Annelation of Pyridinium Rings onto Nitrogen Heterocycles

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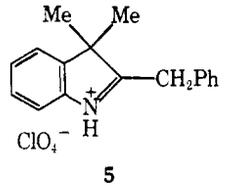
Numerous new fused pyridinium salts were synthesized by the interaction of protonated heterocycles with α,β-unsaturated ketones. The mode of addition was shown to depend on the heterocycle used and sometimes on the reaction conditions. Dihydropyridinium intermediates could be isolated in many cases.

In a preliminary communication[1] we described a simple method for the synthesis of fused pyridinium salts by the reaction of protonated heterocycles with methyl vinyl ketone. In this paper we report the extension of this method to other heterocycles and unsaturated ketones.

The first example of this synthesis[1] was the preparation of 3-methyl-4-phenylpyrido[2,1-*b*]benzothiazolium bromide (**4**) according to Scheme I. The formal Michael addition of 2-benzylbenzothiazolium bromide (**1**) to methyl vinyl ketone (MVK) in acetonitrile gave the adduct **2**. Additions of this type to salts of other nitrogen heterocyclic bases have been reported previously.[2,3] Product **2** was characterized by its IR, NMR spectra, and elemental analysis.

Heating **2** in a variety of solvents caused ring closure of the active methylene and the carbonyl group to give the dihydropyridobenzothiazolium salt **3**. The NMR spectrum (Me_2SO-d_6) of this compound showed a methyl group at δ 2.03 and two methylene triplets centered at δ 3.18 and 4.85. The aromatization of **3** to **4** could be carried out in a variety of ways, e.g., prolonged heating in DMA or Me_2SO, but most easily by heating with Pd/C in DMA. Characteristic peaks in the NMR spectrum (Me_2SO-d_6) of **4** were a methyl group at δ 2.53 and a single proton doublet at δ 10.24 assigned to the hydrogen at position 1.

The extension of this reaction sequence to the other nitrogen heterocyclic salts shown (**5–8**) gave varying results. Under



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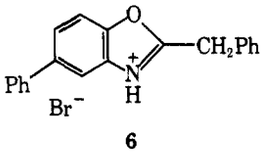

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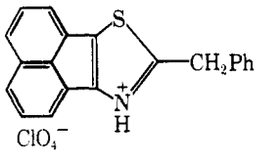

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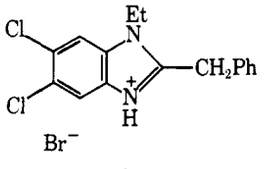
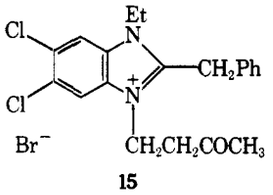


8

appropriate conditions salts **6** and **7** gave in turn Michael adducts (**9** and **12**), ring-closed dihydropyridinium salts (**10** and **13**), and the fully aromatic fused pyridinium salts (**11** and **14**) (Scheme II). Although **8** successfully formed the Michael adduct **15** with MVK, it failed to give an appreciable amount



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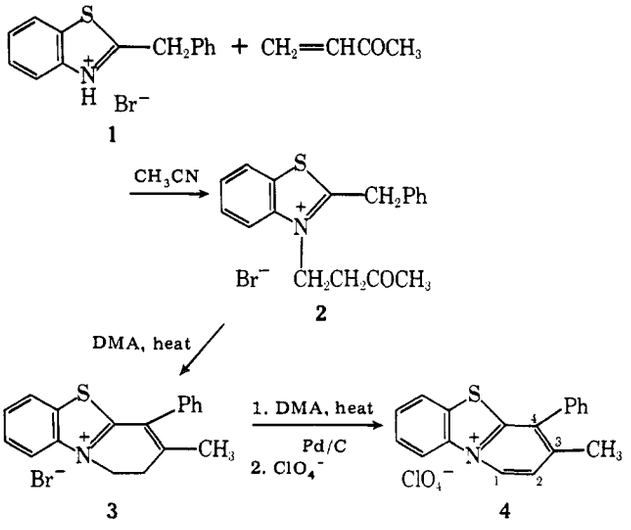
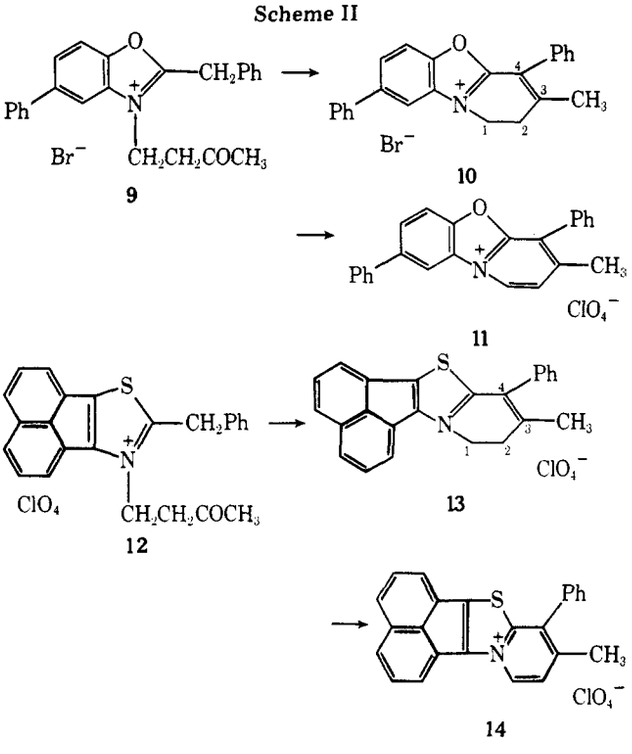
of ring-closed dihydropyridinium salt. This behavior was attributed to the low acidity of the benzylic methylene causing

Scheme I

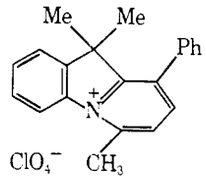


Scheme II



the reverse Michael reaction to compete favorably with ring closure. When the Michael addition was carried out with **5**, the vinyl group of the MVK became attached to the benzylic carbon as opposed to the nitrogen, and cyclization and aromatization occurred to give **16** instead of the expected **17**.

The structure of **16** was established by its NMR spectrum, which showed a methyl peak at δ 3.32 which is at least 0.5 ppm toward lower field than that expected from structure **17**. The



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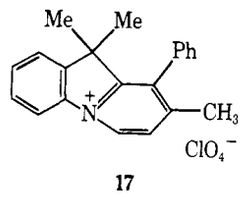
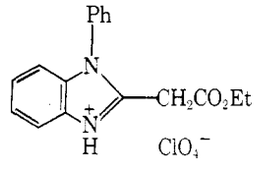


17

spectrum also lacked the doublet at δ 10.0 which is characteristic of a proton α to a positively charged pyridine nitrogen. This reversal of the mode of addition of MVK will be discussed later with reference to 2,3,3-trimethyl-3*H*-indolium salts and other unsaturated ketones.

