

Nitrogen Analogs of Sesquifulvalene.

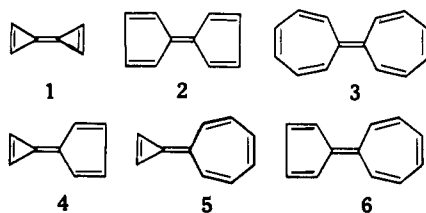
I. Synthesis and Properties^{1a,2}

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The syntheses of a series of pyridine anhydro bases iso-electronic with sesquifulvalene are described. These substances are protonated on carbon rather than on nitrogen. The corresponding conjugate acids are strong enough to be titratable, the pK_a values being in the range 8.5–12. The acidity of a C–H function attached to C-2 or C-4 of a pyridinium nucleus is enhanced by a factor of 10^6 – 10^7 by incorporation of the C–H group in a cyclopentadienyl ring.

Cyclopropenyldenecyclopropene (1), fulvalene (2), heptafulvalene (3), and the unsymmetrical hybrid molecules hypothetically generated from them (4, 5, and 6) are members of a class of cross-conjugated systems of particular theoretical importance.³ Many of the usual criteria for predicting aromaticity are inapplicable to these "pinched" molecules, for which only a single unexcited Kekulé structure can be written. Neither the Hückel $4n + 2$ rule^{3e} nor the "periphery" modification⁴ applies. Moreover, the symmetry of the ground-



(1) (a) We are indebted for the support of part of this work by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Contract No. AF 49(638)-828, by the Office of Ordnance Research (now Army Research Office, Durham) under Contract No. DA-04-495-ORD-532, and by the Camille and Henry Dreyfus Foundation. (b) To whom inquiries should be directed at Madison. (c) This paper is taken from the dissertation presented by Earl Mansfield Evleth, Jr., in partial fulfillment of the requirements for the Ph.D. Degree at the University of Southern California.

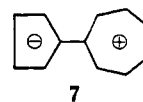
(2) For preliminary communications, see (a) J. A. Berson and E. M. Evleth, Jr., *Chem. Ind.* (London), 901 (1959); (b) *ibid.*, 1362 (1961); (c) J. A. Berson, E. M. Evleth, Jr., and Z. Hamlet, *J. Am. Chem. Soc.*, **82**, 3793 (1960); (d) E. M. Evleth, Jr., J. A. Berson, and S. L. Manatt, *Tetrahedron Letters*, 3087 (1964).

(3) For previous discussions, see *inter alia* (a) J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *J. Am. Chem. Soc.*, **74**, 4579 (1952), (compounds 1, 2, and 4); (b) W. von E. Doering in "Theoretical Organic Chemistry," papers presented to the Kekulé Symposium, London, 1959, p. 35; R. B. Turner, W. R. Meador, W. von E. Doering, L. H. Knox, J. R. Mayer, and D. W. Wiley, *J. Am. Chem. Soc.*, **79**, 4127 (1957) (compounds 2, 3, and 6); (c) B. Pullman, A. Pullman, E. D. Bergmann, H. Berthod, E. Fischer, Y. Hirschberg, D. Lavie, and M. Mayot, *Bull. soc. chim. France*, **73** (1952) (compound 6); (d) J. F. Tinker, *J. Chem. Phys.*, **19**, 981 (1951) (compound 6); (e) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 10; (f) R. D. Brown, *Trans. Faraday Soc.*, **45**, 296 (1949); **46**, 146 (1950); (g) T. Nakajima and S. Katagiri, *Bull. Chem. Soc. Japan*, **35**, 910 (1962); (h) A. J. Silvestri, L. Goodman, and J. A. Dixon, *J. Chem. Phys.*, **36**, 148 (1962). Derivatives of 4 have recently been synthesized: (i) W. M. Jones and R. S. Pyron, *J. Am. Chem. Soc.*, **87**, 1608 (1965); (j) A. S. Kende and P. T. Izzo, *ibid.*, **87**, 1609 (1965).

(4) J. R. Platt, *ibid.*, **22**, 1448 (1954).

state valence-bond wave function, an important clue to aromaticity,⁵ is not directly discernible by inspection, since the structural requirements needed⁵ for application of the criterion are not met.

Cyclopentadienyldenecyclopropene (4) and sesquifulvalene (6) are especially significant examples. Simple resonance theory suggests⁶ that dipolar resonance structures would make unusually large contributions to the ground states of both molecules, since the charge separation in such structures (e.g., 7) might be balanced by the stability associated with the pair of electron



s sextets.⁷ Hückel molecular orbital (HMO) calculations^{3a,c} confirm these qualitative expectations. The ground states are predicted to have high dipole moments, and the bond order at the "pinch," *i.e.*, between each pair of rings, should be exceptionally low. Further, the HMO delocalization energies are substantial, and the ground states have closed-shell electronic configurations, suggesting that the π -electron systems may be unusually stable. In the present paper, we report the details² of the syntheses and properties of a series of nitrogen analogs of sesquifulvalene 6 which are iso- π -electronic with that molecule. The results provide the basis of a comparison with the behavior of the parent hydrocarbon system^{8–10} and of other heterocyclic analogs.^{11–16} The following two papers¹⁷ present a theoretical treatment of the π -electron system by the HMO theory (modified and supplemented by simple parametric techniques and by perturbation methods) and a correlation of the calculations with the observed chemical and physical properties.

Syntheses of N-Alkyl-2- and 4-cyclopentadienyldenyl-1,2- and 1,4-dihydropyridines. In the analogs of ses-

(5) (a) D. P. Craig in "Theoretical Organic Chemistry," papers presented to the Kekulé Symposium, London, 1959, p. 20; (b) D. P. Craig and A. Maccoll, *J. Chem. Soc.*, 964 (1949).

(6) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, pp. 138, 231.

(7) Since resonance theory in its simplest form does not ascribe particular stability to a sextet, the assumption must be intuitively imposed and is justified, as is usually the case in such arguments, by experience.⁶

(8) H. Prinzbach and D. Seip, *Angew. Chem.*, **73**, 169 (1961).

(9) H. Prinzbach and W. Rosswog, *ibid.*, **73**, 543 (1961).

(10) H. Prinzbach and W. Rosswog, *Tetrahedron Letters*, 1217 (1963).

(11) G. V. Boyd, *Proc. Chem. Soc.*, 253 (1960).

(12) G. V. Boyd and L. M. Jackman, *J. Chem. Soc.*, 548 (1963).

(13) F. Kröhnke, K. Ellegast, and E. Bertram, *Ann.*, **600**, 176 (1956).

(14) D. N. Kursanov, N. K. Baranetskaya, and V. N. Setkina, *Proc. Acad. Sci. USSR, Chem. Sect.*, **113**, 191 (1957).

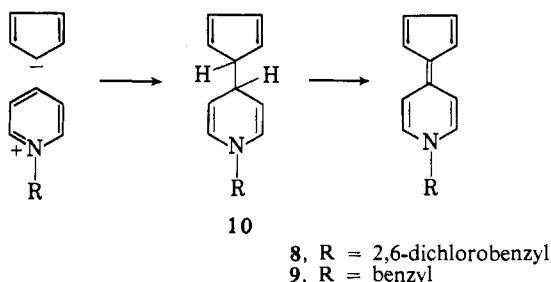
(15) D. N. Kursanov and N. K. Baranetskaya, *Bull. Acad. Sci., USSR, Div. Chem. Sci.*, 341 (1958).

(16) A. Lüttringhaus, E. Futterer, and H. Prinzbach, *Tetrahedron Letters*, 1209 (1963).

(17) E. M. Evleth, Jr., J. A. Berson, and S. L. Manatt, *J. Am. Chem. Soc.*, **87**, 2908 (1965); J. A. Berson, E. M. Evleth, Jr., and S. L. Manatt, *ibid.*, **87**, 2901 (1965).

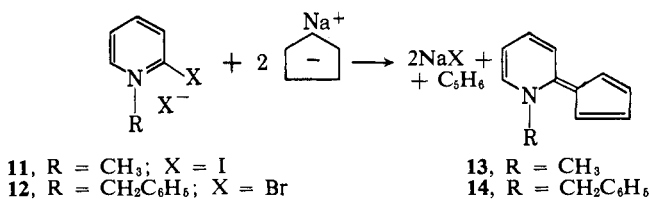
quifulvalene (6) described here, the cycloheptatrienyli-
dene moiety is replaced by an alkylated 1,2- or 1,4-
dihydropyridine ring. The resulting series of substances
use the nitrogen lone pair of electrons in place of one of
the C-C π -bonds of the parent substance 6 to complete
the conjugated system.¹⁸

Shortly after our work began, two substances of this
type were prepared by the action of alkali cyclopentadi-
enides on N-2,6-dichlorobenzyl and N-benzylpyridinium
salts and assigned structures 8 and 9.¹³⁻¹⁵ The final
stages of both syntheses presumably involved dehydro-



genation of an intermediate addition product, an N-alkyl-
4-cyclopentadienyl-1,4-dihydropyridine (10). For reasons
given elsewhere,^{2c} the structural assignments to 8 and
9 required confirmation, since there were no obvious
grounds for excluding the isomeric 2-cyclopentadi-
enylidene-1,2-dihydropyridine structures.²²

Structurally specific syntheses of members of the 2-
and 4-series are achieved by nucleophilic displacement
reactions of 2- or 4-halo² or phenoxy^{11,12}
pyridinium salts with sodium cyclopentadienide, e.g., as shown
below.



The proximate products of the displacements pre-
sumably are the conjugate acids of 13 and 14, from
which the bright orange anhydro bases are generated
by transfer of a proton to the extra cyclopentadienide
anion. The reaction mixtures also contain much
uncharacterized black solid, which interferes with
attempts to isolate the anhydro bases directly; in the
preferred procedure, the products 13 and 14 are ex-
tracted as the conjugate acids with dilute aqueous
hydrochloric acid and then regenerated with alkali.

(18) Heterocyclic analogs of aromatics constructed on these princi-
ples include early examples (furan, pyrrole, and thiophene as analogs of
benzene) and many later ones.¹⁹⁻²¹

(19) Cf. *inter alia* (a) A. G. Anderson, W. F. Harrison, R. G.
Anderson, and A. G. Osborne, *J. Am. Chem. Soc.*, 81, 1255 (1959);
(b) J. Harley-Mason and C. R. Harrison, *J. Chem. Soc.*, 4872 (1963).

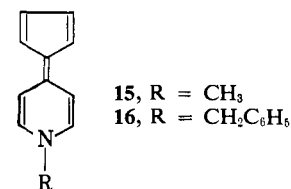
(20) (a) M. Los and W. H. Stafford, *ibid.*, 1680 (1959); (b) J. W.
Armit and R. Robinson, *ibid.*, 121, 827 (1922); 127, 1604 (1925).

(21) (a) G. V. Boyd, *ibid.*, 1978 (1958); (b) C. B. Reese, *J. Am. Chem.
Soc.*, 84, 3978 (1962).

(22) As an addendum to the previous discussion,^{2c} we note that the
reactions leading to 8 and 9 via 10 involve attack at C-4 of the pyridin-
ium ring, but other reactions of pyridinium salts with sodium cyclopent-
adienide, carried out under apparently very similar conditions, are
reported²³ to lead to intermediates that can be converted to azulenes,
presumably by attack at C-2. We have now scrutinized the reaction
mixture from the Kursanov-type^{14,15} synthesis of 9 but are unable to find
the 2-analog 13, azulene, or azulenogens. The reasons for the apparent
differences in behavior remain to be clarified.

