett.*, 3997 (1975).

(4) Z. Yoshida, S. Araki, and H. Ogoshi, *Tetrahedron Lett.*, 19 (1975).

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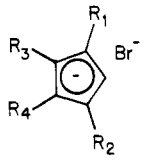
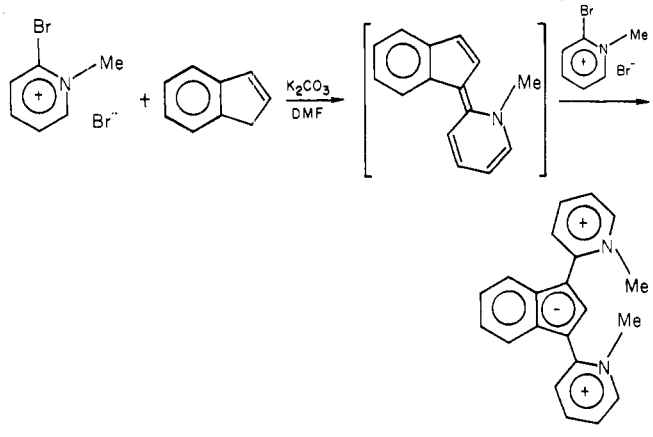


3a, $R_1 = R_2$ = 1-methyl-2-pyridinium; R_3 = H
b, R_1 = 1-methyl-2-pyridinium; R_2 = 1-methyl-4-pyridinium; R_3 = H
c, R_1 = 1-methyl-2-pyridinium; R_2 = 1-benzyl-4-pyridinium; R_3 = H
d, $R_1 = R_2$ = 1-methyl-2-pyridinium; R_3, R_4 = -CH=CHCH=CH-
e, $R_1 = R_2$ = 1-methyl-4-pyridinium; R_3, R_4 = $-(CH)_4-$
f, R_1 = 1-methyl-2-pyridinium; R_2 = 1-methyl-4-pyridinium; R_3, R_4 = $-(CH)_4-$
g, R_1 = 1-methyl-2-pyridinium; R_2 = 1-benzyl-4-pyridinium; R_3, R_4 = $-(CH)_4-$

Discussion

Synthesis. General methods for the preparation of the indenylidene analogues (e.g., **3d**) were reported in our



3d

earlier paper.[3] Symmetrical species such as **3a** and **3d** can be synthesized from cyclopentadiene or indene and 1-alkyl-2-bromopyridinium salts[5] in the presence of base. Fulvalenes presumably are intermediates in these reactions, and, indeed, fulvalenes react with alkylbromopyridinium salts under the same conditions. Although we have prepared only seven cyclopentadienides and indenides, it seems clear that the fulvalene plus pyridinium salt reaction should be capable of yielding a variety of tripolar derivatives. One very interesting possibility would involve cyclopropenium and pyridinium substituents in the same tripolar compound.

The reaction of a fulvalene such as 1 with a bromopyridinium cation can be thought of as occurring via an initial electrophilic attack on a pyridinium-substitued cyclopentadienide (e.g., structure **1b**) by the cation. HMO calculations of the π-electron energies of intermediates resulting from such an addition indicate that the cyclopentadienide atoms adjacent (ortho) to the pyridinium position are preferred over the nonadjacent (meta) atoms (i.e., the ortho intermediate is more stable than the meta analogue). Since the observed products arise from nonadjacent substitution, steric factors presumably then tilt