In order to facilitate ring closure of the Michael adducts from various benzimidazolium salts and MVK, the acidities of the hydrogens involved in the condensations were increased by activating with ethoxycarbonyl groups. When **18** was treated with MVK in acetonitrile, the Michael adduct was not



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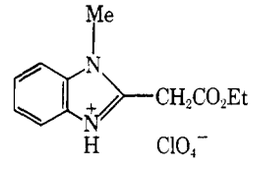

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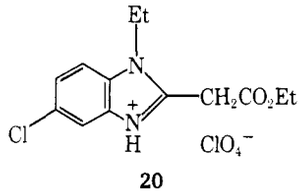
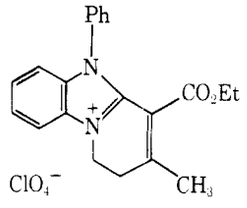


20

isolated in crystalline form. The resulting syrup was boiled in 2,6-lutidine and subsequently treated with ethanol to give the dihydropyridinium salt **21.** Aromatization to **22** was achieved by heating in DMA with Pd/C as before. When **19**



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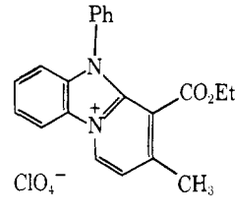

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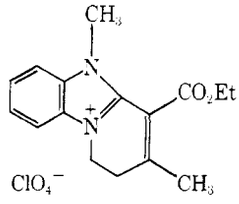
was reacted with MVK in acetonitrile, again a crystalline adduct was not isolated. Ring closure presumably occurred when the resulting syrup was subsequently boiled in pyridine. In addition to the expected product, **23, 24,** or **25** was also



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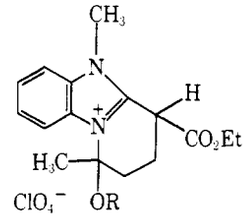
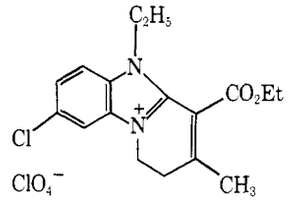


24, R = Et
25, R = H

isolated depending upon whether the workup involved ethanol (to give **24**) or acetic acid (to give **25**). Evidently, the vinyl group of the MVK reacted partially at nitrogen and partially at the activated methylene. The structures of **24** and **25** were assigned from the NMR spectra (90 MHz; 100 atom % Me_2SO-d_6) using decoupling techniques.

The dihydropyridinium ester **26** was prepared from **20** via the procedure used to prepare **23** from **19.** Upon aromatization, loss of the ethoxycarbonyl group and substantial hydrogenolysis of the chlorine–carbon bond also occurred giving an inseparable mixture of **27** and **28.** The mole percentages of the two salts present were estimated from the elemental analyses as both the perchlorate and fluoroborate salts. The NMR (Me_2SO-d_6) of mixed **27** and **28** showed a broadened



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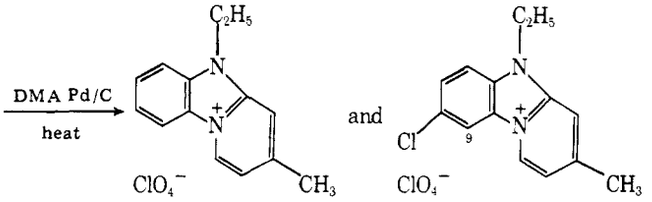
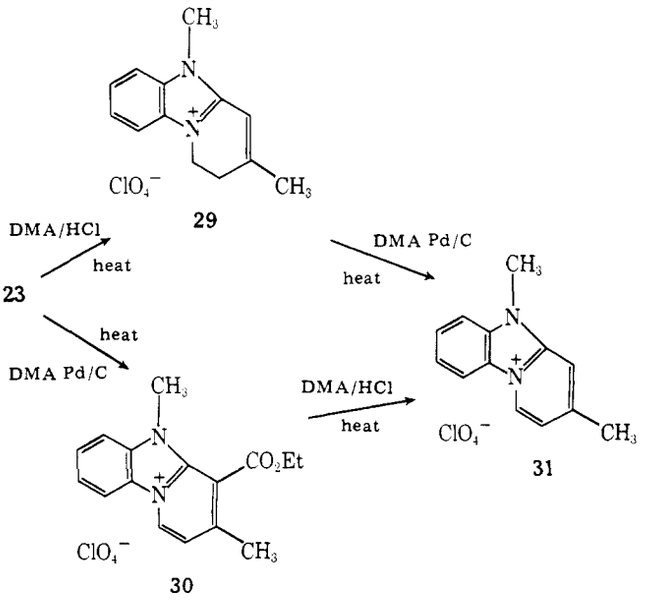


27 (~80%) and 28 (~20%)

doublet at δ 8.53 (J = 8 Hz) assigned to the proton at position 9 in **27;** a small doublet at δ 8.76 (J = 2 Hz) was assigned to the proton at position 9 in **28.** The unexpected loss of the ester group during this reaction suggested that hot DMA containing HCl might be an effective medium for carrying out the ester hydrolysis of compounds of this type.

In support of this suggestion it was found that the dihydropyridinium ester **23** could be selectively aromatized or hydrolyzed and decarboxylated. The resulting quaternary salts **29** and **30** were then converted to **31.** Boiling DMA con-

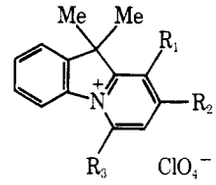


29, 30, 31

taining 5% of concentrated hydrochloric acid was very effective at hydrolyzing and decarboxylating the esters if part of the solvent was allowed to boil off. The use of a reflux condenser resulted in substantially lower yields.

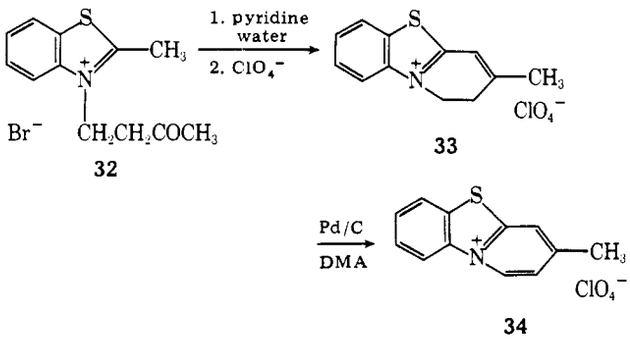
With Michael adducts containing a 2-methyl group of sufficient acidity, e.g., the 2-methylbenzothiazolium adduct **32,** the ring closure reaction to form **33** does occur but only to the

Table I[a]



Registry no.	R_1	R_2	R_3	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N	Mp, °C	Yield, %	CH_3, ppm
55867-79-3	CH_3	H	CH_3	59.3	5.0	4.3	59.6	5.3	4.6	217	27	3.20
55868-11-6	H	CH_3O-Ph	CH_3	63.5	5.2	3.4	63.7	5.2	3.6	298–300	50	3.22
62476-17-9	H	Ph	Ph	69.8	5.0	3.1	69.4	5.1	3.1	>310	30	
55953-69-0	H	CH_3O-Ph	Ph	67.8	5.1	2.9	67.8	5.3	2.9	258	26	
55953-76-9	H	Ph	CH_3O-Ph	67.8	5.1	2.9	67.5	5.3	2.9	245	43	
62476-19-1	CH_3	CH_3O-Ph	CH_3	67.3	5.9	3.4	67.1	5.9	3.3	290	25	3.32

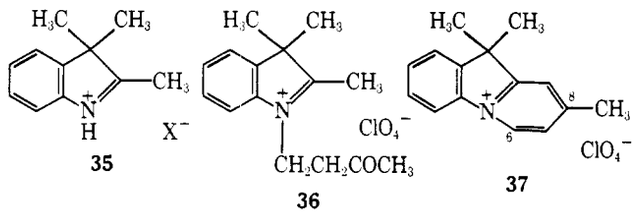
[a] Satisfactory analytical data (±0.4% for C, H, N) were reported for all new compounds listed in the table.



32 33 34

extent of a 17% yield owing to the competition with the reverse Michael reaction. Aromatization to **34** was carried out in the normal manner.

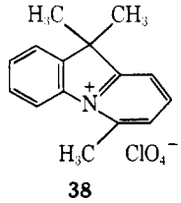
In the case of the reaction of 2,3,3-trimethyl-3*H*-indolium perchlorate (**35**) with MVK either neat or in acetonitrile the product was the open-chain adduct **36** which when heated in



35 36 37

pyridine formed the aromatic compound **37.** No dihydro intermediate was observed.

If, however, the initial reaction of **35** with MVK was run in DMA at room temperature no **36** was obtained and the only

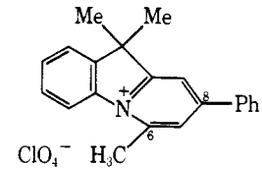


38

product was **38** analogous to **16** in which carbon alkylation predominated.

The two products **37** and **38** could readily be distinguished by the methyl resonances in their NMR spectra: **37** at δ 2.79 and **38** at δ 3.33.