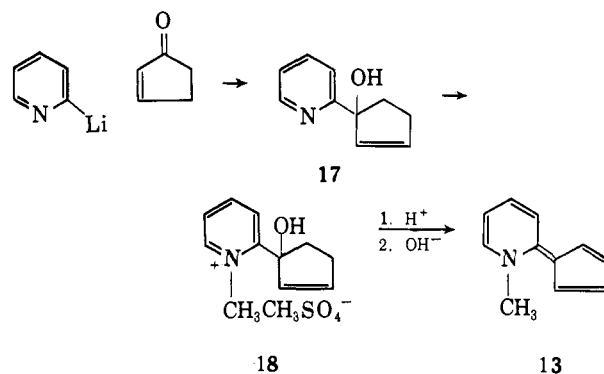
(23) K. Hafner, *Angew. Chem.*, 70, 419 (1958).

By analogous reactions, N-methyl- and N-benzyl-4-
cyclopentadienylidene-1,4-dihydropyridines 15 and 16
(\equiv 9) are prepared from the corresponding N-alkyl-4-
halopyridinium salts. Compound 16 has physical
properties identical with those previously recorded



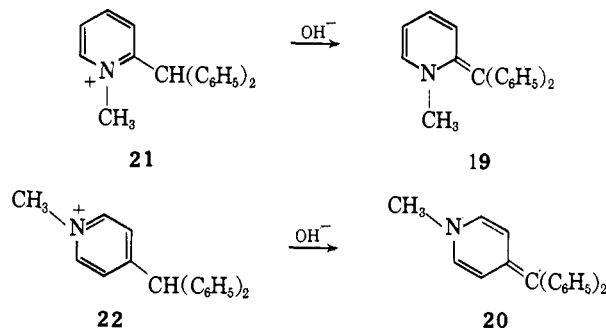
by Kursanov for the product prepared by the oxidative
substitution (cf. 9).²⁴

The structure of the N-methyl derivative in the 2-
series (13) already is fairly clear from the method of
synthesis; only the remote possibility of an elimina-
tion-addition mechanism in the nucleophilic displace-
ment step would introduce any ambiguity. The
structure is confirmed by an alternative synthesis.
2-Pyridyllithium and cyclopentenone give the tertiary
alcohol 17, which is converted to the methosulfate 18
and dehydrated to 13. The last step of the sequence
produces only a spectroscopically detectable amount of
13, but additional confirmation of the structure is
provided by catalytic hydrogenation of 13 (5.1 moles)
to 1-methyl-2-cyclopentylpiperidine, isolated and iden-
tified as the hydriodide.



Similarly, hydrogenation of the N-methyl derivative
in the 4-series (15) gives N-methyl-4-cyclopentylpiperi-
dine, isolated and identified as the methiodide.

Preparation of Benzo Derivatives. Tschitschibabin²⁵
showed that the benzhydrylidenedihydropyridines 19
and 20 could be prepared by abstraction of a proton
(with strong alkali) from the corresponding metho
salts 21 and 22. Essentially the same procedure is

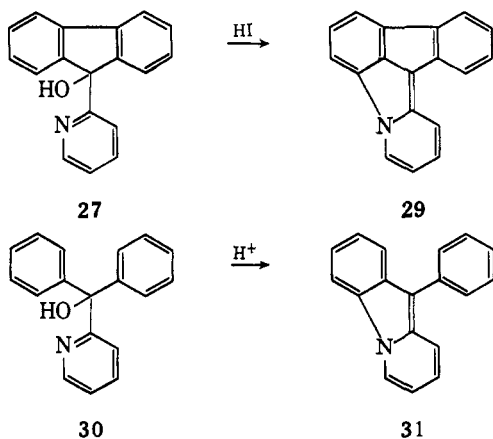
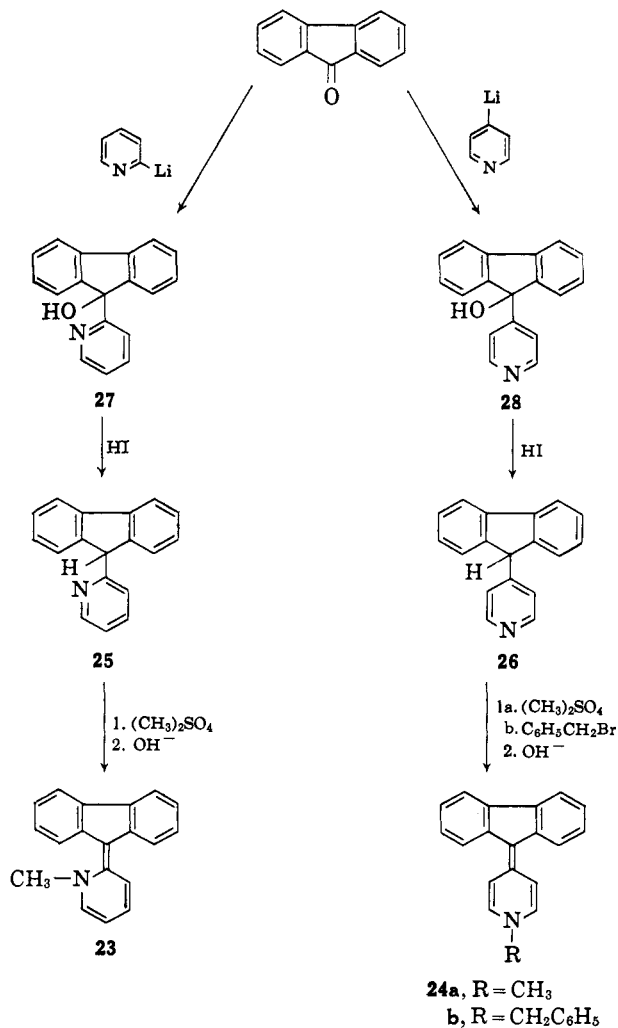


(24) The assigned structure 9 is confirmed by a subsequent degrada-
tion. See D. N. Kursanov and N. K. Baranetskaya, *Izvest. Akad. Nauk
SSSR, Otd. Khim. Nauk*, 1703 (1962).

(25) G. E. Tschitschibabin and S. W. Benewolenskaya, *Ber.*, 61,
547 (1928).

applicable to the synthesis of the fluorenylidene analogs **23**, **24a**, and **24b**. The 2- and 4-(9'-fluorenyl)pyridines **25** and **26** required as precursors are readily obtained by hydriodic acid reduction of the alcohols **27** and **28** which result from the action of 2- or 4-pyridyllithium on fluorenone.²⁶

Although Wasserman and Waterfield²⁷ found that strong acids smoothly converted the carbinol **30** to the brightly colored benzopyrrocoline **31**, this type of

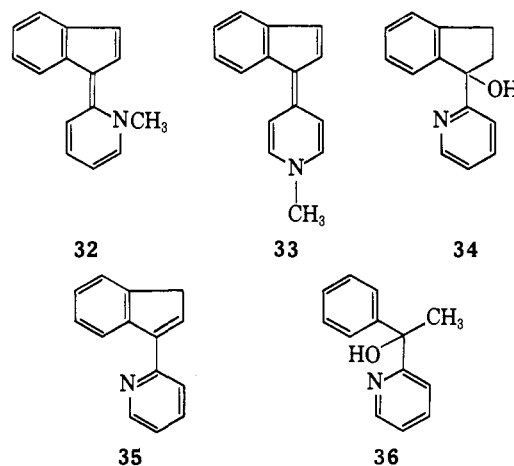


(26) F. J. McCarty, C. H. Tilford, and M. G. Van Campen, Jr., *J. Am. Chem. Soc.*, **79**, 472 (1957).

(27) H. H. Wasserman and W. R. Waterfield, *Chem. Ind. (London)*, 1220 (1961).

cyclodehydration, which would give **29**, does not appear to be of major importance with our closely analogous carbinol **27** under the strongly acidic but strongly reducing conditions of the hydriodic acid reduction.

The indenylidene analogs **32** and **33** are prepared by a sequence starting with 1-indanone and 2- (or 4-) pyridyllithium, which give 2'- (or 4'-) pyridyl-1-indanol (the 2'-isomer is already known^{26,28}); acid-catalyzed dehydration to 1-(2'- (or 4'-) pyridyl)-1-indene,²⁹ methylation, and then neutralization of the methosalts with alkali afford the anhydro bases **32** and **33** as red-purple needles. Compound **32** is obtained as an apparently homogeneous stereoisomer, despite the formal possibility of *cis-trans* isomerism. We have no evidence on its configuration.



The dehydration of the carbinol **34** in 85% sulfuric acid²⁹ or in 12 *N* hydrochloric acid gives the indene **35** rather than a benzopyrrocoline, despite the fact that the conditions, in contrast to the previous case, are nonreducing. This result is in accord with the observation of Wasserman and Waterfield²⁷ that when one of the phenyl groups of **30** is replaced by methyl (as in **36**), cyclodehydration to a benzopyrrocoline fails.

Reactions and Properties of the Anhydro Bases. Reactions with Electrophiles. N-Methyl-2-cyclopentadienylidene-1,2-dihydropyridine (**13**) reacts rapidly with a variety of electrophilic substances. Both bromine and nitrosyl chloride give amorphous, water-soluble products, which are unstable and rapidly decompose to gummy, intractable tars. Although we have not pursued the nature of these reactions further, it seems likely that they are initiated by electrophilic attack in the five-membered ring, as is the case with protonation. Carbonyl compounds such as benzoyl chloride, acetyl chloride, acetic anhydride, benzaldehyde, and the like convert **13** to ill-defined materials from which we are thus far unable to isolate discrete substances.

The color of all the anhydro bases is instantaneously discharged by proton acids, a change that is reversed by alkali. Although the salts formed with acids are water soluble, a crystalline perchlorate of **13** can be obtained by treatment of an ethyl acetate solution of the anhydro base with a cold 1:1 mixture of 70% perchloric acid and ethyl acetate. This substance is

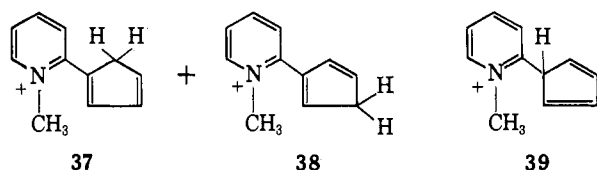
(28) D. W. Adamson and J. W. Billingham, *J. Chem. Soc.*, 1039 (1950).

(29) The 2'-isomer **35** is known; cf. P. A. Barrett, *ibid.*, 325 (1958).

unstable; it changes to an amorphous powder on keeping and gradually decomposes above 80°, without melting, to a black cindery material. The infrared spectrum of the perchlorate shows no absorption corresponding to the ammonium N-H stretching frequency. Protonation of **13** thus occurs on carbon. Compound **13** is completely protonated in ethanol or dioxane solutions containing perchloric acid or in solution in anhydrous trifluoroacetic acid; the characteristic ultraviolet-visible spectrum of **13** free base, showing four maxima at about 210, 272, 360, and 420 m μ , is replaced in the acid media by a simplified, hypsochromically shifted one with maxima at about 230–260 and 342 m μ . The characteristic spectrum of **13** is quantitatively regenerated from the trifluoroacetic acid solution by alkali, even after storage.

Trifluoroacetic acid solutions of **13** contain the two conjugate acids **37** and **38**, resulting from protonation in the five-membered ring. The two species are revealed by the nuclear magnetic resonance (n.m.r.) spectrum of the solution, which shows, in addition to aromatic and olefinic absorptions (area = 7.00), two N-methyl peaks (area = 3.05) and two sets of methylene signals (area = 2.09). The observed ratio 7.00:2.09 is very close to the theoretical (7:2) for both **37** and **38** and indicates the absence of any significant quantity of the third type of C-protonated species, **39**, for which the theoretical ratio is 8.