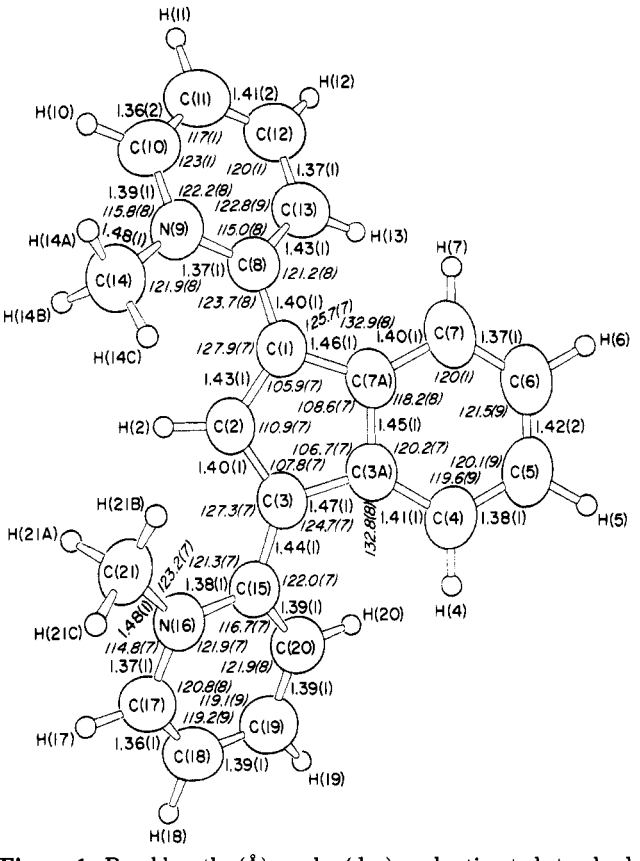


Figure 1. Bond lengths (Å), angles (deg), and estimated standard deviations (in parentheses) for 1,3-bis(1′-methyl-2′-pyridinium)indenide bromide (**3d**). The twist and tilt[10] angles are 31.8 and 8.9° for the C(1)–C(8) bond and 34.3 and 7.6° for the C(3)–C(15) bond.

the overall energy balance in favor of the nonadjacent position.

Since charge densities in the five-membered rings of compounds like 1 and 1-methyl-2-cyclopentadienylidene-1,2-dihydropyridine are in the range of 0.3–0.4 e,[6] it seems likely that fulvalenes should be somewhat less reactive than cyclopentadienide. This is borne out by consideration of the reaction conditions used to prepare fulvalenes from bromopyridinium salts with those used in the synthesis of the bis(alkylpyridinium)cyclopentadienides. The fulvalenes are prepared[2] from the reaction of bromopyridinium salts with ≥2 equiv of cyclopentadienide,[7] conditions which disfavor the reaction of fulvalene with unreacted pyridinium cation. In the two reactions reported here, which produce bis(alkylpyridinium)cyclopentadienides (**3a** and **3d**), 1-methyl-2-bromopyridinium bromide and cyclopentadiene or indene are used in 2:1 molar ratios, favoring the formation of the tripolar products. In our earlier paper,[3] the formation of **3d** from an excess of indene was probably the result of the reaction conditions: a DMF solution of indene and the pyridinium salt stirred together with solid potassium carbonate. It is likely that only low concentrations of indenide were formed under these conditions, unlike the fulvalene-forming reactions[2] in which cyclopentadienide was irreversibly produced before addition of the pyridinium salt. Thus the fulvalene, formed as the reaction proceeds, is able to effectively compete with the relatively low indenide concentrations for the pyridinium salt.[8]

(5) The most inexpensive and convenient method of preparing a 1-methyl-2-bromopyridinium salt is by the reaction of methyl iodide and 2-bromopyridine to give 1-methyl-2-bromopyridinium iodide. However, we elected to use 1-methyl-2-bromopyridinium bromide (from methyl bromide) for the preparation of the tripolar compounds to avoid possible problems with mixtures of bromide- and iodide-containing products.

(6) H. L. Ammon and G. L. Wheeler, *J. Am. Chem. Soc.*, **97**, 2326 (1975).

(7) One equivalent of cyclopentadienide presumably is consumed by proton abstraction from the initial pyridinium–cyclopentadienide adduct.