2,3,3-Trimethylindolium perchlorate (**35**) also proved to be the most reactive of all the salts studied in terms of its reaction with other unsaturated ketones. When it was heated



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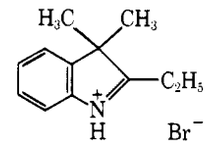
with benzylideneacetone at 100 °C, addition and cyclization occurred to form **39,** the 8-phenyl analogue of **38.**

Some other pyridoindolium salts formed by the carbon alkylation of both the 2-methylindolium salt **35** and the 2-



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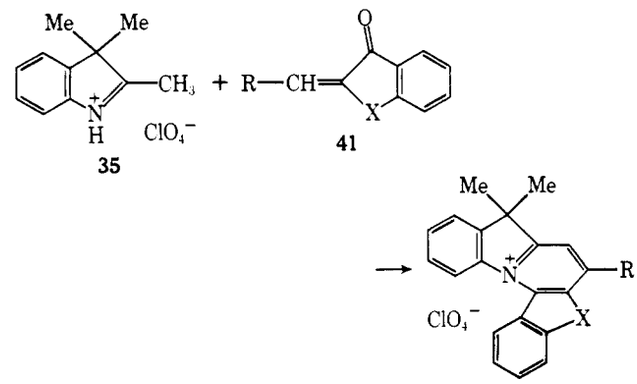
ethylindolium salt **40** with unsaturated ketones are shown in Table I.

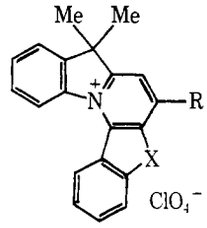
The 3*H*-indolium salt **35** will also react with unsaturated ketones where the ketone function is contained in a ring; for



35 41 42

example, 2-benzylidene-1-indanone **41** (R = Ph; X = CH_2) gives the indenopyridoindolium salt **42** (R = Ph; X = CH_2).

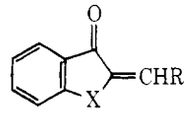
Table II[a]



Registry no.	R	X	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N	Mp, °C	Yield, %
55953-71-4	Ph	CH_2	70.5	4.8	3.1	70.5	5.1	2.8	259–261	48
62476-21-5	CH_3O–Ph	CH_2	68.6	4.9	2.9	68.5	4.9	2.8	229–230	29
61049-39-6	2-furyl	CH_2	66.8	4.5	3.1	66.5	4.8	3.0	229–230	18
61049-41-0	CH_3O_2C–Ph	O	64.8	4.2	2.7	64.8	4.1	2.6	300	26
62476-23-7	Ph	C=O	68.4	4.2	3.0	68.4	4.5	2.8	300	11

[a] Satisfactory analytical data (±0.4% for C, H, N) were reported for all new compounds listed in the table.

Table III



R	X	Mp, °C	Lit. mp, °C
Ph	CH_2	111	111[a]
CH_3O–Ph	CH_2	141	141[a]
2-furyl	CH_2	119	119[a]
Ph	C=O	152	152[b]
CH_3O_2C–Ph	O	204[d]	[c]

[a] Y. Poirier and N. Lozac'h, *Bull. Soc. Chim. Fr.*, 1062 (1966). [b] L. Geita and G. Vanags, *Zh. Ohshch. Khim.*, 27, 3107 (1957). [c] Anal. Calcd for $C_{17}H_{12}O_4$: C, 72.9; H, 4.3. Found: C, 73.1; H, 4.1. [d] Registry no., 61049-42-1.

Other examples of this type of product where X and R are varied are shown in Table II. The necessary intermediates for the synthesis of the compounds listed in Table II are given in Table III.

From the variety of examples discussed, it can be seen that this new annelation method provides a means for the synthesis of novel heterocycles by a simple one-step or two-step process. Although the yields seldom exceed 50%, the simplicity of the process more than compensates for this.

Experimental Section

All melting points were taken on a Thomas-Hoover melting point apparatus and are corrected. The IR spectra were measured as potassium bromide pressings on a Perkin-Elmer 257 grating spectrophotometer. TheNMR spectra were recorded with a Varian A-60 or Brüker 90-MHz instrument, and absorption values are given in parts per million downfield from tetramethylsilane added as an internal standard. Gas chromatography was run on an FM 650 chromatograph using a 6-ft column of 10% OV-17 packing.

Most of the salts used were prepared by addition of the appropriate acid to a solution of the heterocyclic base in ether. After filtration they were generally used without further purification.

2-Benzylbenzothiazole was prepared as described by Hofmann[4] and converted to the hydrobromide.

2-Benzyl-3-(3-oxo-1-butyl)benzothiazolium Bromide (2). 2-Benzylbenzothiazolium bromide (1, 24.5 g) in acetonitrile (100 mL) was treated with methyl vinyl ketone (6 g) and stirred overnight at room temperature. The starting material dissolved and the product precipitated: yield 19.9 g (66%); mp 144 °C; IR 1710 cm^{-1}; NMR (MeOD) δ 5.05 (s, 2 H, CH_2Ph), 2.2 (s, 3 H, CH_3CO), 3.4 (t, 2 H, $-CH_2CO$), 5.07 (t, 2 H, N^+CH_2).

Anal. Calcd for $C_{18}H_{18}BrNOS$: C, 57.4; H, 4.8; N, 3.7. Found: C, 57.3; H, 5.1; N, 3.8.

1,2-Dihydro-3-methyl-4-phenylpyrido[2,1-*b*]benzothiazolium Bromide (3). The adduct 2 (10 g) was heated to reflux in dimethylacetamide (50 mL). The solution was then cooled and the product collected, yield 8 g. Recrystallization from ethanol gave mp 208–210 °C: NMR (Me_2SO-d_6) δ 2.03 (s, 3 H, CH_3), 3.18 (t, 2 H, $-CH_2C=$), 4.85 (t, 2 H, $-CH_2N^+$), 7.4–8.4 (m, 9 H, aryl).

Anal. Calcd for $C_{18}H_{16}BrNS$: C, 60.3; H, 4.5; N, 3.9; S, 8.9. Found: C, 60.0; H, 4.6; N, 3.9; S, 8.9.

3-Methyl-4-phenylpyrido[2,1-*b*]benzothiazolium Perchlorate (4). The dihydro compound 3 (1 g) was refluxed in dimethylacetamide (20 mL) in the presence of 10% palladium on charcoal (0.1 g) for 2 h. The product was isolated by filtration and converted to the perchlorate: yield 0.6 g after recrystallization from ethanol; mp 218–219 °C; NMR (Me_2SO-d_6) δ 2.53 (s, 3 H, CH_3), 7.7 (s, 5 H, Ph), 7.81–9.23 (m, 5 H, aryl), 10.24 (d, 1 H, J = 7 Hz, H_1).

Anal. Calcd for $C_{18}H_{14}ClNO_4S$: C, 57.5; H, 3.8; N, 3.7; S, 8.5. Found: C, 57.6; H, 3.9; N, 3.6; S, 8.6.

2-Benzyl-5-phenylbenzoxazole (Free Base of 6). 2-Amino-4-phenylphenol (89 g) and phenylacetic acid (65 g) were heated together at 200–220 °C for 3 h. The product was treated with aqueous sodium hydroxide and the mixture extracted with chloroform. Removal of the chloroform gave an oil which was crystallized from hexane (Norit carbon) to give white needles (67 g, 49%), mp 52–54 °C.

Anal. Calcd for $C_{20}H_{15}NO$: C, 84.2; H, 5.3; N, 4.9. Found: C, 84.2; H, 5.5; N, 4.9.

2-Benzyl-3-(3-oxo-1-butyl)-5-phenylbenzoxazolium Bromide (9). 2-Benzyl-5-phenylbenzoxazolium bromide (6, 1.7 g) was suspended in acetonitrile (25 mL) and methyl vinyl ketone (0.7 g) added with rapid stirring. The solid dissolved and after 40 min the solution was poured into ether (150 mL). The product (0.8 g, 40%) was collected and had mp 106–108 °C, IR 1710 cm^{-1}. Attempts to recrystallize this material led to decomposition.