The intensities of the two methylene signals of this solution are in the ratio 68:32, with the downfield



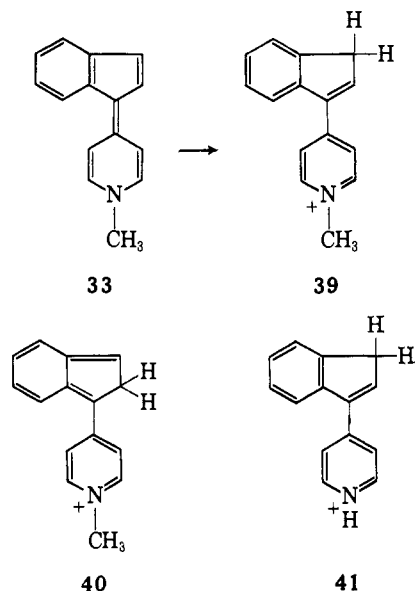
absorption being the stronger. The inductive effect of the cationic nitrogen might be expected to cause a stronger paramagnetic shift on the absorption of the methylene protons nearer to it, which would suggest that the downfield absorption is due to **37** rather than **38**.^{2b} It is possible, however, that this relationship could be reversed by ring current and local diamagnetic shielding effects.¹²

N-Methyl-4-cyclopentadienylidene-1,4-dihydropyridine (**15**) is also completely decolorized in acid solution, the long wave length electronic maximum shifting from 429 to 354 m μ . It is not yet known whether two conjugate acids corresponding to **37** and **38** are present in this case,³⁰ but the similarity of the spectrum of the conjugate acid of **15** to that of the 2-isomer suggests that protonation again has occurred in the five-membered ring.

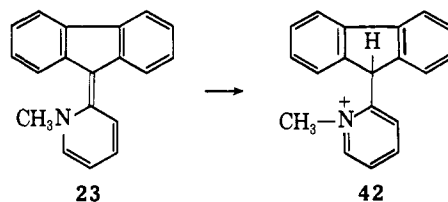
Addition of perchloric acid to a dioxane solution of the indenylidene anhydro base of the 4-series (**33**) causes a hypsochromic shift of the long wave length maximum to 331 m μ ; other bands occur at 251 and 217 m μ . The conjugate acid **39** probably predominates in solution. The *o*-quinone methide structure (**40**) would be exceedingly reactive and would decompose irreversibly, which would produce a type of anomalous behavior on titration that is not observed; the re-

(30) N-Butyl-2,6-dimethyl-4-cyclopentadienylidene-1,4-dihydropyridine perchlorate shows two kinds of methylene n.m.r. absorptions in trifluoroacetic acid, but the low-field signal is the weaker one.¹²

maining alternatives would all be in conflict with the observed ultraviolet spectrum. This spectrum corresponds closely to that of an acidified solution of 3-4'-pyridylindene (which must surely contain the cation **41**) and is thus in agreement with the previous conclusion.



Protonation of the fluorenylidene anhydro bases **23** and **24a** occurs at C-9 of the fluorene system (e.g., **23** \rightarrow **42**). The ultraviolet spectra of dioxane-perchloric acid solutions ($\lambda\lambda_{\text{max}}$ 262, 302 m μ for **24a** and 269 and 302 m μ for **23**) correspond very well to the summed spectra of fluorene and pyridinium cation.



The effect of structure on basicity of the members of the series is examined by quantitative $\text{p}K_a$ measurements. Since these substances are virtually insoluble in water, it is necessary to resort to indirect methods to obtain $\text{p}K_a$ values on the water scale.

Hall³¹ has shown that a good correlation exists between the electrical potential $E_{1/2}$ of a half-neutralized solution of a nitrogen base in nonaqueous solvent and the $\text{p}K_a$ of the base in aqueous solution. The correlation holds for a variety of solvents and bases,³¹ and has been applied by Kosower and co-workers^{32,33} to additional cases. Hall's potentiometric method provides one measure of basicity used in the present work.

A second method applicable to our series is the spectrophotometric one using the Hammett acidity function,³⁴ which involves the basic assumption that the ratio of dissociation constants of a pair of acids of a given charge type is invariant with medium changes.

(31) H. K. Hall, *J. Phys. Chem.*, **60**, 63 (1956).

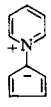
(32) E. M. Kosower and B. C. Ramsey, *J. Am. Chem. Soc.*, **81**, 856 (1959).

(33) E. M. Kosower and T. S. Sorensen, unpublished; T. S. Sorensen, Dissertation, University of Wisconsin, 1961.

(34) For a review, see M. A. Paul, *Chem. Rev.*, **57**, 1 (1957).

Although this assumption is invalid for some solvent systems,³⁴ its use in the present cases appears to be justified by the results to be described. The data for the series are collected in Table I. Also shown are the values now found potentiometrically for Tschitschibabin's²⁵ benzhydrylidene bases (**19** and **20**) and Kosower's value³² for pyridinium cyclopentadienide,³⁵ **43**.

Table I. pK_a Values for Conjugate Acids of Pyridinium Anhydro Bases

Compd.	In H_2O^a	In 10% dioxane- CH_3CN^b	In 10% dioxane- H_2O^b	In H_2O^c
13	9.1	8.69	8.73	8.87
14	...	8.34	8.51	8.65
32	...	11.0, 11.1 ^d	...	11.25
23	11.4	11.34, ^e 11.73, ^f 11.59 ^{d,e,g}	...	11.72
19	12.5
15	...	9.16	9.03	9.17
16	8.8	8.61	8.64	8.78
33	...	8.79	...	8.96
24a	...	9.86	...	10.03
24b	...	9.19	...	9.36
20	12.1 ^h
	10.0 ⁱ

^a Potentiometric; determined in acetonitrile solvent and calculated by the method of Hall (see text). ^b Spectrophotometric. ^c Estimated by adding 0.14 pK_a units to the dioxane-water value. ^d In pure dioxane. ^e Piperidine buffer. ^f Diphenylguanidine buffer. ^g Average of two determinations, 11.57 and 11.61. ^h Average of two determinations, 12.0 and 12.1. ⁱ W. K. McEwen, *J. Am. Chem. Soc.*, **58**, 1124 (1936); cf. A. Streitwieser, Jr., *Tetrahedron Letters*, No. 68, 23 (1960).

The potentiometric pK_a values correspond to measured values of $E_{1/2}$, read off a Hall plot used as a calibration curve; the Hall plot is obtained by measuring $E_{1/2}$ values for a series of known nitrogen bases and graphing these vs. aqueous pK_a values taken from the literature or independently measured spectrophotometrically in the present work. The derived pK_a values are probably reliable to about 0.2–0.3 of a unit, the major source of error being the scatter of the “known” points about the correlation curve. It is striking that the empirical Hall correlation is fairly smooth, even in solvents of very low dielectric strength,³² despite the large ion-pairing effects that must be present.

The usual technique in Hammett acidity function measurements involves spectrophotometric determination of the acid–base concentration ratios for both the unknown and an indicator acid–base system. This is inconvenient in the present cases because the strong absorption of the unknowns throughout most of the ultraviolet region precludes the use of most of the readily available indicator bases of the proper charge type (chargeless). The necessary concentration ratio of the known can, however, be set up stoichiometrically by a buffer technique, in which a relatively high concentration of the known (100-fold or more greater

than the unknown) is established. From the buffer ratio so fixed, the known pK_a of the buffer conjugate acid, and the spectrophotometrically determined acid–base concentration ratio of the unknown, the pK_a of the unknown conjugate acid can be calculated from the usual Hammett equations. Although an extended discussion of the acidity data is deferred to the next paper,¹⁷ we note several qualitative trends here.

The relationship between the spectrophotometric pK_a values and true pK_a values for aqueous solution is not immediately apparent. Strict adherence to the Hammett acidity function would require that the pK_a values so derived be solvent independent. In those cases (**13**, **14**, **15**, and **16**) where experimental circumstances permit direct tests, the requirement seems to be fulfilled, at least approximately. Thus, the average change in derived pK_a for these four compounds resulting from the medium change 10% dioxane–acetonitrile to 10% dioxane–water (a change of roughly 50 in dielectric constant) is +0.03 unit, which is certainly within experimental error. There seems to be a small but perhaps real medium effect on the spectrophotometric pK_a values associated with a change from 10% dioxane–water to pure water. This is illustrated in Table II, which lists data for three

Table II. Effect of Solvent on Spectrophotometric pK_a Values of Three Nitrogenous Conjugate Acids

Conjugate acid of	Aq. dioxane, %	pK_a
1,2,3-Triphenylguanidine	0	9.01
	1	8.98
	5	8.95
	10	8.84
1,2-Diphenylguanidine	0	10.04
	10	9.96
1,2-Diphenylacetamidine	0	8.45
	10	8.28

familiar nitrogen bases. The average change is about +0.14 unit, which is not unreasonable in comparison to the change of +0.19 to +0.26 unit reported³⁶ for another series of nitrogen bases examined in 20% dioxane–water and in pure water. Accordingly, it seems proper to give the spectrophotometric “pure aqueous” pK_a value as 0.14 unit greater than the observed 10% dioxane value and 0.17 unit greater than the 10% dioxane–acetonitrile value. At worst, this suggests a small departure from strict Hammett behavior. Although we cannot claim a high degree of accuracy in the absolute pK_a values, it seems unlikely that they are seriously in error, since for the three cases (**13**, **23**, and **16**) where direct comparisons are available, the derived spectrophotometric “pure aqueous” pK_a is identical with the potentiometric pK_a within the combined experimental error.

The pK_a values listed in Table I for the 1-methyl-2-cyclopentadienylidene-1,2-dihydropyridine (**13**) system must be dissected into two, since two conjugate acids (**37** and **38**) are formed. The spectrophotometric determination gives only the summed conjugate acid–base ratio (**37** + **38**):**13**, and the pK_a derived from this

(35) D. Lloyd and N. S. Sneezum, *Chem. Ind.*, (London), 1221 (1955); *Tetrahedron*, **3**, 334 (1958).

(36) H. P. Marshall and E. Grunwald, *J. Am. Chem. Soc.*, **76**, 2000 (1954).

ratio does not refer to a specific acid. The individual pK_a values can be calculated from the ratio **37**:**38**, which is known from the analysis, already described, of the n.m.r. spectrum of a trifluoroacetic acid solution. If it is assumed that the acidity function is obeyed in trifluoroacetic acid, then the **37**:**38** ratio is the same in aqueous solution and in the other solvents examined. The relationship between the apparent spectrophotometric equilibrium constant and the true dissociation constants for the individual acids is given by eq. 1.

$$K_{\text{apparent}} = \frac{K_1 K_2}{K_1 + K_2} \quad (1)$$

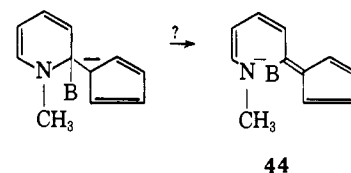
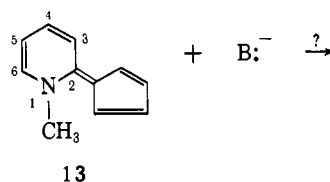
On this basis, $pK_1 = 8.70$ and $pK_2 = 8.37$ in aqueous solution. This dissection is independent of whether K_1 is assigned to **37** and K_2 to **38** or *vice versa*; the higher pK_a value applies to whichever conjugate acid is the more abundant. Note that the derived values are both lower than pK_{apparent} , which is 8.87. Similar corrections presumably are required for the other cyclopentadienylidene anhydro bases **14**, **15**, and **16**, although the necessary n.m.r. data are not yet available. If one of the acids of a pair connected through a common conjugate base is much stronger than the other, very little of it will exist at equilibrium, and the measured acid concentration will approach that of the weaker acid. The largest discrepancy between the measured acid concentration and that of the "weaker" acid will occur when both acids are of equal strength, in which case the true pK_a would be less than pK_{apparent} by log 2. For example, the value for **15** might require correction to 8.87.