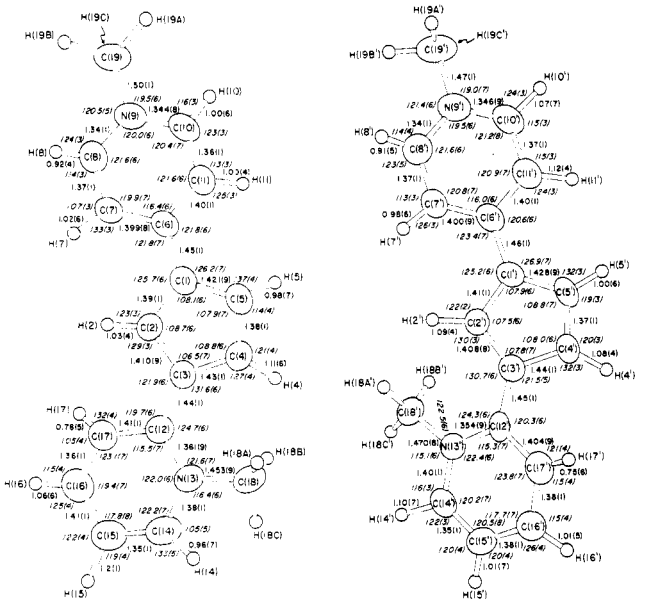


Figure 2. Bond lengths (Å), angles (deg), and estimated standard deviations (in parentheses) for the two crystallographically unique 1-(1′-methyl-2′-pyridinium)-3-(1″-methyl-4″-pyridinium)cyclopentadienide bromides (**3b**). The twist and tilt[10] angles are as follows: C(1)–C(6), 2.6 and 0.4°; C(3)–C(12) 8.8 and 2.1°; C(1′)–C(6′), 0.4 and 2.1°; C(3′)–C(12′), 24.1 and 1.9°.

Structure. Bond lengths and angles for the tripolar indenide **3d** superimposed on an ORTEP drawing of the structure are shown in Figure 1. The two pyridinium rings are twisted out of the plane of the indenide five-membered ring by angles of 31.8° (N(1) ring) and 34.3° (N(2) ring). The C(8)–C(1)–C(2)–C(3)–C(15) distances of 1.40, 1.43, 1.40, and 1.44 Å suggest that the N(2) ring has more pyridinium character (more positive charge) than the N(1) ring. The C(1)–C(7A) and C(3)–C(3A) bond lengths of 1.46 and 1.47 Å, respectively, are typical of C_{sp^2}–C_{sp^2} single bonds and quite different from those expected for the indenide portion[9] of a "tripolar" structure, such as **2c**. While the bond lengths indicate little or no indenide character for the central ring, there is a clear pattern for delocalization over the two heterocyclic rings via connecting atoms C(1), C(2), and C(3), and it would appear that the compound is best represented as a hybrid of resonance structures similar to those of **2a** and **2b**, with little or no contribution from **2c**.

It is improbable that the small difference in the twist of the two heterocyclic rings relative to the indenide nucleus, or other intramolecular effects, would be sufficient to produce the apparent inequality in positive-charge delocalization in the heterorings, which normally would be expected to be identical. A rationale for the apparent localization of greater positive charge on the N(2) ring may be found in the packing of the bromide ions around the organic cations in the crystal. The proximity of three anions to the N(2) ring, as opposed to two such approaches for the N(1) ring, may provide the electrostatic stabilization necessary for the extra buildup of positive charge on the N(2) ring.

The two symmetry-independent molecules in the **3b** crystal represent the *Z* and *E* isomers, related by rotation about the bond linking the cyclopentadienide and the 2-substituted-pyridinium rings (Figure 2). Carbon–carbon distances in the five-membered rings suggest, as in the case of **3d**, that the major contributors to the resonance hybrid are structures like **2a** and **2b**. The C(1)–C(5)–C(4)–C(3) distances are fairly typical of single–double–single bonds in fulvenoid five-membered rings and, together with the C(1)–C(2)–C(3) distances of intermediate value, are evidence for the absence of any significant contribution by tripolar cannonical form **2c**.

The twist angles of the 4-substituted pyridinium rings relative to the five-membered rings are small (2.6 and 0.4°). These angles and the inter-ring contact distances are very similar to those observed in 1-(2,6-dichlorobenzyl)-4-cyclopentadienylidene-1,4-dihydropyridine,[6] a compound which should have a substantially greater degree of inter-ring C=C character than **3b**. While the 2-substituted pyridinium to five-membered ring twist angles of 8.8 and 24.1° necessarily are larger, the 8.8° value is considerably less than the minimum of 20° that we had expected on the basis of other investigations. Again, crystal-packing effects seem to have a noticeable influence. First, there are 3.35- and 3.39-Å contacts between this 8.8° pyridinium ring and one in an adjacent molecule that would become shorter with further twist, and, second, the closet Br^- contacts in the crystal involve the 4-methylpyridinium ring in the unprimed molecule, which would favor an increased contribution of canonical form **2b** to the resonance hybrid and a concomitant decrease in the C(3)–C(12) twist.

Experimental Section

Melting points were determined on a Fisher-Johns hot-stage apparatus and are uncorrected. Microanalyses were performed by Dr. Frank Kasler, Department of Chemistry, University of Maryland. In addition to the reported NMR data, all products were characterized with infrared and ultraviolet–visible spectroscopic data. The NMR spectra were recorded on Varian EM-360 and A-60D spectrometers in Me_2SO-d_6 with 1% Me_4Si.