1,2-Dihydro-4,8-diphenyl-3-methylpyrido[2,1-*b*]benzoxazolium Bromide (10). 2-Benzyl-5-phenylbenzoxazolium bromide (6, 6.7 g) and methyl vinyl ketone (2.8 g) in dry acetonitrile (100 mL) were stirred at room temperature for 104 h. The product (4 g, 55%) was isolated by filtration and after recrystallization from chloroform–hexane had mp 300–313 °C dec; NMR (MeOD) δ 2.12 (s, 3 H, CH_3), 3.25 (m, 2 H, CH_2), 4.75 (m, 2 H, CH_2N^+).

Anal. Calcd for $C_{24}H_{20}BrNO$: C, 69.0; H, 4.8; N, 3.4; Br, 19.1. Found: C, 68.6; H, 4.9; N, 3.3; Br, 19.0.

4,8-Diphenyl-3-methylpyrido[2,1-*b*]benzoxazolium Perchlorate (11). 1,2-Dihydro-4,8-diphenyl-3-methylpyrido[2,1-

b]benzoxazolium bromide (**10**, 2.0 g) was dissolved in dimethyl sulfoxide and heated. The clear solution turned deep blue and after a few minutes of heating went yellow. Sodium perchlorate (0.6 g) in isopropyl alcohol (20 mL) was added to the cooled solution followed by an excess of ether. The product was separated by decantation and recrystallized from ethanol: yield 1.1 g; mp 252–254 °C; NMR (Me_2SO) δ 2.6 (s, 3 H, CH_3), 9.72 (d, J = 7 Hz, 1 H, N^+=CH–).

Anal. Calcd for $C_{24}H_{18}ClNO_5$: C, 66.1; H, 4.2; N, 3.2. Found: C, 65.8; H, 4.3; N, 3.3.

8-Benzylacenaphtho[1,2-*d*]thiazole (Free Base of 7). 2-Bromoacenaphthenone[5] (8.65 g, 0.035 mol) and phenylthioacetamide (5.3 g, 0.035 mol) in toluene (400 mL) were heated at 70–80 °C for 2 h with stirring. The tan solid was filtered and dried to give 9.73 g. This solid was heated in concentrated sulfuric acid (20 mL) at 60–80 °C for 5 min, and the dark solution was added to water (50 mL) and stirred for 30 min. The resulting solid was stirred in warm sodium carbonate solution and, after cooling, the crude product was extracted into ether. The ether layer was evaporated and the residue was recrystallized from methanol, yield 5.1 g (49%), mp 98–104 °C. A second recrystallization from ligroin gave mp 103–105 °C.

Anal. Calcd for $C_{20}H_{13}NS$: C, 80.2; H, 4.4; N, 4.7; S, 10.7. Found: C, 79.9; H, 4.1; N, 4.4; S, 10.5.

9-(3-Oxo-1-butyl)-8-benzylacenaphtho[1,2-*d*]thiazolium Perchlorate (12). To 8-benzylacenaphtho[1,2-*d*]thiazole (4.8 g, 0.016 mol) in cold ether (300 mL) was added dropwise with stirring 70% perchloric acid until no more salt separated. The salt was filtered, washed with ether, and dissolved in dry acetonitrile (180 mL). Methyl vinyl ketone (10 mL) was added, and the mixture was stirred at room temperature for 3 days. The solution was evaporated and the syrup was warmed in methanol, then cooled to give crystalline product, yield 5.85 g (78%), mp 167–170 °C dec. A second recrystallization from methanol gave mp 172–173 °C dec: NMR (CD_3CN) δ 2.2 (s, 3 H, $-COCH_3$), 3.4 (t, 2 H, J = 6.5 Hz, $-CH_2CO-$), 4.9 (s, 2 H, $-CH_2Ph$), 5.0 (t, 2 H, J = 6.5 Hz, N^+CH_2); IR 1714 cm^{-1}.

Anal. Calcd for $C_{24}H_{20}ClNO_5S$: C, 61.3; H, 4.3; N, 3.0; S, 6.8. Found: C, 61.6; H, 4.2; N, 2.7; S, 6.6.

1,2-Dihydro-3-methyl-4-phenylpyrido[2′,1′:8,9]acenaphtho-[1,2-*d*]thiazolium Perchlorate (13). 9-(3-Oxo-1-butyl)-8-benzylacenaphtho[1,2-*d*]thiazolium perchlorate (**12** 4.7 g, 0.01 mol) was boiled in pyridine (125 mL) until the blue solution turned yellow-brown. The pyridine was evaporated, and the syrup was heated in methanol until crystalline: yield 3.75 g (83%); mp 243–245 °C dec; NMR (CD_3CN) δ 2.05 (s, 3 H, CH_3), 3.17 (t, 2 H, J = 8.5 Hz, $-CH_2C$=), 4.87 (t, 2 H, J = 8.5 Hz, N^+CH_2); IR 1590, 1610 cm^{-1}.

Anal. Calcd for $C_{24}H_{18}ClNO_4S$: C, 6.37; H, 4.0; N, 3.1; S, 7.1. Found: C, 63.2; H, 3.9; N, 3.0; S, 6.9.

3-Methyl-4-phenylpyrido[2′,1′:8,9]acenaphthothiazolium Perchlorate (14). 1,2-Dihydro-3-methyl-4-phenylpyrido[2′,1′:8,9]-acenaphtho[1,2-*d*]thiazolium perchlorate (**13**, 1.36 g, 0.003 mol) was refluxed with stirring for 30 min in dimethylacetamide (20 mL) containing 10% palladium on charcoal (0.25 g). The solution was cooled, filtered, and poured into stirring ether (1 L). After 1 h the product was filtered and recrystallized from water: yield 0.62 g (46%); mp 151 °C (becomes glassy); NMR (CD_3CN) δ 2.53 (s, 3 H, CH_3); IR 1600 cm^{-1}.

Anal. Calcd for $C_{24}H_{16}ClNO_4S \cdot \frac{1}{2}H_2O$: C, 62.8; H, 3.7; N, 3.0; S, 7.0. Found: C, 62.5; H, 3.9; N, 2.7; S, 7.2.

2-Benzyl-5,6-dichloro-1-ethylbenzimidazolium Bromide (8). 4,5-Dichloro-*N*-ethyl-*o*-phenylenediamine dihydrochloride[6] (14 g) and phenylacetyl chloride (8 g) were dissolved in pyridine (35 mL) and heated under reflux for 1.5 h. The mixture was cooled, poured into water, and extracted with ether. The dried ether solution was distilled and the fraction 210–240 °C (0.5 mm) collected. It was recrystallized from isopropyl alcohol, mp 107–110 °C, yield 7.9 g (53%).

The free base was dissolved in ether and treated with an excess of hydrogen bromide in acetic acid. The precipitate was filtered, washed with ether followed by cold acetone, and dried, mp 182–205 °C.

Anal. Calcd for $C_{16}H_{13}BrCl_2N_2$: C, 49.8; H, 3.9; N, 7.3. Found: C, 49.4; H, 3.9; N, 7.1.

2-Benzyl-5,6-dichloro-1-ethyl-3-(3-oxo-1-butyl)benzimidazolium Bromide (15). 2-Benzyl-5,6-dichloro-1-ethylbenzimidazolium bromide (**8**, 6 g, 0.0155 mol) and methyl vinyl ketone (20 mL, excess) were stirred in *N*,*N*-dimethylacetamide (100 mL) for 5 days. The resulting mixture was stirred in ether (1.5 L) for 2 h and then filtered. The product was washed with ether and dried to give 6.8 g (96.3%): mp 172–173 °C; NMR ($CDCl_3$) δ 1.37 (t, 3 H, J = 7 Hz, CH_3C-), 2.16 (s, 3 H, CH_3CO), 3.55 (t, 2 H, J = 6 Hz, $-CH_2CO$), 4.63 (q, 2 H, J = 7 Hz, $-CH_2Me$), 4.89 (t, 2 H, J = 6 Hz, $-CH_2N^+$), 5.15 (s, 2 H, $-CH_2Ph$), 7.1–7.5 (m, 5 H, Ph), 8.1 (s, 1 H), and 8.46 (s, 1 H).