In a general way, the effect of annelation on the acidities of the conjugate acids is in accord with that found³⁷ for the series cyclopentadiene > indene > fluorene. The successive fusion of benzo rings onto the five-membered ring steadily decreases the acidity in both the 2- and 4-series. The profound electronic effect of the cyclopentadienylidene ring is demonstrated by the sharp increase in acidity associated with completion of a fluorenylidene system by *ortho-ortho* junction of a benzhydrylidene system (**20** → **24a**, and **19** → **23**).^{38a} Although pK_a values for simple N-alkyl-1,*x*-dihydro-*x*-alkylpyridinium cations are unknown, they must be in the range of 14 to 15, since these substances form anhydro bases only in strong caustic.^{38b} The replacement of a 2- or 4-alkyl group by a cyclopentadienyl group thus increases the acidity by six to seven powers of ten (**13**, **14**, **15**, and **16**, Table I).

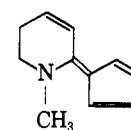
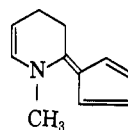
The electron-withdrawing inductive effect of a phenyl group seems to be detectable in the pK_a values. In each of the three pairs (**13** → **14**, **15** → **16**, and **24a** → **24b**) in which a hydrogen of the N-methyl group is replaced by phenyl, a slightly stronger acid results.

Reactions with Nucleophiles. By analogy to fulvenes,³⁹ **13** might be expected to react with strong base to give a cyclopentadienide. Cleavage of the heterocyclic ring

by release of a negatively charged nitrogen fragment⁴⁰ then would produce a (γ -aminobutadienyl)-



fulvene like the intermediate in the Ziegler-Hafner azulene synthesis.^{23,41-43} In the event, however, this kind of cleavage does not seem to occur. Thus, N-methyl-2-cyclopentadienylidene-1,2-dihydropyridine (**13**) can be recovered in substantial amounts after having been subjected for several hours to the action of a boiling solution of phenyllithium in benzene. Lithium aluminum hydride reduces **13** first to a dihydro and then to a tetrahydro stage, but the dihydro derivative (which may well be a mixture) is not formed primarily by attack at C-2 of the pyridine ring, since the product still contains a fulvene system (λ_{max} 243 and 340 $m\mu$). It is probably **45** and/or **46**; over palladium-charcoal it consumes exactly 4 moles of hydrogen and gives 1-methyl-2-cyclopentylpyridine. Further lithium alu-



minium hydride treatment of the dihydro material produces a liquid tetrahydro derivative, which again may be a mixture. The fulvene system is absent in this product (λ_{max} 243 $m\mu$). Catalytic hydrogenation consumes 3 moles of gas and again produces 1-methyl-2-cyclopentylpyridine.

Spectra. All of the anhydro bases prepared in this study show intense, sharp maxima near 6.1 μ in the C=C stretching region of the infrared spectrum. This region is one in which fulvenes, benzofulvenes, and dibenzofulvenes all show strong maxima, some with molar extinction coefficients⁴⁴ as high as 100, or about ten times that of ordinary *cis* double bonds.⁴⁵ Strong bands in this region are also reported for several dihydropyridines.³³

The electronic spectra of the anhydro bases in various solvents and under several conditions of acidity were measured and are discussed in an accompanying paper.^{1c}

(40) For nucleophilic displacements of 6-aminofulvenes, see K. Hafner, C. König, M. Kreuder, G. Ploss, G. Schulz, E. Sturm, and K. H. Vöpel, *Angew. Chem. Intern. Ed. Engl.*, **2**, 123 (1963).

(41) K. Ziegler and K. Hafner, *Angew. Chem.*, **67**, 301 (1955).

(42) K. Hafner and H. Kaiser, *Ann.*, **618**, 140 (1958).

(43) K. Hafner, *ibid.*, **606**, 79 (1957).

(44) J. C. Wood, R. M. Elofson, and D. M. Sanders, *Anal. Chem.*, **30**, 1339 (1958).

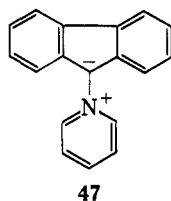
(45) Cf. R. N. Jones and C. Sandorfy, "Techniques of Organic Chemistry," Vol. IX, "Chemical Applications of Spectroscopy," W. West, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p. 370.

(37) See Table I, footnote *i*.

(38) (a) For a discussion of how much of this effect is attributable to increased coplarity and how much to the distinctive anion-stabilizing ability of the five-membered ring in the related case of 9-phenylfluorene vs. triphenylmethane, see A. Streitwieser, Jr., J. I. Brauman, J. H. Hammons, and A. H. Pudjaatmaka, *J. Am. Chem. Soc.*, **87**, 384 (1965). (b) H. Decker, *Ber.*, 2493 (1905).

(39) For a review of fulvene chemistry, see E. D. Bergmann, in "Progress in Organic Chemistry," Vol. 3, J. W. Cook, Ed., Academic Press Inc., New York, N. Y., 1955, p. 103.

Stability. The electronic arrangement in the series of anhydro bases of the 2- and 4-series seems to be associated with far greater stability toward decomposition than that of the truly zwitterionic analogs 1-pyridinium cyclopentadienide (43)^{33,35} and 1-pyridinium fluorenylide (47).⁴⁶ The last two substances appear to be



exceedingly unstable to light and heat, in contrast to the compounds of the 2- and 4-series. Storage for several years at room temperature in a nitrogen atmosphere produces little apparent change in the anhydro bases, and N-methyl-4-cyclopentadienylidene-1,4-dihydropyridine (15) can be stored at refrigerator temperature for 1 year without change in its ultraviolet-visible spectrum. N-Methyl-2-fluorenylidene-1,2-dihydropyridine (23) can be recovered unchanged after storage in air. Its benzene solutions are only slowly altered by light, and it is unaffected when a suspension in water is boiled. The cyclopentadienylidene compounds are somewhat more sensitive than the fluorenylidene and indenylidene ones, but they still seem to be far easier to isolate and handle than the simple, notoriously unstable⁴⁷ pyridone methides derived from 2- or 4-alkylpyridinium salts. We do not observe the instability reported¹¹ for 15 and 33.

Experimental⁴⁸

N-Methyl-2-cyclopentadienylidene-1,2-dihydropyridine (13). *A. From Cyclopentadienylsodium and 2-Iodopyridine Methiodide.* A solution of 0.080 mole of cyclopentadienylsodium in 150 ml. of 1,2-dimethoxyethane was prepared by rapidly stirring a suspension of 1.84 g. of sodium dispersed in xylene (supplied by Ethyl Corp. as 50% sodium, 0.5% oleic acid) under a nitrogen atmosphere with 100 ml. of dimethoxyethane and adding dropwise over a 15-min. period a solution of 11 ml. of cyclopentadiene in 50 ml. of dimethoxyethane.⁴⁹ The temperature of the reaction mixture was held below 30°. The resulting colorless solution (which turned pink only if air was admitted) was stirred vigorously and treated during 10 min. with 12.1 g. (0.035 mole) of powdered 2-iodopyridine methiodide⁵⁰ while maintaining a nitrogen atmosphere. At the first addition of the salt, the reaction mixture turned a deep green, finally becoming a jet black toward the end of the reaction. The reaction was only mildly

(46) F. Kröhnke, *Angew. Chem.*, **65**, 605 (1953).

(47) G. E. Tschitschibabin, *Ber.*, **60**, 1607 (1927); cf. also L. C. Anderson and N. V. Seeger, *J. Am. Chem. Soc.*, **71**, 343 (1949).

(48) Melting and boiling points are uncorrected. Microanalyses are by A. Elek, Elek Microanalytical Laboratories, Los Angeles, Calif., and by Joseph F. Alicino, P. O. Box 267, Metuchen, N. J. Infrared spectra of potassium bromide disks were taken with the Perkin-Elmer Infracord spectrometer. The n.m.r. spectrum of 13 in trifluoroacetic acid was determined at 60 Mc. with the Varian A-60 instrument. We are indebted to L. F. Johnson of Varian Associates for the spectrum and interpretation.

(49) Cf. G. Wilkinson, in "Organic Syntheses," Coll. Vol. IV, N. Rabjohn, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, p. 474.

(50) H. L. Bradlow and C. A. Vanderwerf, *J. Org. Chem.*, **16**, 1143 (1951).

exothermic. After the reaction mixture had been stirred for an additional 2 hr., a total of 20 ml. of water was added. At this time the reaction mixture was a deep red. The solvent was then removed by heating the reaction vessel to 50° *in vacuo*. When the reaction mixture was nearly dry, 100 ml. of benzene and 50 ml. of water were added. After separating the deep red organic phase, titration of the light yellow aqueous phase with 0.12 *N* hydrochloric acid showed the presence of 0.010 mole of base. The organic phase was dried over magnesium sulfate. After filtration, the organic phase was reduced by evaporation to approximately one-half of its former volume, whereupon a large quantity of black amorphous material began to deposit from solution. The benzene solution was then extracted with 50 ml. of 0.24 *N* hydrochloric acid. This yielded a nearly colorless benzene phase and a deep black, aqueous phase. The benzene layer was discarded and the aqueous phase was brought to a pH of 8–9 by the addition of 5% sodium carbonate solution. This mixture was extracted with three 100-ml. portions of benzene. After having been dried over magnesium sulfate, the extract was evaporated to 30 ml. After cooling to room temperature 60 ml. of petroleum ether (40–60°) was added and the flask stored overnight in the refrigerator. This yielded 0.15 g. of bright orange needles, m.p. 55–57°. The remaining aqueous phase was made strongly basic by the addition of concentrated sodium hydroxide, extracted with benzene, and worked up in an identical manner. This yielded an additional 1.00 g. of orange needles, m.p. 72–73°. The combined mother liquors were evaporated to 20 ml. and diluted with petroleum ether (40–60°) to yield a final crop of 0.75 g. of orange needles. The total yield was 1.95 g. (35% yield, based on the 2-iodopyridine methiodide). The 57 and 73° materials were dimorphs of the same compound (13). They showed the same infrared and ultraviolet-visible spectra. When a molten sample of the 57° form was seeded with a crystal of the 73° form it resolidified and remelted at 73°. In later repetitions of this preparation, only the 73° form was obtained.

For analysis, the compound was recrystallized from ether-pentane or from benzene-petroleum ether (b.p. 40–60°). The analytical samples melted at 56–57° and 74.5–75°, respectively.

Anal. Calcd. for C₁₁H₁₁N: C, 84.04; H, 7.05; N, 8.91. Found (for the 57° form): C, 84.05; H, 7.16; N, 8.94. Found (for the 75° form): C, 84.12; H, 7.11; N, 8.97.