1-Methyl-2-bromopyridinium Bromide. Methyl bromide (6 g, 0.06 mol) was condensed into a thick-walled glass tube and cooled in a dry ice bath containing 2-bromopyridine (7.9 g, 0.05 mol) in 10 mL of methylene chloride. The tube was sealed and allowed to stand at room temperature for 2 days. The tube was cooled, opened, and allowed to warm to room temperature in a hood. The solid which had formed was filtered and recrystallized from acetonitrile, giving 5 g (35%) of white needles, mp 216 °C dec (lit.[11] mp 225–226 °C dec).

1-Methyl-4-bromopyridinium Bromide. This compound was prepared in a manner similar to that for the 2-bromo derivative only with 4-bromopyridine. Recrystallization from acetonitrile gave white needles, 160 °C dec. (The only literature reference to this compound found[12] prepared it in a similar manner but gave no melting point.)

1,3-Bis(1′-methyl-2′-pyridinium)indenide Bromide (3d). 1-Methyl-2-bromopyridinium bromide (4.2 g, 0.0166 mol), indene (0.97 g, 0.0083 mol), and powdered potassium carbonate (4.0 g, 0.029 mol) were stirred together in 50 mL of DMF for 24 h. The solvent was removed in vacuo and the residue extracted with methylene chloride, which was then filtered and evaporated to give 2.2 g (70%) of a gummy solid. Recrystallization from methanol gave the product as red needles: mp >230 °C dec; NMR δ 4.32 (s, 6 H, methyl), 6.0–8.7 (m, 13 H, pyridyl and indenyl). An X-ray crystallographic analysis is reported in this paper.

(8) Berson, Evleth, and Hamlet[2] reported a minor component (not purified) produced in the reaction of cyclopentadienide and 1-methyl-4-bromopyridinium iodide which was insoluble in benzene (the infrared spectrum indicated it was "polymeric").

(9) The five-membered-ring distances in indenyl lithium tetramethylenediamine [W. E. Rhine and G. D. Stucky, *J. Am. Chem. Soc.*, **97**, 737 (1975)] are C(3a)–C(7a) = 1.429 Å, C(7a)–C(1) = 1.401 Å, C(1)–C(2) = 1.380 Å, C(2)–C(3) = 1.370 Å, and C(3)–C(3a) = 1.414 Å.

(10) The terms twist and tilt refer to the angular relationship between the least-squares planes of two rings joined by a bond. The twist component refers to a rotation about the connecting bond, while the tilt component refers to the tip of one plane above or below the other plane.

(11) G. B. Barlin and J. A. Benbow, *J. Chem. Soc., Perkin Trans.* **2**, 790 (1974).

(12) G. Coppens, F. Declerck, C. Gillet, and J. Nasielski, *Bull. Soc. Chim. Belg.*, **72**, 25 (1963).

Table I. Crystal, Intensity Measurement and Refinement Data

	3d	3b
molec formula	$C_{21}H_{19}N_2Br$	$C_{17}H_{17}N_2Br \cdot {}^1/_2H_2O$
crystzn solvent	DMF	methanol
cryst shape and size	red needle, 0.2 × 0.1 mm, cut to 0.3 mm long	orange block, 0.25 × 0.25 × 0.20 mm
space group	$P2_1/n$	$P\bar{1}$ [c]
unit cell parameters (esd)	a = 24.899 (2) Å b = 7.681 (1) Å c = 9.265 (1) Å β = 90.92 (1)°	a = 15.267 (1) Å b = 9.8582 (6) Å c = 11.2147 (6) Å α = 89.54 (1)° β = 98.70 (1)° γ = 67.15 (1)°
Z	4	4
V, Å^3	1771.50	1533.41
ρ, g cm^{-3}	1.421	1.460
2θ scan speed, deg min^{-1}	1.0	2.0
time per bkgd, s	20	20
max 2θ (sin θ/λ)	50° (0.6076)	50° (0.6076)
tot no. of unique data (data 3σ above bkgd)	3115 (2623)	5411 (3189)
least-squares weights	$w = 1$ for $F_o < 30$, otherwise $w = (30/F_o)^2$	$w = 1/\sigma^2 (F_o)$
R [a]	0.061	0.059
R_w [b]	0.088	0.047

[a] $R = \Sigma \|F_o - F_c\| / \Sigma F_o$. [b] $R_w = [\Sigma w(F_o - F_c)^2 / \Sigma w F_o^2]^{1/2}$. [c] The crystal data cell parameters are a = 11.215 Å, b = 14.607 Å, c = 9.858 Å, α = 105.61°, β = 90.46°, γ = 80.59°. The transformation to this cell is 0,0,1/−1,1,0/0,−1,0.