Anal. Calcd for $C_{20}H_{21}BrCl_2N_2O \cdot \frac{1}{2}H_2O$: C, 51.6; H, 4.8; N, 6.0. Found: C, 51.4; H, 4.7; N, 5.8.

All attempts to cyclize this compound by heating in a variety of solvents with or without the presence of base were unsuccessful. Either starting material was recovered or the 3-oxo-1-butyl group was lost.

2-Benzyl-3,3-dimethyl-3*H*-indolium Perchlorate (5). 3-Methyl-1-phenylbutan-2-one[7] (4 g) and phenylhydrazine (2.7 g) in acetic acid (20 mL) were refluxed for 1 h. The reaction mixture was then evaporated to dryness and dissolved in ether. The ether solution was extracted with 2 N HCl (3 × 60 mL). The product was recovered by basification and extraction with methylene chloride. Removal of the solvent gave a semisolid product which was converted first to the hydrobromide and then to the perchlorate salt, yield 3 g. After recrystallization from ethanol, the product melted at 173–175 °C.

Anal. Calcd for $C_{17}H_{18}ClNO_4$: C, 60.8; H, 5.4; N, 4.2. Found: C, 60.5; H, 5.4; N, 4.2.

If the crude indole was not converted to the salt immediately, it underwent a rapid aerial oxidation[8,9] to the 2-benzoyl derivative. Some of the indole (ca. 1 g) was dissolved in isopropyl alcohol and left at room temperature. The oxidation was monitored by gas chromatography on 10% OV-17 packing. Workup by recrystallization from ethanol gave 2-benzoyl-3,3-dimethyl-3*H*-indole: mp 80–81 °C; 0.4 g; mass spectrum *m*/*e* 249.

Anal. Calcd for $C_{17}H_{15}NO$: C, 81.9; H, 6.1; N, 5.6. Found: C, 81.9; H, 6.2; N, 5.5.

6,10,10-Trimethyl-9-phenyl-10*H*-pyrido[1,2-*a*]indolium Perchlorate (16). 2-Benzyl-3,3-dimethyl-3*H*-indolium perchlorate (**5**, 1.7 g) and methyl vinyl ketone (1 g) were stirred at room temperature in acetonitrile (10 mL) overnight. The product was isolated by dilution with ether and recrystallized from methanol: yield 0.8 g; mp 260 °C; NMR (Me_2SO-d_6) δ 1.7 [s, 6 H, $C(CH_3)_2$], 3.32 (s, 3 H, CH_3), 7.3–8.4 (m, 11 H, aryl).

Anal. Calcd for $C_{21}H_{20}ClNO_4$: C, 65.4; H, 5.2; N, 3.6. Found: C, 65.3; H, 5.3; N, 3.9.

4-Ethoxycarbonyl-1,2-dihydro-3-methyl-5-phenyl-5*H*-pyrido[2,1-*b*]benzimidazolium Perchlorate (21). To ethyl *N*-phenyl-2-benzimidazolylacetate[10] (14.02 g, 0.05 mol) in ether (1 L) 70% perchloric acid was added dropwise with stirring until no more reddish syrup separated. The ether was decanted, and the syrup was stirred with fresh ether for 15 min and again decanted. The syrup was dissolved in dry acetonitrile (300 mL), methyl vinyl ketone (25 g) was added, and the solution was stirred for 10 days at room temperature. The acetonitrile and excess methyl vinyl ketone were evaporated giving a syrup which would not crystallize. This syrup was boiled for 1 min in 2,6-lutidine (25 mL) and the solution was evaporated to dryness. The residue was warmed in ethanol to induce crystallization. The solid was recrystallized from ethanol to give 8.0 g (37%): mp 213–214 °C; NMR (Me_2SO-d_6) δ 2.37 (s, 3 H, CH_3), 3.15 (t, 2 H, J = 7.5 Hz, $-CH_2C$=), 4.7 (t, 2 H, J = 7.5 Hz, $-N^+CH_2$); IR 1740 cm^{-1}.

Anal. Calcd for $C_{21}H_{21}ClN_2O_6$: C, 58.3; H, 4.9; Cl, 8.2; N, 6.5. Found: C, 58.6; H, 4.9; Cl, 8.2; N, 6.5.

4-Ethoxycarbonyl-3-methyl-5-phenyl-5*H*-pyrido[2,1-*b*]-benzimidazolium Perchlorate (22). Compound **21** (4.33 g, 0.01 mol) was refluxed for 1 h with stirring in dimethylacetamide (50 mL) containing 10% palladium on charcoal (0.5 g). The mixture was cooled and filtered, and the filtrate was stirred with ether (1 L) for 15 min. The product was filtered and recrystallized from ethanol: yield 2.14 g (49.7%); mp 230–232 °C dec; NMR (Me_2SO-d_6) δ 2.63 (s, 3 H, CH_3), 9.9 (d, 1 H, J = 7 Hz, N^+CH); IR 1738 cm^{-1}.

Anal. Calcd for $C_{21}H_{19}ClN_2O_6$: C, 58.5; H, 4.4; N, 6.5. Found: C, 58.3; H, 4.5; N, 6.4.

Ethyl *N*-Methyl-2-benzimidazolylacetate (Free Base of 19). *N*-Methyl-*o*-phenylenediamine (48.9 g, 0.4 mol) and ethyl carboethoxyacetimidate hydrochloride[11] (78.3 g, 0.4 mol) were refluxed in ethanol (250 mL) for 3 h. The hot mixture was filtered to remove ammonium chloride, and the filtrate was evaporated to a syrup. The syrup in chloroform was washed twice with water, dried ($MgSO_4$), and evaporated. The residue was recrystallized twice from ether with dry ice cooling: yield 61 g (70%); mp 66–67 °C; NMR ($CDCl_3$) δ 1.1 (t, 3 H, J = 7 Hz, CH_3 of ethyl), 3.4 (s, 3 H, CH_3), 3.7 (s, 2 H, $-CH_2CO$), 3.9 (q, 2 H, J = 7 Hz, $-CH_2-$ of ethyl).

Anal. Calcd for $C_{12}H_{14}N_2O_2$: C, 66.0; H, 6.5; N, 12.8. Found: C, 65.6; H, 6.5; N, 12.9.

4-Ethoxycarbonyl-1,2-dihydro-3,5-dimethyl-5*H*-pyrido-[2,1-*b*]benzimidazolium Perchlorate (23) and 1-Ethoxy-4-ethoxycarbonyl-1,5-dimethyl-1,2,3,4-tetrahydro-5*H*-pyrido[2,1-*b*]benzimidazolium Perchlorate (24). To ethyl *N*-methyl-2-benzimidazolylacetate (6.55 g, 0.03 mol) in ether (1 L) 70% perchloric acid was added dropwise with stirring until no more syrup separated. The ether layer was decanted, and the syrup was stirred for 15 min with fresh ether and decanted again. The syrup was dissolved in acetonitrile (100 mL) and methyl vinyl ketone (10 g) was added. This mixture

was stirred for 4 weeks at room temperature. The acetonitrile and excess methyl vinyl ketone were evaporated, and the residual syrup was stirred for 1 day under ether. The ether was decanted, and the syrup was taken up and boiled for 1 min in pyridine (50 mL). The pyridine was evaporated and the syrup was dissolved in hot ethanol (500 mL). This solution was concentrated and cooled to give the dihydro product (**23**). Recrystallization from ethanol gave 2.0 g (18%): mp 202 °C dec; NMR (Me_2SO-d_6) δ 2.44 (s, 3 H, $\geq CH_3$), 3.0 (t, 2 H, J = 7.5 Hz, $-CH_2\leq$), 3.9 (s, 3 H, NCH_3), 4.6 (t, 2 H, J = 7.5 Hz,2 $^+NCH_2-$); IR 1735 cm^{-1}.

Anal. Calcd for $C_{16}H_{19}ClN_2O_6$: C, 51.9; H, 5.2; Cl, 9.6; N, 7.6. Found: C, 51.9; H, 5.2; Cl, 9.8; N, 7.2.