B. By Dehydration of N-Methyl-2-(1'-hydroxy-2'-cyclopentenyl)pyridinium Methosulfate (18). A solution of 0.30 mole of 2-lithiopyridine in ether was prepared according to Wibaut, *et al.*,^{51a,b} and the deep red solution was treated dropwise at –50° with 24.5 g. (0.30 mole) of 1-cyclopenten-3-one.^{51c} At the end of the addition, the reaction mixture was a white slurry. It was warmed to 0°, treated with 100 ml. of water, and warmed to room temperature. The aqueous phase was separated and extracted with 50 ml. of

(51) (a) H. L. Otto, J. P. Wibaut, and C. W. Grownendaal, *Rec. trav. chim.*, **78**, 446 (1959); (b) J. P. Wibaut and L. G. Heeringa, *ibid.*, **74**, 1003 (1955); (c) K. Alder and F. H. Flock, *Chem. Ber.*, **89**, 1732 (1956).

ether. The organic phases were combined and dried over sodium sulfate and filtered, and the ethereal extract was concentrated on the steam bath. Final traces of solvent were removed by heating on the steam bath *in vacuo*. This yielded 44 g. of a red oil, which contained a ketonic impurity, λ_{\max} 5.85 μ . Attempts at bulb-to-bulb distillation *in vacuo* failed to effect a separation. Trituration of the crude product followed by cooling overnight resulted in the separation of a crystalline product.

Several recrystallizations from petroleum ether followed by sublimation *in vacuo* (40° at 0.3 mm.) were necessary before analytically pure material could be obtained. This gave fine white crystals of 2-(1'-hydroxy-2'-cyclopentenyl)pyridine (17), m.p. 34–35°. The sublimed sample was very hygroscopic.

Anal. Calcd. for $C_{10}H_{11}NO$: C, 74.52; H, 6.88. Found: C, 74.47; H, 6.93.

The infrared spectrum (film) of this material showed a very strong maximum at 3.04 and no maxima in the region between 5.5 and 6.0 μ .

A 0.40-g. quantity of the alcohol 17 and 0.30 ml. of dimethyl sulfate were dissolved in 10 ml. of benzene, and the resulting solution was heated on the steam bath for 1 hr. A dark red oil gradually deposited. This was extracted from the benzene phase with 10 ml. of water and treated with 10 ml. of hydrochloric acid, and the solution was heated for 1 hr. on the steam bath. After having been cooled and made basic to litmus, the reaction mixture was extracted with benzene. The visible spectrum of the extract showed two maxima at 432 and 371 $m\mu$ in the approximate optical density ratios of 1:2. This curve was identical in shape and position of the maxima with that obtained for N-methyl-2-cyclopentadienylidene-1,2-dihydropyridine (13). Titration of the benzene extract with 0.5 N perchloric acid in dioxane indicated the presence of 0.0003 mole of base. The acidified benzene extract was colorless. The color was regenerated and extracted into fresh benzene by the addition of sodium hydroxide solution. Attempts to isolate 13 from the extract were fruitless.

The perchlorate of 13 was obtained when a cold solution of perchloric acid in ethyl acetate (prepared by diluting one volume of ice-cold 70% perchloric acid with one volume of ethyl acetate) was added dropwise to an ice-cold solution of 100 mg. of 13 in 10–15 ml. of ethyl acetate. The addition was continued until the color was completely discharged. The resulting precipitate (92 mg.) was collected and recrystallized from acetone–ether to give white needles which decomposed gradually above 80° to a black, cindery material without melting.

Anal. Calcd. for $C_{11}H_{12}ClNO_4$: C, 51.26; H, 4.69. Found: C, 51.50; H, 5.20.

1-Methyl-2-cyclopentylpiperidinium Iodide. A.

From 1-(2'-Pyridyl)-1-cyclopentene. A solution of 3.85 g. of 1-(2'-pyridyl)-1-cyclopentene,⁵² b.p. 132–133°, in 10 ml. of benzene was treated with excess

(52) (a) H. L. Lochte, P. F. Krause, Jr., and E. N. Wheeler, *J. Am. Chem. Soc.*, **75**, 4477 (1953). (b) The substance was prepared by dehydration of 1-(2'-pyridyl)-1-cyclopentanol, which was in turn prepared in two ways: (a) as described,^{52a} by the Emmert reaction between pyridine and cyclopentanone, and (b) by the action of 2-lithiopyridine on cyclopentanone. The alcohols from both sources had m.p. 82–83° and showed no melting point depression when mixed with each other (lit.^{52a} m.p. 82–83°).

methyl iodide and allowed to stand overnight. The resulting precipitate (6.75 g., m.p. 105–110°) was recrystallized several times from ethanol–ethyl ether to give the methiodide, m.p. 109.5–110°.

Anal. Calcd. for $C_{11}H_{14}IN$: C, 46.01; H, 4.91. Found: C, 46.14; H, 4.88.

A solution of 0.318 g. of the methiodide in 10 ml. of ethanol at room temperature and atmospheric pressure over prerduced platinum oxide (0.05 g.) absorbed 4.0 moles of hydrogen. Filtration of the catalyst, concentration of the ethanol solution to dryness, and recrystallization of the residue from ethanol–ethyl acetate gave colorless crystals, m.p. 141–142°.

Anal. Calcd. for $C_{11}H_{22}IN$: C, 44.88; H, 7.51. Found: C, 44.75; H, 7.17.

B. By Catalytic Hydrogenation of 13. A stirred solution of 0.1950 g. of the anhydro base 13 in 20 ml. of ethanol in which was suspended 30 mg. of 10% palladium–charcoal consumed 5.0 moles of hydrogen during 7.5 hr., whereupon the reaction stopped. (Hydrogenation was also readily and quantitatively effected in dimethoxyethane solution with Adams catalyst.) The reaction mixture was filtered and treated with about 1 ml. of 47% hydriodic acid, and the ethanol was removed *in vacuo* under nitrogen. The residue was made alkaline with dilute aqueous sodium hydroxide, and the free base was extracted with ether and dried over potassium hydroxide pellets. The ether solution was decanted and treated dropwise with a saturated benzene solution of hydriodic acid until no further precipitate appeared. The crude product was a yellow solid, m.p. 110–115°. Several treatments with charcoal and recrystallizations from ethanol–ethyl acetate were necessary before a relatively pure sample was obtained. In two different runs, materials of m.p. 137–139° (alone or mixed with an authentic sample prepared as in part A) and m.p. 142–143° were obtained. The infrared spectra of the samples prepared in parts A and B were identical.

N-Benzyl-2-cyclopentadienylidene-1,2-dihydropyridine (14) was prepared from N-benzyl-2-bromopyridinium bromide,⁵³ m.p. 156–157° (lit.⁵³ m.p. 156–157°), and cyclopentadienylsodium in dimethoxyethane. It was obtained as deep red blocks, m.p. 141–142° from benzene–petroleum ether.

Anal. Calcd. for $C_{17}H_{15}N$: C, 87.52; H, 6.48; N, 6.01. Found: C, 87.45; H, 6.61; N, 5.99.

N-Methyl-4-cyclopentadienylidene-1,4-dihydropyridine (15)

A. From Cyclopentadienylsodium and 4-Bromopyridine Methiodide. 4-Bromopyridine methiodide was formed when 10.0 g. of 4-bromopyridine was added to a solution of 55 g. of methyl iodide in 50 ml. of benzene. The mixture was allowed to stand at room temperature for 1 hr. At the end of this period a large amount of solid had formed. At this time another 10.1 g. of 4-bromopyridine was added and the reaction mixture was allowed to stand for another hour. A final portion of 10.2 g. of 4-bromopyridine was added and the reaction mixture was allowed to stand for 1 week in the dark. The crude product was then collected by filtration after suspending in 50 ml. of benzene. After washing the filter cake with an additional 50 ml. of benzene the product was dried *in vacuo*. A

(53) B. R. Baker and F. J. McEvoy, *J. Org. Chem.*, **20**, 118 (1955).

total of 64 g. of dark green amorphous solid was collected. This material was purified by Soxhlet extraction with acetonitrile. Several recrystallizations from acetonitrile were necessary before an analytically pure sample could be obtained. The light yellow crystalline solid decomposed at about 235°.

Anal. Calcd. for C₆H₇BrIN: C, 24.02; H, 2.35; N, 4.67. Found: C, 23.62; H, 2.30; N, 4.55.

In the same manner as previously described for the synthesis of **13** and **15**, 10 g. of solid 4-bromopyridine methiodide was allowed to react with 0.066 mole of cyclopentadienylsodium in 500 ml. of dimethoxyethane at room temperature. After having been stirred for 15 min., the jet black reaction mixture was decomposed by pouring into 500 ml. of water. The resulting black solid was collected by filtration and dried *in vacuo*. A total of 7 g. of black amorphous powder was collected. This material was extracted in a Soxhlet apparatus with benzene for 2 hr. The extract (50 ml.) was diluted to 200 ml. with petroleum ether (b.p. 40–60°) and cooled in the refrigerator. A deep black solid (0.76 g.) was isolated on filtration of the cooled extract. This material had an infrared spectrum (KBr) that was identical with the subsequently isolated analytically pure material. The infrared spectrum (KBr) of the undissolved material from the Soxhlet extraction suggested that it was polymeric. The material isolated from the soluble fraction was recrystallized from benzene to yield bright golden plates decomposing above 200°. This material was identical in physical appearance, infrared spectrum, and visible spectrum with that obtained by method B.

B. From Cyclopentadienylsodium and 1-Methylpyridinium Iodide. A solution of 0.080 mole of cyclopentadienylsodium in 250 ml. of dimethoxyethane was treated with 20 g. (0.090 mole) of 1-methylpyridinium iodide, m.p. 115–116° (lit.⁵⁴ m.p. 115–116°). The mixture was rapidly stirred at room temperature. Within 5 min. after the addition of the pyridinium halide the base concentration of the reaction mixture had dropped from 0.0033 mole/ml. to 0.0014 mole/ml. During the course of the stirring, the color of the mixture became gradually darker. After stirring at room temperature (ca. 25°) for a period of 20 hr., the reaction mixture was decomposed by the addition of 25 ml. of water. The solvent was removed by heating to 40° *in vacuo*. After ca. 75% of the solvent had been removed, several hundred milliliters of water was added and the resulting solid was collected by filtration. After drying *in vacuo* the black, amorphous solid weighed 13.2 g. This material was extracted in a Soxhlet apparatus for 24 hr. with benzene (200 ml.). The resulting black extract was filtered through a small quantity of charcoal and diluted with 30 ml. of petroleum ether (b.p. 40–60°). On cooling, 0.5 g. of bright yellow sheets crystallized. An additional 0.2 g. of the same material was isolated by concentrating the mother liquor. The residue was re-extracted for 5 days with benzene to yield, on identical work-up, an additional 0.4 g. of the same material as isolated above. The total yield was thus 1.1 g. (8%). The infrared spectrum of each of the fractions was identical with that of the analytically pure material. The mother liquors from the above isolation were concentrated to dryness and the in-

frared spectrum (KBr) taken. The spectrum showed no absorption at 13.0 and 14.0 μ , indicating the absence of 2-cyclopentadienylidene-1,2-dihydro-1-methylpyridine (**13**), which absorbs at these wave lengths. In addition the visible spectrum (benzene) showed no absorption maximum in the region of 360 m μ or between 600 and 700 m μ , but did show the band at 426 m μ corresponding to the finally isolated product **15**.

The first fraction of **15** was recrystallized twice from hot benzene and collected by filtering under nitrogen. This gave beautiful golden yellow plates which darkened and decomposed on heating above 200° (sealed capillary under nitrogen).