1,3-Bis(1′-methyl-2′-pyridinium)cyclopentadienide Bromide (3a). This compound was prepared in the same manner as the corresponding indenide with freshly distilled cyclopentadiene rather than indene. Recrystallization from ethanol–benzene gave a 27% yield of a light orange-brown crystalline solid, mp 98–100 °C. Analyses suggested the compound crystallized as a hydrate: NMR δ 4.31 (s, 6 H, methyl), 6.75 (d, 2 H, five-membered ring), 7.24–7.42 (m, 3 H, five-membered ring and pyridyl), 7.90–8.30 (m, 4 H, pyridyl), 8.44–8.56 (m, 2 H, pyridyl). Anal. Calcd for $C_{17}H_{17}N_2Br$: C, 62.01; H, 5.17; N, 8.51. Calcd for $C_{17}H_{17}N_2Br \cdot H_2O$: C, 58.78; H, 5.48; N, 8.07. Found: C, 59.68; H, 5.50; N, 8.07.

1-(1′-Methyl-2′-pyridinium)-3-(1″-methyl-4″-pyridinium)cyclopentadienide Bromide (3b). 1-Methyl-4-cyclopentadienylidene-1,4-dihydropyridine was prepared by method A of Boyd, Ellis, and Harms[13] with sodium cyclopentadienide and 1-methylpyridinium iodide. This compound (0.32 g, 0.002 mol) was dissolved in 3 mL of DMF, and 1-methyl-2-bromopyridinium bromide (0.25 g, 0.002 mol) was added. There was an immediate, slightly exothermic reaction. After being stirred at room temperature for 1 h, the mixture was evaporated in vacuo and leached with 200 mL of acetonitrile which was then filtered and evaporated. Recrystallization from methanol gave red needles, mp 233–235 °C dec. The yield was 0.25 g (75%). Analyses indicated the compound crystallized as a hemihydrate, which was confirmed by X-ray crystallographic analysis: NMR δ 4.00 (s, 3 H, 4″-pyridyl methyl), 4.18 (s, 3 H, 2′-pyridyl methyl), 6.62–6.82 (m, 2 H, 2′-pyridyl), 7.26 (m, 1 H, 2′-pyridyl), 7.49 (m, 1 H, five-membered ring), 7.72–7.80 (m, 2 H, 4″-pyridyl), 7.95–8.18 (m, 2 H, five-membered ring), 8.20–8.36 (m, 2 H, 4′-pyridyl), 8.40–8.54 (m, 1 H, 2′-pyridyl). Anal. Calcd for $C_{17}H_{17}N_2Br$: C, 62.01; H, 5.20; N, 8.51; Br, 24.27. Calcd for $C_{17}H_{17}N_2Br \cdot {}^1/_2H_2O$: C, 60.37; H, 5.36; N, 8.28; Br, 23.62. Found: C, 60.22; H, 5.15; N, 8.40; Br, 22.94.

1-(1′-Methyl-2′-pyridinium)-3-(1″-benzyl-4″-pyridinium)cyclopentadienide Bromide (3c). This was prepared in the same way as the 1″-methyl derivative from 1-benzyl-4-cyclopentadienylidene-1,4-dihydropyridine (made by method A of Boyd et al.[13]). The product precipitated from the reaction solution and was recrystallized from methanol to give orange-red needles, mp 128–130 °C. The yield was 50%. Analyses suggested the compound crystallized as a hydrate: NMR δ 4.18 (s, 3 H, 2′-pyridyl methyl), 5.47 (s, 2 H, benzyl), 6.62–6.82 (m, 2 H, 2′-pyridyl), 7.30 (m, 1 H, 2′-pyridyl), 7.38–7.64 (m, 6 H, five-membered ring and phenyl), 7.72–7.80 (m, 2 H, 4″-pyridyl), 7.98–8.20 (m, 2 H, five-membered ring), 8.34–8.56 (m, 3 H, 4″-pyridyl and 2′-pyridyl). Anal. Calcd for $C_{23}H_{21}N_2Br$: C, 68.15; H, 5.19; N, 6.91. Calcd for $C_{23}H_{21}N_2Br \cdot H_2O$: C, 65.24; H, 5.44; N, 6.62. Found: C, 65.16; H, 5.31; N, 6.80.