The ethanol filtrate from above was evaporated to a syrup which was dissolved in a minimum of chloroform and chromatographed on a 3 ft silica gel column (chloroform). Elution of the column was carried out with chloroform, mixture of chloroform and acetonitrile, and finally pure acetonitrile. Two of the middle fractions slowly gave a crystalline material after evaporation. The solid was washed with ether, filtered, and recrystallized from ethanol to give 2.0 g (16%), mp 166–168 °C, of the tetrahydro product: NMR (100 atom % Me_2SO-d_6) δ 1.07 (t, 3 H, J = 7 Hz, CH_3 of ethoxy), 1.19 (t, 3 H, J = 7 Hz, CH_3 of ethoxycarbonyl), 1.87 (s, 3 H, CH_3CN), 2.0–2.7 (m, 4 H, $-CH_2CH_2-$), 2.89 (q, q, 1 H, J = 7, 9 Hz, one of the $-CH_2-$ hydrogens of the ethoxy), 3.68 (q, q, 1 H, J = 7, 9 Hz, the other $-CH_2-$ hydrogen of the ethoxy), 4.03 (s, 3 H, CH_3N), 4.25 (q, 2 H, J = 7 Hz, $-CH_2-$ of ethoxycarbonyl), 4.85 (broad s, 1 H, EtOOCCH slightly coupled to $-CH_2CH_2-$), 7.5–8.2 (m, 4 H, aromatics); IR 1737 cm^{-1}.

Anal. Calcd for $C_{18}H_{25}ClN_2O_7$: C, 51.9; H, 6.05; Cl, 8.5; N, 6.7. Found: C, 51.6; H, 5.9; Cl, 8.6; N, 6.8.

4-Ethoxycarbonyl-1,2-dihydro-3,5-dimethyl-5*H*-pyrido[2,1-*b*]benzimidazolium Perchlorate (23) and 4-Ethoxycarbonyl-1,5-dimethyl-1-hydroxy-1,2,3,4-tetrahydro-5*H*-pyrido[2,1-*b*]benzimidazolium Perchlorate (25). The hydroperchlorate salt from ethyl *N*-methyl-2-benzimidazolylacetate (**19**, 32.8 g, 0.15 mol) was reacted for 1 week in acetonitrile (250 mL) containing methyl vinyl ketone (100 mL) as described in the preparation of **23** and **24**. However, the residue obtained after having been boiled with pyridine and evaporation was treated with pure, dry tetrahydrofuran in place of ethanol. The insoluble solid was the dihydro product **23**, yield 19.2 g (34.5%).

The tetrahydrofuran filtrate was evaporated to a syrup which became crystalline on treatment with hot acetic acid followed by cooling. Recrystallization from acetic acid gave 12.3 g (21.1%), mp 119–121 °C, of the tetrahydro product (**25**): NMR (CD_3CN) δ 1.23 (t, 3 H, J = 7 Hz, CH_3- of ethoxycarbonyl), 1.8 (s, 3 H, CH_3CN), 2.2–2.8 (m, 4 H, $-CH_2CH_2-$), 3.95 (s, 3 H, CH_3N), 4.2 (q, 2 H, J = 7 Hz, $-CH_2-$ of ethoxycarbonyl), 4.5 (m, 1 H, EtOOCCH), 5.4 (broad, 1 H, –OH), 7.5–8.3 (m, 4 H, aromatics); IR 1730 cm^{-1}.

Anal. Calcd for $C_{16}H_{21}ClN_2O_7 \cdot \frac{1}{2}H_2O$: C, 48.3; H, 5.5; N, 7.04. Found: C, 48.3; H, 5.4; N, 7.1.

Ethyl 5-Chloro-1-ethyl-2-benzimidazolylacetate (Free Base of 20). 2-Amino-4-chloro-*N*-ethylaniline[12] (34.1 g, 0.2 mol) and ethyl carboethoxyacetimidate hydrochloride (39.1 g, 0.2 mol) were reacted in ethanol (150 mL) in the manner described for the preparation of ethyl *N*-methyl-2-benzimidazolylacetate. The product was recrystallized from ether with dry ice cooling and then from petroleum ether: yield 35.2 g (66%); mp 44–45 °C; NMR ($CDCl_3$) δ 1.1 (t, 3 H, J = 7 Hz, CH_3C), 1.2 (t, 3 H, J = 7 Hz, other CH_3C), 3.7 (s, 2 H, $-CH_2CO$), 3.9 (q, q, 4 H, J = 7, 7 Hz, $-CH_2-$ of the two ethyls).

Anal. Calcd for $C_{13}H_{15}ClN_2O_2$: C, 58.5; H, 5.7; N, 10.5; Cl, 13.3. Found: C, 58.3; H, 5.8; N, 10.4; Cl, 13.7.

8-Chloro-4-ethoxycarbonyl-5-ethyl-1,2-dihydro-3-methyl-5*H*-pyrido[2,1-*b*]benzimidazolium Perchlorate (26). The hydroperchlorate salt from ethyl 5-chloro-1-ethyl-2-benzimidazolylacetate (**20**, 32 g, 0.12 mol) was reacted for 2 weeks in acetonitrile (250 mL) containing methyl vinyl ketone (70 mL) as described in the preparation of **23**. The residue obtained after having been boiled with pyridine and evaporated was treated with isopropyl alcohol (800 mL) and the somewhat sticky solid was filtered. This solid became more crystalline on stirring in aqueous sodium perchlorate solution. The product was filtered and recrystallized from ethanol/acetonitrile (2/1): yield 12.8 g (25.5%); mp 232–233 °C dec; NMR (Me_2SO-d_6) δ 2.36 (s, 3 H, CH_3), 3.02 (t, 2 H, J = 7.5 Hz, $-CH_2CMe$), 4.26 (t, 2 H, J = 7.5 Hz, N^+CH_2-), 7.7 (d, d, 1 H, J = 9, 2 Hz, H_7), 8.1 (d, 1 H, J = 9 Hz, H_6), 8.2 (d, 1 H, J = 2 Hz, H_9); IR 1725 cm^{-1}.

Anal. Calcd for $C_{17}H_{20}Cl_2N_2O_6$: C, 48.8; H, 4.8; Cl, 16.9; N, 6.7. Found: C, 48.4; H, 4.8; Cl, 16.6; N, 6.7.

Attempted Dehydrogenation of 8-Chloro-4-ethoxycarbonyl-5-ethyl-1,2-dihydro-3-methyl-5*H*-pyrido[2,1-*b*]benzimidazolium Perchlorate. Compound **26** (6.29 g, 0.015 mol) was refluxed for 1 h with stirring in dimethylacetamide (100 mL) containing 10% palladium on charcoal (2 g). The mixture was cooled and filtered, and the filtrate was stirred with ether (1.5 L) for 1 h. The product was filtered, washed with ether, and dried. Surprisingly, the infrared spectrum showed only a trace of carbonyl. Recrystallizations from ethanol and then from water gave 2.35 g of carbonyl-free material of mp 262–264 °C dec. The product consisted of an inseparable mixture of 5-ethyl-3-methyl-5*H*-pyrido[2,1-*b*]benzimidazolium perchlorate (78% by weight or 80% mole fraction) and 8-chloro-5-ethyl-3-methyl-5*H*-pyrido[2,1-*b*]benzimidazolium perchlorate (22% by weight or 20% mole fraction) via elemental analysis. The product mixture was converted to the mixed chloride salts with Amberlite IRA-400 chloride anion exchange resin, and then to the mixed fluoroborate salts by adding fluoroboric acid to an aqueous solution of the chloride salts. Elemental analysis of the mixed fluoroborate salts fit for 74% weight or 76% mole fraction of the chlorine free salt and 26% by weight or 24% mole fraction of the 8-chloro salt. The reaction was repeated with nearly identical results. NMR (Me_2SO-d_6): δ 1.4 (t, 3 H, J = 7 Hz, CH_3 of ethyl), 2.63 (s, 3 H, $ArCH_3$), 4.64 (q, 2 H, J = 7 Hz, $-CH_2-$ of ethyl), 8.53 (d, 1 H, J = 8 Hz, H_9), 9.42 (d, 1 H, J = 7 Hz, H_1). A small band at δ 8.76 (d, J = 2 Hz) is probably due to H_9 in the 8-chloro component.