Anal. Calcd. for C₁₁H₁₁N: C, 84.04; H, 7.05; N, 8.91. Found: C, 83.97; H, 7.11; N, 8.86.

This material was stored under nitrogen at 0° in a well-sealed container because of its reported¹¹ instability. Not only was the physical appearance and infrared spectrum unchanged after storage for 1 year under these conditions, but the visible spectrum showed λ_{\max} (dioxane) 429 m μ (ϵ 33,000) vs. that of a freshly prepared sample of λ_{\max} 429 m μ (ϵ 32,500).

In order to determine the possible existence of azulene or azulenogens in the material remaining from the isolation of **15**, 1.0 g. of the residue from the mother liquors was heated with 7.1 g. of benzidine⁴² for 2 hr. at 230–250°. The deep red reaction mixture was extracted with hot benzene, poured onto an alumina column, and eluted with benzene. No blue band developed during the elution. The visible absorption spectrum of the benzene extract showed no absorption maximum in the 600–700-m μ region.

Although the residue from the reaction of cyclopentadienylsodium and 1-methylpyridinium iodide yielded only 4-cyclopentadienylidene-1,4-dihydro-1-methylpyridine by benzene extraction, it was obvious from the infrared spectrum of the extracted residue that other components were present. These were not identified.

1-Benzyl-4-cyclopentadienylidene-1,4-dihydropyridine (9, 16). *A. From Cyclopentadienylsodium and 1-Benzyl-4-bromopyridinium Bromide.* 1-Benzyl-4-bromopyridinium bromide was formed when a solution of 9.5 ml. of benzyl bromide and 10 g. of 4-bromopyridine

was allowed to stand at room temperature for several days. The resulting solid was suspended in benzene, collected by filtration, washed with several small portions of benzene, and dried *in vacuo* to give 20 g. of material. Three recrystallizations from acetonitrile-ethyl acetate yield light yellow plates, m.p. 205–209°.

Anal. Calcd. for C₁₃H₁₁Br₂N: C, 43.80; H, 3.37; N, 4.26. Found: C, 44.17; H, 3.47; N, 4.38.

A mixture of 4.7 g. (0.014 mole) of 1-benzyl-4-bromopyridinium bromide and 0.030 mole of cyclopentadienylsodium (in dimethoxyethane) was stirred vigorously for 1 hr. at room temperature. The reaction mixture was hydrolyzed by pouring into 1 l. of water. The resulting black solid (2.9 g.) was collected by filtration, dried *in vacuo*, and extracted (Soxhlet) with hot benzene for 6 hr. The extract was concentrated in the usual manner to yield 0.82 g. (25%) of an orange solid. Two recrystallizations from benzene yielded beautiful golden yellow plates that decomposed on heating above 200° (sealed under nitrogen). These properties agree with those reported by Kursanov, *et al.*¹⁴

(54) A. Hantzsch, *Ber.*, **42**, 81 (1909).

Anal. Calcd. for $C_{17}H_{15}N$: C, 87.52; H, 6.48; N, 6.01. Found: C, 87.44; H, 6.57; N, 6.07.

The infrared spectra of the analytical sample, of the initially isolated material (0.82 g.), and of the sample prepared from N-benzylpyridinium bromide and cyclopentadienylsodium (*vide infra*) were identical.

*B. From Cyclopentadienylsodium and 1-Benzylpyridinium Bromide.*¹⁴ 1-Benzylpyridinium bromide was formed when a mixture of 61 g. of benzyl bromide and 50 ml. of anhydrous acetone was heated to reflux on the steam bath and treated dropwise, while maintaining reflux, with a solution of 30 ml. of pyridine in 300 ml. of acetone. On cooling, light brown crystals separated from solution. These were collected by filtration under a nitrogen atmosphere. After having been dried *in vacuo*, the material melted at 109–111°. One recrystallization from acetonitrile yielded white needles, m.p. 110–111° (lit.⁵³ m.p. 98–100°). The compound was extremely hygroscopic.

Anal. Calcd. for $C_{12}H_{12}BrN$: C, 57.61; H, 4.84. Found: C, 57.33; H, 5.18.

A mixture of 33 g. (0.13 mole) of 1-benzylpyridinium bromide and 0.12 mole of cyclopentadienylsodium in 250 ml. of dimethoxyethane was stirred for 20 hr. at 35°. The deep brown reaction mixture was then hydrolyzed with 20 ml. of water and the solvent was removed by heating (40–50°) *in vacuo*. The residual material was suspended in 500 ml. of water and collected by filtration. The filter cake was then washed with two equal portions, 100 ml. each, of petroleum ether (b.p. 40–60°) and dried *in vacuo* to give 12.7 g. of material, which was leached with hot benzene and filtered, and the filtrate was cooled to room temperature to give 1.0 g. (first crop) of a red crystalline solid. The mother liquor was concentrated to about one-tenth of its former volume and cooled. An additional 1.3 g. of a red crystalline solid was collected (second crop). Both crops had identical infrared spectra (KBr). These spectra were identical with those obtained from the previously prepared sample of 1-benzyl-4-cyclopentadienylidene-1,4-dihydropyridine. A single crystallization from benzene using a small amount of charcoal yielded beautiful golden yellow plates that decomposed on heating above 200° (sealed tube under nitrogen). The visible spectrum of this material showed a single absorption band, λ_{max} (dioxane) 430 m μ (ϵ 35,700) (lit.¹⁵ λ_{max} (methanol) *ca.* 430 m μ (ϵ 28,000)).

1-(4'-Pyridyl)-1-cyclopentanol. An ethereal solution of 0.064 mole of 4-lithiopyridine and 7.5 ml. of cyclopentanone was allowed to react at –60°. Work-up in the manner described in the synthesis of **17** gave 4.8 g. of a white crystalline solid, m.p. 80–82°. Several recrystallizations from petroleum ether (b.p. 40–60°) yielded a colorless crystalline material, m.p. 86–87°.

Anal. Calcd. for $C_{10}H_{13}NO$: C, 73.59; H, 8.03. Found: C, 73.63; H, 8.09.

4-Cyclopentylpyridine. A solution of 4.2 g. of the 1-(4'-pyridyl)-1-cyclopentanol in 50 ml. of hydriodic acid was heated at reflux for 3 hr. After treatment with 50 ml. of ammonium hydroxide, the reaction mixture was worked up in the manner described above for hydriodic acid reductions. Distillation of the product *in vacuo* gave 3.01 g. of a colorless liquid, b.p. 114–115° (12 mm.), n_D^{20} 1.5307 (lit.⁵⁵ n_D^{20} 1.5306

for a sample prepared by another route). The picrate was prepared in and recrystallized from chloroform, m.p. 130–131° (lit.⁵⁵ m.p. 131–132°).

4-Cyclopentyl-1,1-dimethylpiperidinium Iodide. A. From 4-Cyclopentylpyridine. A solution of 1.004 g. of 4-cyclopentylpyridine in 25 ml. of ethanol and 1.0 ml. of concentrated hydrochloric acid over platinum absorbed 3.05 moles of hydrogen. On working up the reaction mixture in the usual manner (*vide supra*) *ca.* 1 g. of the substituted piperidine was isolated. A 0.2-g. quantity of this material was converted to the methiodide by treatment with methyl iodide (2 ml.). Several recrystallizations from ethanol-ethyl acetate gave colorless blocks, m.p. 229–230°.

Anal. Calcd. for $C_{12}H_{24}IN$: C, 46.60; H, 7.82. Found: C, 46.57; H, 7.67.

B. By Hydrogenation of 1-Methyl-4-cyclopentadienylidene-1,4-dihydropyridine. A solution of 0.0604 g. of **15** in 50 ml. of ethanol consumed 5.1 moles of hydrogen over platinum. The mixture was filtered, 1.0 ml. of 3 *N* sulfuric acid was added, and the mixture was then taken to dryness. A few pellets of sodium hydroxide was added to the residue and the resulting mixture was extracted with ether, dried, and treated with 1 ml. of methyl iodide. A solid separated. The solvent was evaporated and the residue was dried *in vacuo* to give material, m.p. 218–222°. After treatment with charcoal, several recrystallizations from ethyl acetate-ethanol yielded a colorless crystalline solid, m.p. 228–229°, alone or mixed with an authentic sample of 4-cyclopentyl-1,1-dimethylpiperidinium iodide. The infrared spectra (KBr) of both materials were identical.

9-(2'-Pyridyl)-9-fluorene (27), m.p. 130–131° (lit.²⁶ m.p. 130–131°), was reduced to 9-(2'-pyridyl)fluorene (**25**) by heating a solution of 7.50 g. of **27** in 50 ml. of 47% hydriodic acid at reflux. After the transient appearance of a purple oil, the reaction mixture became homogeneous and colorless. Solvent was boiled off until the reaction temperature reached 140°. After having cooled, the reaction mixture was treated with excess ammonium hydroxide and the product was extracted into petroleum ether (b.p. 40–60°), dried over sodium sulfate, and concentrated to dryness to give 7.3 g. of crude product. A single recrystallization from 20 ml. of petroleum ether gave 5.7 g. of a colorless crystalline material, m.p. 78–80°. An additional recrystallization from petroleum ether yielded an analytically pure sample of **25**, m.p. 78–79°.

Anal. Calcd. for $C_{18}H_{13}N$: C, 88.86; H, 5.38. Found: C, 89.06; H, 5.41.

The *picrate* was prepared in ethanol and recrystallized twice from glacial acetic acid, m.p. 195–196° dec.

A solution of 0.545 g. of **25** in 50 ml. of ethyl acetate absorbed 3.1 moles of hydrogen at atmospheric pressure over platinum catalyst. Filtration and evaporation gave 0.50 g. of crystalline solid. Several recrystallizations from petroleum ether (b.p. 40–60°) gave colorless crystalline 9-(2'-piperidyl)fluorene, m.p. 113.5–114.0°.

Anal. Calcd. for $C_{18}H_{19}N$: C, 86.70; H, 7.68. Found: C, 86.89; H, 7.80.

(55) H. L. Lochte and E. N. Wheeler, *J. Am. Chem. Soc.*, **76**, 5548 (1954).

Sury and Hoffmann⁵⁶ report that the reaction of 2-bromopyridine and fluorenylsodium gave **25** which, in contrast to our sample, was a liquid. The *picrate*⁵⁶ melted at 182–184°. Catalytic hydrogenation⁵⁶ of the liquid gave a material melting at 104–105°. We occasionally observed that **27** oiled out of solution and would only crystallize on vigorous scratching of the side of the flask.

1-Methyl-2-fluorenylidene-1,2-dihydropyridine (23). A solution of 2.90 g. of 9-(2'-pyridyl)fluorene (**27**) and 4.0 ml. of dimethyl sulfate in 20 ml. of benzene was heated for 3 hr. on the steam bath. The reaction mixture gradually deposited a solid. This material (4.15 g.) was dissolved in 50 ml. of water. On the addition of 50 ml. of 5% aqueous sodium carbonate solution, 2.68 g. of a deep purple solid precipitated. Soxhlet extraction with petroleum ether (b.p. 40–60°) gave 2.40 g. (79%) of **23** as deep purple blocks, m.p. 171–172° dec. A single recrystallization from benzene-petroleum ether (b.p. 40–60°) yielded short purple needles, m.p. 171–172° dec.

Anal. Calcd. for C₁₉H₁₅N: C, 88.67; H, 5.88; N, 5.44. Found: C, 88.76; H, 6.00; N, 5.37.