1-(1′-Methyl-2′-pyridinium)-3-(1″-methyl-4″-pyridinium)indenide Bromide (3f). This compound was prepared in the same way as for the cyclopentadienide derivative with 1-methyl-4-indenylidene-1,4-dihydropyridine prepared by method A of Boyd et al.[13] The product was filtered from the reaction mixture (62% crude yield) and recrystallized from methylene chloride or (preferably) methanol to give red needles, mp 243–245 °C. Analyses suggested that the compound may have crystallized as a partial hydrate or methanolate: NMR δ 4.30 (s, 3 H, 2′-pyridyl methyl), 3.91 (s, 3 H, 4″-pyridyl methyl), 7.0–8.8 (m, 13 H, indenyl and pyridyl). Anal. Calcd for $C_{21}H_{19}N_2Br$: C, 66.49; H, 5.01; N, 7.39. Calcd for $C_{21}H_{19}N_2Br \cdot {}^1/_2H_2O$: C, 65.97; H, 5.15; N, 7.22. Calcd for $C_{21}H_{19}N_2Br \cdot {}^1/_2CH_3OH$: C, 65.32; H, 5.31; N, 7.09. Found: C, 65.22; H, 5.04; N, 7.51.

1-(1′-Methyl-2′-pyridinium)-3-(1″-benzyl-4″-pyridinium)indenide Bromide (3g). This compound was prepared in the same manner as for the 1″-methyl compound from 1-benzyl-4-indenylidene-1,4-dihydropyridine in 44% crude yield. Recrystallization from acetonitrile gave red needles: mp 245–246 °C; NMR δ 4.34 (s, 3 H, 2′-pyridyl methyl), 5.43 (s, 2 H, 4″-pyridyl benzyl), 7.0–8.85 (m, 18 H, indenyl and pyridyl). Anal. Calcd for $C_{27}H_{23}N_2Br$: C, 71.21; H, 5.09; N, 6.15. Found: C, 70.95; H, 5.04; N, 6.03.

1,3-Bis(1′-methyl-4′-pyridinium)indenide Bromide (3e). This compound was prepared in the same manner as the unsymmetric 1,3-pyridiniumindenides from 1-methyl-4-indenylidene-1,4-dihydropyridine and 1-methyl-4-bromopyridinium bromide. Recrystallization from acetonitrile gave a 30% yield of red needles with a metallic green shine; mp 255–258 °C. Analyses suggested the compound crystallized as a hydrate: NMR δ 3.99 (s, 6 H, methyl), 7.16 (m, 2 H, benzo), 7.90–8.16 (m, 4 H, benzo and pyridyl), 8.16–8.35 (m, 2 H, pyridyl), 8.37 (s, 1 H, five-membered ring). Anal. Calcd for $C_{21}H_{19}N_2Br$: C, 66.49; H, 5.01; N, 7.39. Calcd for $C_{21}H_{19}N_2Br \cdot H_2O$: C, 63.47; H, 5.31; N, 7.05. Found: C, 62.90; H, 5.14; N, 7.12.

X-ray Crystallographic Studies of 3b and 3d. Crystal, X-ray intensity measurement, and refinement data are listed in Table I. The final cell parameters and intensity measurements were made with a Picker FACS-I diffractometer with graphite-crystal-monochromatized Mo Kα radiation (Kα λ = 0.71069 Å). The intensity data were collected with the θ–2θ scan method.[14] The

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(14) A detailed description of the experimental procedures used in our X-ray laboratory may be found in H. L. Ammon, *J. Am. Chem. Soc.*, **95**, 7093 (1973).

3b structure was solved with heavy-atom Patterson techniques, while **3d** was determined with direct methods.[15] The structures were refined by full-matrix least-squares techniques with minimization of $\sum w(F_o - F_c)^2$. Anisotropic temperature factors were used for C, N, O, and Br; isotropic terms were used for H. Few of the H atoms in **3d** refined well, and these atoms were fixed at idealized positions for the last several least-squares cycles. The F_c's were corrected for isotropic secondary extinction,[16] and only those terms for which $I_c > 3\sigma(I)$ were included in the calculations. The f curves for C, N, O, and Br were obtained from the analytical functions of Cromer and Mann;[17] the H values were interpolated from data tabulated by Stewart, Davidson, and Simpson.[18]

(15) All of the crystallographic calculations were performed on a UNIVAC 1108 computer at the University of Maryland's Computer Science Center, with the X-ray 72 system [J. M. Stewart, G. J. Kruger, H. L. Ammon, C. Dickinson, and S. R. Hall, Report TR-192, Computer Science Center, University of Maryland, College Park, MD, 1972] of programs.