Anal. Calcd for $(C_{14}H_{15}ClN_2O_4)$ (0.80) + $(C_{14}H_{14}Cl_2N_2O_4)$ (0.20): C, 52.9; H, 4.7; N, 8.8; Cl, 13.4. Found: C, 52.5; H, 5.0; N, 8.5; Cl, 13.1.

Anal. Calcd for $(C_{14}H_{15}BF_4N_2)$ (0.76) + $(C_{14}H_{14}BClF_4N_2)$ (0.24): C, 54.9; H, 4.9; N, 9.1; Cl, 2.8. Found: C, 54.5; H, 5.3; N, 8.8; Cl, 2.5.

4-Ethoxycarbonyl-3,5-dimethyl-5*H*-pyrido[2,1-*b*]benzimidazolium Perchlorate (30). Compound **23** (2.22 g, 0.006 mol) was refluxed for 1 h with stirring in dimethylacetamide (30 mL) containing 10% palladium on charcoal (0.4 g). The mixture was cooled and filtered, and the filtrate was stirred with ether (600 mL) for 1 h. The product was filtered and recrystallized from ethanol: yield 1.18 g (53.5%); mp 242–245 °C dec; NMR (Me_2SO-d_6) δ 2.67 (s, 3 H, CH_3Ar), 4.03 (s, 3 H, CH_3N), 7.82 (d, 1 H, J = 7 Hz, $^+NC=CH-$), 9.7 (d, 1 H, J = 7 Hz, $^+NCH=$); IR 1740 cm^{-1}.

Anal. Calcd for $C_{16}H_{17}ClN_2O_6$: C, 52.1; H, 4.6; N, 7.6. Found: C, 52.0; H, 4.9; N, 8.0.

1,2-Dihydro-3,5-dimethyl-5*H*-pyrido[2,1-*b*]benzimidazolium Perchlorate (29). Compound **23** (7.92 g, 0.0213 mol) was boiled for 40 min with stirring in dimethylacetamide (50 mL) containing concentrated hydrochloric acid (3 mL) as approximately half of the solvent was permitted to boil off. The mixture was cooled and stirred with ether (1 L) overnight. The ether was decanted and the crude solid was dissolved in hot water (300 mL), treated with Norit carbon (2 g), and filtered. On cooling, some gum separated upon the sides of the flask. The clear liquid was decanted into a beaker, treated with sodium perchlorate (20 g), and cooled with ice. The crude product which separated was filtered and recrystallized from ethanol/acetonitrile (5/1): yield 3.28 g (51.6%); mp 206–210 °C dec; NMR (CD_3CN) δ 2.2 (s, 3 H, $=CCH_3$), 2.85 (broad t, 2 H, J = 8.0 Hz, $-CH_2CMe$), 3.86 (s, 3 H, NCH_3), 4.4 (t, 2 H, J = 8.0 Hz, $-N^+CH_2-$), 6.7 (m, 1 H, H_4); IR 1640 cm^{-1}.

Anal. Calcd for $C_{13}H_{15}ClN_2O_4$: C, 52.3; H, 5.1; N, 9.4. Found: C, 52.3; H, 5.1; N, 9.4.

3,5-Dimethyl-5*H*-pyrido[2,1-*b*]benzimidazolium Perchlorate (31). Compound **29** (2.0 g, 0.0067 mol) was refluxed for 1 h with stirring in dimethylacetamide (40 mL) containing 10% palladium on charcoal (0.5 g). The reaction mixture was worked up as described in the preparation of **20**, and the crude product was recrystallized twice from ethanol, yield 1.15 g (58%), mp 240–245 °C.

The identical material was also prepared by boiling compound **30** for 1 h with stirring in dimethylacetamide containing concentrated hydrochloric acid as previously described in the preparation of **29**: yield 1.09 g (55%); NMR (Me_2SO-d_6) δ 2.6 (s, 3 H, $ArCH_3$), 4.04 (s, 3 H, NCH_3), 8.54 (d, 1 H, J = 8 Hz, H_9), 9.42 (d, 1 H, J = 7 Hz, H_1); IR 1657 cm^{-1}.

Anal. Calcd for $C_{13}H_{13}ClN_2O_4$: C, 52.6; H, 4.4; N, 9.4. Found: C, 52.4; H, 4.5; N, 9.4.

3-(3-Oxo-1-butyl)-2-methylbenzothiazolium Bromide (32). 2-Methylbenzothiazolium bromide (37 g, 0.16 mol) and methyl vinyl ketone (34.5 g, 0.49 mol) in dimethylacetamide (75 mL) were stirred at room temperature overnight. The solid was filtered and washed in turn with acetone and ether, yield 35 g (73%). After two recrystallizations from ethanol, the yield was 31 g (65%): mp 152–153 °C dec; IR 1704 cm^{-1}; NMR (Me_2SO-d_6) δ 2.19 (s, 3 H, CH_3CO), 3.55 (s + t, 5 H, $CH_3C=N^+$ and CH_2CO), 4.93 (2 H, J = 6 Hz, $^+NCH_2-$), 7.9 (m, 2 H, aryl), 8.55 (m, 2 H, aryl).

Anal. Calcd for $C_{12}H_{14}BrNOS \cdot H_2O$ (prolonged drying leads to decomposition): C, 45.3; H, 5.1; N, 4.4; S, 10.1. Found: C, 45.6; H, 5.1; N, 4.6; S, 10.5.

1,2-Dihydro-3-methylpyrido[2,1-*b*]benzothiazolium Per-

chlorate (33). Compound **32** (2.0 g, 0.0067 mol) was boiled for 30 min in a mixture of water (150 mL) and pyridine (5 mL). The solution was evaporated to dryness, and the residue was washed with ether. The crude product was dissolved in water (15 mL), sodium perchlorate (3 g) was added, and product separated upon cooling: yield 0.35 g (17.5%); mp ~195 °C; NMR (CD_3CN) δ 2.23 (broad s, 3 H, CH_3), 3.0 (t, 2 H, J = 8.5 Hz, $-CH_2CMe$), 4.68 (t, 2 H, J = 8.5 Hz, N^+CH_2), 6.95 (q, 1 H, J = 1.5 Hz, HC=CMe); IR 1580, 1628 cm^{-1}.

Anal. Calcd for $C_{12}H_{12}ClNO_4S$: C, 47.8; H, 4.0; Cl, 11.8. Found: C, 48.0; H, 3.9; Cl, 11.5.

3-Methylpyrido[2,1-*b*]benzothiazolium Perchlorate (34). 1,2-Dihydro-3-methylpyrido[2,1-*b*]benzothiazolium perchlorate (**33**, 5.22 g, 0.0173 mol) was refluxed with stirring for 3 h in dimethylacetamide (50 mL) containing 10% palladium on charcoal (1.7 g). The mixture was cooled and filtered, and the filtrate was stirred for 15 min in ether (2 L). The crude brown product was scraped from the sides of the beaker, and the mixture was filtered. The solid was dissolved in water, treated with Norit carbon, and filtered. Sodium perchlorate (15 g) was dissolved in the chilled filtrate whereupon the product crystallized: yield 3.42 g (66%); mp 202–204 °C dec; NMR (CD_3CN) δ 2.75 (s, 3 H, CH_3), 9.7 (d, 1 H, J = 7 Hz, N^+CH); IR 1625 cm^{-1}.

Anal. Calcd for $C_{12}H_{10}ClNO_4S \cdot H_2O$: C, 45.4; H, 3.8; N, 4.4. Found: C, 45.7; H, 4.2; N, 4.4.