This compound was very soluble in benzene. A benzene solution was not decolorized on shaking with water but was decolorized on shaking with dilute hydrochloric acid. A sample was stored at room temperature for a period of *ca.* 4 months without apparent decomposition; m.p. 171°. Longer storage (1 year) at room temperature caused decomposition. After heating a suspension of 0.0135 g. at 90° (3 hr.) in 2 ml. of water, 0.0119 g., m.p. 172°, was recovered unchanged. Benzene solutions gradually deposited insoluble material on exposure to air and light. Bubbling oxygen through a benzene solution of **27** caused a precipitate to form.

9-(4'-Pyridyl)-9-fluorenol (28) was prepared by the reaction of 4-lithiopyridine with fluorenone. It was obtained as a white crystalline solid, m.p. 266–267° (from benzene).

Anal. Calcd. for C₁₈H₁₃NO: C, 83.38; H, 5.05. Found: C, 83.10; H, 4.64.

9-(4'-Pyridyl)fluorene (26) was obtained when 9-(4'-pyridyl)-9-fluorenol (1.70 g.) was reduced in the usual manner with 33 ml. of 47% hydriodic acid to give 1.50 g. of a colorless crystalline solid, m.p. 140–141°. Two recrystallizations from methanol gave material, m.p. 144–145°.

Anal. Calcd. for C₁₈H₁₃N: C, 88.86; H, 5.38; N, 5.76. Found: C, 88.98; H, 5.56; N, 5.77.

1-Methyl-4-fluorenylidene-1,4-dihydropyridine (24a). A 0.43-g. quantity of **26** was dissolved in 10 ml. of benzene and alkylated by the addition of 0.4 ml. of dimethyl sulfate. The precipitated salt was dissolved in 10 ml. of water and treated with 50 ml. of 2 *N* aqueous sodium hydroxide. The precipitated anhydro base was collected by filtration and dried *in vacuo*. The bright orange powder was then dissolved in 100 ml. of benzene and filtered, and the filtrate was evaporated to 50 ml. After the addition of 25 ml. of petroleum ether (b.p. 40–60°), the solution was allowed to cool to 0° to give bright orange needles, m.p. 184–186°. Two additional recrystallizations from benzene-petro-

leum ether gave 0.25 g. of bright orange needles, m.p. 187–188°. Since the reported¹¹ melting point (178–179°) was lower than obtained in this work, the material was submitted for elemental analysis.

Anal. Calcd. for C₁₉H₁₃N: C, 88.67; H, 5.88; N, 5.44. Found: C, 88.75; H, 6.01; N, 5.39.

1-Benzyl-4-fluorenylidene-1,4-dihydropyridine (24b) was prepared in the same manner from 0.359 g. of **26** by decomposing the benzyl chloride salt in aqueous sodium hydroxide. Several recrystallizations of the crude material (0.35 g.) from benzene-petroleum ether (b.p. 40–60°) gave red plates, m.p. 209–210°.

Anal. Calcd. for C₂₅H₁₉N: C, 90.05; H, 5.74. Found: C, 90.07; H, 5.84.

1-Methyl-2-indenylidene-1,2-dihydropyridine (32). A solution of 0.85 g. of 1-(2'-pyridyl)-1-indene (**35**), m.p. 81–82° (lit.²⁹ m.p. 80–82°), and 0.6 ml. of dimethyl sulfate in 10 ml. of benzene was heated on the steam bath. Within a few minutes a second liquid phase began to separate from solution. The reaction mixture was cooled and the benzene-insoluble phase was extracted into 50 ml. of water. The benzene phase was discarded and 50 ml. of 5% sodium carbonate solution was added to the aqueous phase. This caused the precipitation of a large quantity of purple oil, which was extracted with benzene. The benzene layer was dried over sodium sulfate and concentrated to dryness on the steam bath under a stream of nitrogen. The residue was a gummy red solid, which crystallized from petroleum ether. This substance was purified by recrystallization from petroleum ether (Soxhlet) to give short, red-purple needles, m.p. 161–162° dec.

Anal. Calcd. for C₁₅H₁₃N: C, 86.92; H, 6.32; N, 6.76. Found: C, 86.73; H, 6.30; N, 6.86.

Samples of this material were apparently stable for several months at room temperature but gradually decomposed. After storage at 0° in nitrogen for approximately 2 years the material had turned to a tarry liquid.

1-(4'-Pyridyl)-1-indanol. The reaction of 4-lithiopyridine with 1-indanone at –70° gave 5.4 g. (65%) of a crystalline solid melting at 154–156°. Two recrystallizations from ether-hexane yielded colorless crystalline material, m.p. 157–158°.

Anal. Calcd. for C₁₄H₁₃N: C, 79.59; H, 6.20; N, 6.63. Found: C, 79.59; H, 6.15; N, 6.63.

1-(4'-Pyridyl)-1-indene. A solution of 3.4 g. of 1-(4'-pyridyl)-1-indanol in 30 ml. of concentrated hydrochloric acid (12 *N*) was heated for 3 hr. on the steam bath. The reaction mixture was cooled and slowly poured into 60 ml. of concentrated ammonium hydroxide. The resulting mixture was extracted with ether and the ether extract was dried over potassium carbonate and concentrated to dryness under a stream of nitrogen. A light brown oil (3.0 g.) remained. When 2 g. of this material was distilled *in vacuo* (150° at 1 mm.) only 0.6 g. of lightly colored distillate was obtained. The undistilled material (residue) was a deep red glass, m.p. 140–160°, which distilled *in vacuo* (*ca.* 0.001 mm.) at very high temperatures (300–500°) to give deeply red liquid-solid mixtures. The distillate collected at 150° (0.6 g.) did not crystallize on standing in the cold (0°). On standing in contact with air at room temperature it visibly darkened

(56) E. Sury and K. Hoffmann, *Helv. Chim. Acta*, 37, 2133 (1954).

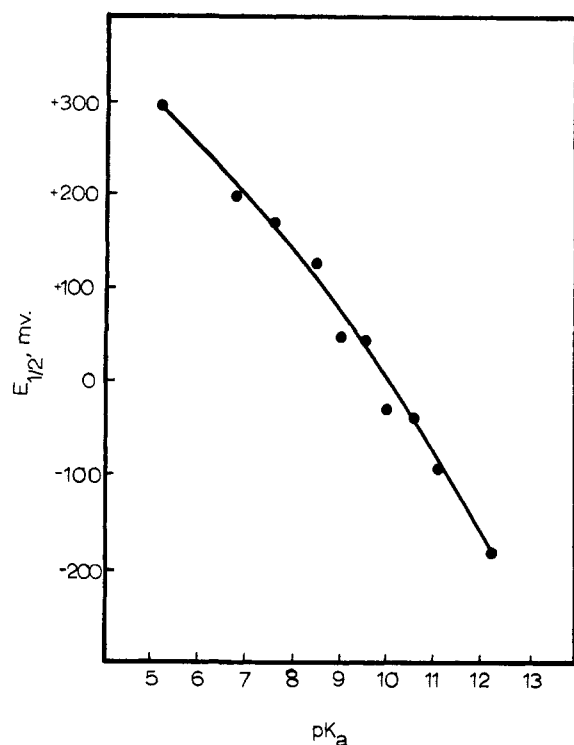


Figure 1. Hall potentiometric correlation of acidities of standard bases

within 1 to 2 hr., becoming extremely viscous within 1 day. In another preparation 0.5 g. of the alcohol was converted to 0.25 g. of the lower boiling distillate on heating in 6 *N* hydrochloric acid for 1 hr. The extreme instability of this material prevented convenient elemental analysis. A freshly distilled sample (0.1309 g.) was titrated in acetonitrile with standard perchloric acid (0.451 *N*) in dioxane.

Anal. Calcd. (neut. equiv.): 193. Found: 194.

The $E_{1/2}$ was +290 mv., indicating $pK_a = 5.1 \pm 0.2$ (*vide infra*). The ultraviolet spectrum showed maxima in absolute ethanol at 215 $m\mu$ ($\log \epsilon$ 4.15), 233 (4.21), sh. 280 (*ca.* 3.7), and sh. 295 (3.3). In ethanolic perchloric acid solution (1.5×10^{-3} *M*), the maxima occurred at 217 $m\mu$ ($\log \epsilon$ 4.11), 251 (4.27), and 331 (3.64).

1-Methyl-4-indenylidene-1,4-dihydropyridine (33). A mixture of dimethyl sulfate (1 g.) and 0.95 g. of a freshly distilled sample of 1-(4'-pyridyl)-1-indene in 10 ml. of benzene gave 1.8 g. of a solid salt, which was dissolved in 20 ml. of water. The addition of aqueous sodium hydroxide caused the precipitation of a brown-red solid, which was dried *in vacuo* and leached with boiling benzene. The mixture was filtered and the extract was concentrated and cooled to give 0.58 g. of purple-red needles. An analytical sample was recrystallized from benzene-petroleum ether (b.p. 40–60°) to give purple-red crystals, m.p. *ca.* 215° dec.

Anal. Calcd. for $C_{15}H_{13}N$: C, 86.92; H, 6.32; N, 6.76. Found: C, 87.03; H, 6.34; N, 6.67.

This material could be sublimed *in vacuo* (*ca.* 0.001 mm.) at 200–210° to give a bright orange sublimate, m.p. 215° dec. The melting points were taken in sealed capillary tubes (under nitrogen), but the samples began to darken visibly above 180° so that the exact decomposition point was indeterminate. The infrared

spectra (KBr) of the recrystallized and sublimed samples were identical. A sample stored under nitrogen at 0° did not visibly decompose (no color change) over a period of several months. Also a sample stored at room temperature in the open air did not exhibit visible decomposition. This material is reported in the literature¹¹ to decompose within several minutes under nitrogen.

Acidity Constants. A. Potentiometric. Acetonitrile for use as a solvent was purified by heating 5 l. of technical material at reflux with 1 lb. of phosphorus pentoxide for several days and distilling the product through a 6-ft. fractionating column. The column was packed with cylinders of stainless steel screening ("Penn State packing"), and the reflux ratio was held at about 20:1. The first few milliliters of distillate was discarded, and the remainder was collected and stored under nitrogen. The material had b.p. 81.5–82.0°, n_D^{20} 1.3444. Dioxane was purified by boiling 5 l. of the technical material over 0.5 lb. of sodium for 1 week and fractionating at a reflux ratio of 20:1 in the column described above. The first 500 ml. of distillate was discarded and the remainder was stored under nitrogen. The product had b.p. 102–102.1°, n_D^{20} 1.4221.

The standard substances used as calibration points for the Hall plot (Figure 1) are listed in Table III. These were obtained either from commercial sources or by synthesis according to literature procedures. The substances were purified by distillation or crystallization, whichever was appropriate. The liquids had boiling points and refractive indices and the solids had melting points in good agreement with literature values.