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(17) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).

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Registry No. 1a, 1916-70-7; **3a**, 73198-81-9; **3b**, 73210-17-0; **3c**, 73198-82-0; **3d**, 58805-28-0; **3e**, 73198-83-1; **3f**, 73210-18-1; **3g**, 58805-30-4; 1-methyl-2-bromopyridinium bromide, 52693-57-9; 2-bromopyridine, 109-04-6; 1-methyl-4-bromopyridinium bromide, 73198-84-2; 4-bromopyridine, 1120-87-2; indene, 95-13-6; cyclopentadiene, 542-92-7; 1-benzyl-4-cyclopentadienylidene-1,4-dihydropyridine, 729-28-2; 1-methyl-4-indenylidene-1,4-dihydropyridine, 1916-68-3; 1-benzyl-4-indenylidene-1,4-dihydropyridine, 58805-29-1.

Supplementary Material Available: Tables of the atomic coordinates and temperature factors and crystal packing diagrams for **3b** and **3d** (8 pages). Ordering information is given on any current masthead page.

(18) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

Synthesis of 3,4-Dihydro-4-(2-hydroxyphenyl)pyrido[2,3-*d*]pyrimidin-2(1*H*)-ones by a Novel Rearrangement of a 5*H*-[1]Benzopyrano[2,3-*b*]pyridine Derivative

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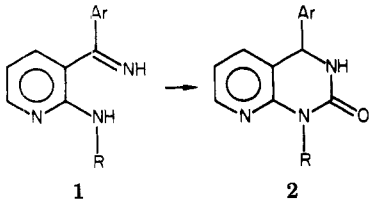
The benzopyrano[2,3-*b*]pyridine **4** undergoes a facile base-induced ring rearrangement in the form of its monoanion derivatives **5** or **7** to afford the pyrido[2,3-*d*]pyrimidin-2(1*H*)-ones **8a** and **8b**, respectively. Deuteration experiments confirm the formation of the urea dianion **6** which does not rearrange but initially reacts with iodomethane at 0–20 °C and subsequently rearranges to **8b**.

As part of an investigation of the chemistry and biological activity of a series of 5*H*-[1]benzopyrano[2,3-*b*]-pyridin-5-ylureas,[1] we have observed a novel base-induced ring rearrangement of the 1,3-dimethylurea derivative **4** to give the 3,4-dihydro-4-(2-hydroxyphenyl)pyrido[2,3-*d*]pyrimidin-2(1*H*)-ones **8a** and **8b** (Scheme I). The only previously reported synthesis of this class of compounds has involved the cyclization of a 2-aminopyridine derivative (**1**) followed by reduction of the 3,4 double bond to give **2**.[2]



1 **2**

In the present case, reaction of 5*H*-[1]benzopyrano-[2,3-*b*]pyridin-5-ol (**3**) with 1,3-dimethylurea under acid-catalyzed conditions ($HOAc/CH_3CN$) gave **4** in 65% yield. Treatment of **4** with 1 molar equiv of LiN-*i*-Pr_2 (LDA) in THF at −40 °C gave the monoanion **5** which afforded **8a** (62%) after warming to room temperature. When **5** was treated at −40 °C with excess iodomethane and warmed to 20 °C, rearrangement also occurred to give **8a** and not the 1,1,3-trimethylurea derivative.

The formation of a carbanion α to nitrogen in amides with LDA has been reported recently.[3] By contrast, we are unaware of any examples of metalation on carbon α to a urea nitrogen. When **4** was treated with 2 molar equiv of LDA in THF at −40 °C to form the dianion **6** followed by the addition of 2 molar equiv of iodomethane and warming to 25 °C, **8b** was isolated (44%). TLC of the crude product before recrystallization showed one major component corresponding to **8b**.

The ^1H NMR spectrum of **4** is reported in the Experimental Section and is readily interpretable. In the mass spectrum, the molecular ion at m/e 269 is abundant, and

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(1) A complete description of this research will be published separately.

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