2,3,3-Trimethyl-1-(3-oxo-1-butyl)-3*H*-indolium Perchlorate (36) and 8,10,10-Trimethyl-10*H*-pyrido[1,2-*a*]indolium Perchlorate (37). 2,3,3-Trimethyl-3*H*-indolium perchlorate (**35**, X = ClO_4^-) (20 g) and methyl vinyl ketone (40 mL) were heated together on the steam bath for 15 min. The reaction mixture was chilled until solid and then filtered to yield 20 g of crude adduct **36.** A sample was recrystallized for analysis from isopropyl alcohol: mp 168–170 °C; IR 1720 cm^{-1}; NMR (Me_2SO-d_6) δ 1.52 [s, 6 H, $C(CH_3)_2$], 2.15 (s, 3 H, CH_3CO), 2.86 (s, 3 H, $CH_3C=N^+$), 3.25 (t, 2 H, J = 6 Hz, CH_2CO), 4.59 (t, 2 H, J = 6 Hz, CH_2N^+), 7.72 (m, 4 H, aromatic).

Anal. Calcd for $C_{15}H_{20}ClNO_5$: C, 54.6; H, 6.1; N, 4.3. Found: C, 54.9; H, 6.0; N, 4.6.

The same product was also obtained by reaction in acetonitrile at room temperature for 12 h.

The open-chain adduct **36** was dissolved in pyridine (100 mL) and the solution refluxed for 1 h. The pyridine solution was reduced to half volume and diluted with ether. The product **37** was isolated by filtration and purified by recrystallization from ethanol: yield 9 g, 36%; mp 206 °C; NMR (Me_2SO) δ 1.73 [s, 6 H, $C(CH_3)_2$], 2.79 (s, 3 H, CH_3), 7.62–8.60 (m, 6 H, aryl), 9.6 (d, 1 H, J = 6 Hz, $^+NCH=$).

Anal. Calcd for $C_{15}H_{16}ClNO_4$: C, 58.2; H, 5.2; N, 4.5. Found: C, 58.5; H, 5.1; N, 4.6.

6,10,10-Trimethyl-10*H*-pyrido[1,2-*a*]indolium Perchlorate (38). 2,3,3-Trimethyl-3*H*-indolium bromide (**35**, X = Br^-) (10 g) and methyl vinyl ketone (5.6 g) were dissolved in dry dimethylacetamide and stirred for 3 days at room temperature. The reaction mixture was poured into ether (500 mL), and the liquid was decanted from the gummy product. After conversion to the perchlorate, the product was purified by recrystallization from methanol: yield 3.2 g, 26%; mp 215–218 °C; NMR (Me_2SO) δ 1.72 [s, 6 H, $C(CH_3)_2$], 3.33 (s, 3 H, CH_3), 7.58–8.71 (m, 7 H, aryl).

Anal. Calcd for $C_{15}H_{16}ClNO_4$: C, 58.2; H, 5.2; N, 4.5. Found: C, 57.8; H, 5.4; N, 4.3.

6,10,10-Trimethyl-8-phenyl-10*H*-pyrido[1,2-*a*]indolium Perchlorate (39). 2,3,3-Trimethyl-3*H*-indolium perchlorate (1 g) and 4-phenylbut-3-en-2-one (3 g) were heated together on the steam bath for 10 h. The cooled reaction mixture was diluted with ether and the precipitated material recrystallized from methanol: yield 0.35 g, 22%; mp 288–289 °C; NMR (Me_2SO) δ 3.15 (s, 3 H, CH_3).

Anal. Calcd for $C_{21}H_{20}ClNO_4$: C, 65.4; H, 5.2; N, 3.6. Found: C, 65.5; H, 5.1; N, 3.6.

2-Ethyl-3,3-dimethyl-3*H*-indolium Bromide (40). 2-Methylpentan-3-one[13,14] (10 g) and phenylhydrazine (10.8 g) were dissolved in acetic acid (50 mL) and refluxed for 2 h. The remainder of the workup was identical with that described above for the 2-benzyl derivative **5**, yield of crude indole 11 g. Gas chromatography at 170 °C on a 6 ft column of OV-17 packing gave only one peak.

The product was dissolved in ether and treated with excess 40% HBr in acetic acid. The hydrobromide salt was filtered off and recrystallized from isopropyl alcohol: mp 205 °C; NMR (Me_2SO) δ 3.1 (q, 2 H, CH_2), 1.4 (t, 3 H, CH_3), 1.5 [s, 6 H, $C(CH_3)_2$].

The salts listed in Table I were synthesized by heating the appropriate starting materials either neat or in DMF solution above 100 °C for several hours.

5,8-Dihydro-8,8-dimethyl-6-phenylindeno[1′,2′-6,5]pyrido[1,2-*a*]indolium Perchlorate (42, X = CH_2). 2,3,3-Trimethyl-3*H*-indolium perchlorate (**35**, X = ClO_4^-) (1 g) and 2-benzylideninden-1-one (**41**, 2 g) were heated together at 140–150 °C for 24 h. The product was isolated by dissolving the melt in methanol and chilling in the refrigerator, yield 0.9 g.

The compounds listed in Table II were synthesized similarly to the above.

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Registry No.—**1**, 54507-57-2; **2**, 38494-40-5; **3**, 37937-74-9; **4**, 62476-25-9; **5**, 54507-77-6; **6**, 54507-59-4; **6** free base, 62476-26-0; **7** free base, 55868-14-9; **8**, 62476-27-1; **8** free base, 62476-28-2; **9**, 38494-46-1; **10**, 37937-75-0; **11**, 55867-38-4; **12**, 55868-16-1; **13**, 55868-18-3; **14**, 55868-22-9; **15**, 62476-29-3; **16**, 54507-79-8; **18** free base, 7767-16-0; **19**, 54507-69-6; **19** free base, 2735-61-7; **20**, 62476-30-6; **20** free base, 55868-51-4; **21**, 62476-32-8; **22**, 55868-28-5; **23**, 62476-33-9; **24**, 62476-35-1; **25**, 62476-36-2; **26**, 55868-50-3; **27**, 62476-02-2; **27** fluoroborate, 62476-03-3; **28**, 55868-41-2; **28** fluoroborate, 62476-04-4; **29**, 55868-39-8; **30**, 62476-05-5; **31**, 62476-07-7; **32**, 51588-76-2; **33**, 55868-13-8; **34**, 62476-09-9; **35** (X = ClO_4^-), 53057-95-7; **35** (X = Br^-), 53642-08-3; **36**, 62476-11-3; **37**, 55867-89-5; **38**, 55867-61-3; **39**, 55868-00-3; **40**, 62476-12-4; **40** free base, 18781-53-8; **41** (R = Ph; X = CH_2), 5706-12-7; **41** (R = $MeOC_6H_4$-*p*; X = CH_2), 5706-14-9; **41** (R = 2-methylfuranyl; X = CH_2), 6072-59-1; **41** (R = Ph; X = C=O), 5381-33-9; $R_3COCH=CHR_2$ (R_2 = H; R_3 = CH_3), 78-94-4; $R_3CO-CH=CHR_2$ (R_2 = $MeOC_6H_4$-*p*; R_3 = CH_3), 943-88-4; $R_3CO-CH=CHR_2$ (R_2, R_3 = Ph), 94-41-7; $R_3COCH=CHR_2$ (R_2 = $MeOC_6H_4$-*p*; R_3 = Ph), 959-33-1; $R_3COCH=CHR_2$ (R_2 = Ph; R_3 = $MeOC_6H_4$-*p*), 959-23-9; 2-amino-4-phenylphenol, 1134-36-7; phenylacetic acid, 103-82-2; 2-bromoacenaphthenone, 16269-27-5; phenylthioacetamide, 645-54-5; 4,5-dichloro-*N*-ethyl-*o*-phenylenediamine dihydrochloride, 62476-13-5; phenylacetyl chloride, 103-80-0; 3-methyl-1-phenylbutan-2-one, 2893-05-2; phenylhydrazine, 100-63-0; 2-benzoyl-3,3-dimethyl-3*H*-indole, 62476-14-6; *N*-methyl-*o*-phenylenediamine, 4760-34-3; ethylcarboethoxyacetimidate HCl, 2318-25-4; 2-amino-4-chloro-*N*-ethylaniline, 62476-15-7; 2-methylbenzothiazolium bromide, 874-45-3; 4-phenylbut-3-en-2-one, 122-57-6; 2-methylpentan-3-one, 565-69-5.

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