Table III. Standard Nitrogen Bases. pK_a Values of Aqueous Solutions and E.m.f. Values at Half-Neutralization of Acetonitrile Solutions

Compd.	$E_{1/2}$, mv.	No. of titra-tions ^a	Aqueous pK_a^b
Pyridine	+297 ± 10	5	5.17 ^c
α -Picoline	+255	2	5.97 ^c
2,6-Lutidine	+200	2	6.74 ^c
<i>s</i> -Collidine	+172 ± 5	3	7.59 ^d
1,2-Diphenylacetamidine	+128	1	8.46, 8.30 ^f
<i>s</i> -Triphenylguanidine	+50 ± 10	6	9.01 ^g
Benzylamine	+42	1	9.34 ^g
1,2-Diphenylguanidine	-30 ± 5	5	10.04, 10.12 ^g
<i>n</i> -Butylamine	-35 ± 10	1	10.61 ^g
Piperidine	-94 ± 2	2	11.13 ^g

^a Acetonitrile solutions titrated with perchloric acid-dioxane as described in text. ^b Determined in the reference indicated. ^c H. C. Brown and X. R. Mihm, *J. Am. Chem. Soc.*, 77, 1723 (1955). ^d H. C. Brown, S. Johnson and H. Podall, *ibid.*, 76, 5556 (1954). ^e This work. ^f G. Schwarzenbach and K. Lutz, *Helv. Chim. Acta*, 23, 1162 (1940). ^g N. F. Hall and N. R. Sprinkel, *J. Am. Chem. Soc.*, 54, 3469 (1932).

Titration were performed with a Beckman Model G pH meter with glass and calomel electrodes (Models 1190-42 and 1170). The meter was standardized frequently with a diisobutylamine-perchloric acid-acetonitrile buffer. Typical readings for a buffer ratio of 0.218 were -59 ± 1 mv. The titrant was made up by diluting 4 ml. of 70% perchloric acid to 100.0 ml.

with purified dioxane. Solutions thus prepared were about 0.45 *N* and were standardized against aqueous sodium hydroxide or against acetonitrile solutions of *s*-triphenylguanidine. The perchloric acid–dioxane solutions darkened slightly over a period of months, but titrations of *s*-triphenylguanidine with both fresh and aged acid solutions gave identical values for $E_{1/2}$ and for neutral equivalent.

A sample of about 5×10^{-4} to 10^{-3} mole of the base was dissolved in 50–75 ml. of purified acetonitrile. The electrodes, which were kept in distilled water when not in use, were removed and carefully dried with cellulose tissue, introduced into the nonaqueous solution, and allowed to equilibrate for several minutes while the solution was magnetically stirred and purged with a stream of nitrogen. The titrant was delivered from a 2-ml. microburet in aliquots of 0.05 ml. at first and 0.002 ml. in the region of the half-neutralization point. The potential was recorded 15–30 sec. after each aliquot had been added. In the case of the anhydro bases, the color was discharged at the end point. The breaks in the titration curve at neutralization were extremely sharp, a 600-mv. change over 0.03 ml. being typical. The neutral equivalents estimated from the titration curves for the anhydro bases are given in Table IV and are in good agreement with the

Table IV. Spectrophotometric Determination of pK_a' of *s*-Triphenylguanidine

Optical density ^a				pH'	pK_a' ^b
270 m μ	275 m μ	280 m μ	285 m μ		
0.571	0.542	0.493	0.429	<i>c</i>	...
0.287	0.243	0.205	0.165	<i>d</i>	...
0.438	0.402	0.362	0.308	9.05	8.98
0.472	0.438	0.395	0.339	9.23	8.97
0.429	0.393	0.354	0.303	9.02	9.00
Av. $pK_a' = 8.98 \pm 0.03$					

^a Solvent 1% dioxane–water; phosphate buffer; total concentration of *s*-triphenylguanidine (acid and base) 2.455×10^{-5} *M*.
^b Average of four determinations. ^c In 0.2 *N* aqueous hydrochloric acid. ^d In 0.09 *N* aqueous sodium hydroxide.

calculated values. With the exception of the benzhydrylidene compounds **19** and **20**, which had a second break corresponding to a few per cent of impurity, the anhydro bases showed only one break in the titration curve. The basicities of **19** and **20** were greater than that of any of the standards of Table III, and estimates of the pK_a could be made only by extrapolation of the graph (Figure 1) beyond the point of experimental verification.

The pK_a values of Table I were determined by measuring $E_{1/2}$ for the listed bases and reading off pK_a from Figure 1.

B. Spectrophotometric. If the Hammett acidity function³⁹ is obeyed, the acidity of an acid BH^+ is related to that of a known buffer or indicator acid of the same charge type AH^+ by eq. 2

$$pK_{BH^+} = pK_{AH^+} - \log(C_{AH^+}/C_A) + \log(C_{BH^+}/C_B) \quad (2)$$

where C_{AH^+}/C_A is the acid–base buffer or indicator ratio and C_{BH^+}/C_B is the acid–base ratio for the substance whose acidity is to be measured. Since the

anhydro bases studied here all absorbed strongly in the region of the spectrum where the standard bases absorbed, the standard bases were treated as buffers and used in large excess. The C_{AH^+}/C_A ratio was thus fixed stoichiometrically. The C_{BH^+}/C_B ratio was then measured spectrophotometrically on a solution containing the buffer and the unknown, using a spectral region where the anhydro base had strong absorption but the buffer was transparent. The ratio was determined from eq. 3

$$C_{BH^+}/C_B = \frac{\epsilon_B - \epsilon}{\epsilon - \epsilon_{BH^+}} \quad (3)$$

where ϵ_B and ϵ_{BH^+} are the extinction coefficients, measured independently, of the base and acid forms, and ϵ is the observed extinction coefficient in the presence of buffer. From the known pK_{AH^+} of the buffer acid in aqueous solution, the acid–base ratios, and eq. 2, pK_a values (pK_{BH^+}) for hypothetical aqueous solutions of the anhydro bases were derived.

Phosphate buffer was prepared by mixing 0.2 *N* potassium dihydrogen phosphate with 0.2 *N* sodium hydroxide. Depending on the volume ratios used, a pH range of 6 to 12 could be obtained. Triphenylguanidine–perchloric acid buffer was prepared in dioxane by mixing known amounts of triphenylguanidine and perchloric acid in dioxane. In a typical example, 3.134 g. of triphenylguanidine was dissolved in dioxane and brought to 25.00 ml. (0.436 *N*). This solution was then standardized by potentiometric titration with 0.461 *N* perchloric acid in dioxane. The buffer solutions were then prepared by adding 1.00 ml. of aliquots of the 0.436 *N* triphenylguanidine–dioxane solution to 10.00-ml. volumetric flasks. After this, carefully measured aliquots of 0.461 *N* perchloric acid–dioxane were added by means of a 2-ml. microburet. The ratio of triphenylguanidinium perchlorate to triphenylguanidine was allowed to vary from 0.250 to 2.54 in seven separate buffer solutions. This permitted the measurement of pK_a values of other nitrogen bases in the 8–10 pK_a region. In the same manner diphenylguanidine–perchloric acid and piperidine–perchloric acid buffers were prepared.

Procedure. The pK_a values of *s*-triphenylguanidine, 1,2-diphenylguanidine, and 1,2-diphenylacetamide were determined in water and in 10% dioxane–water (see Table II). In addition *s*-triphenylguanidine was also measured in 1 and 5% dioxane–water. A stock solution of *s*-triphenylguanidine in dioxane was prepared at a concentration of 2.455×10^{-3} mole l^{-1} . A dilution of one to ten of this solution with dioxane gave another stock solution at a concentration of 2.455×10^{-4} mole l^{-1} (in dioxane). If this same dilution was done with water the new stock solution was designated as being 1% dioxane–water. A 5% dioxane–water solution was prepared by diluting 1.00 ml. of the 2.455×10^{-3} mole l^{-1} stock solution (in dioxane) to 5.00 ml. by the addition of dioxane and diluting this solution in turn to 10.00 ml. by the addition of water. This gave a 50% dioxane–water stock solution which could be diluted 1:10 to give a 5% dioxane–water solution. Aqueous solutions of *s*-triphenylguanidine were obtained by dissolving the solid in 0.009 *N* aqueous hydrochloric acid and diluting in the same manner as described above. Stock solutions of

1,2-diphenylguanidine and 1,2-diphenylacetamide were prepared by dissolving these materials in 0.009 *N* aqueous hydrochloric acid and diluting 1:10 with water to give concentrations of 7.2×10^{-4} and 3.89×10^{-4} mole l^{-1} , respectively. The final dilution to spectroscopic concentrations was done by the addition of 1.00 ml. of the above stock solution to 1.00 ml. of dioxane, followed by a final dilution to 10.00 ml. by the addition of the solvent. This gave a solution of 10% dioxane-water. The optical densities were determined at four wave lengths each on solutions of the base and acid forms of the above three compounds. These solutions were prepared by diluting the stock solutions with 0.2 *N* aqueous sodium hydroxide and 0.09 *N* aqueous hydrochloric acid, respectively. The optical densities were determined on solutions in phosphate buffers at varying pH (or pH'). These solutions were prepared by diluting 1.00 ml. of the stock solution to 10.00 ml. with 0.2 *N* phosphate buffer or by diluting 1.00 ml. of the stock solution and 1.00 ml. of dioxane to 10.00 ml. with 0.2 *N* phosphate buffer (for the cases of diphenylacetamide and diphenylguanidine). After each determination the pH or pH' (pH' being the observed pH of the aqueous dioxane solutions) was determined on the Beckman pH meter. The pH meter was standardized (25°) at 9.18 with 0.0100 *M* borax solution. The spectral determinations were done in a constant temperature room maintained at 24° ($\pm 1^\circ$). The pK_a was calculated from eq. 4.

$$pK_a \text{ or } pK_a' = \text{pH (or pH')} + \log (C_{AH^+}/C_A) \quad (4)$$

The values given in Table II all are averages of determinations at four different wave lengths in the range 255–280 $m\mu$ and at three pH values. The average deviation of each value was about 0.03 unit. A typical set of data is given in Table IV.

The pK_a' values of the anhydro bases were determined in the same manner as described above for the standards. Dioxane solutions of the individual anhydro bases were diluted 1:10 in phosphate buffer. The hydrochloric acid and sodium hydroxide solutions were stable over the period of measurement of the optical densities, but the phosphate buffer solutions decomposed quite rapidly, as was indicated by a steady drop in the optical densities. The fall in optical density was linear over the first few minutes. The stock and buffer solutions were mixed, the optical densities were then plotted over the period of the next few minutes, and the value at the time of mixing was obtained by extrapolating back to zero time.

The last series of pK_a values was determined in two nonaqueous solvents, 10% dioxane-acetonitrile and

dioxane. Three buffer systems were used: (a) triphenylguanidine-perchloric acid, (b) diphenylguanidine-perchloric acid, and (c) piperidine-perchloric acid. The preparation of these buffers has been previously described (*vide supra*). Acetonitrile and dioxane stock solutions were prepared by taking 1.00 ml. of the stock solution and 1.00 ml. of the buffer solution and diluting to 10.00 ml. with the appropriate solvent. The optical densities were also recorded for solutions containing 1.00 ml. of the stock solution and 1.00 ml. of the buffer free base. The optical densities of the anhydro base solutions at the wave lengths used were independent of the buffer base. Beer's law was checked in several of the pK_a determinations and was obeyed. In acetonitrile the anhydro base solutions were stable over at least several hours while in dioxane some decomposition was noted with the fluorenylidene compounds **23** and **24a**. The pK_a values for these accordingly were determined by extrapolation as described above. Attempts to determine the pK_a of the benzhydrylidene compounds **19** and **20** failed because of rapid decomposition in the buffer solutions. It was also found that the fluorenylidene compounds **23** and **24a** decomposed slowly in buffered solutions. This necessitated the rapid measurement of the optical densities and extrapolation back to zero time. The nature of the difficulty is not clear, but in any case it is not common to alkylpyridinium salts in general, since the spectrum of 1-methylpyridinium perchlorate was not significantly changed under the conditions used with **23** and **24a**.

Ultraviolet-Visible Absorption Spectra. All electronic absorption spectra were measured on a Cary Model 14 recording spectrophotometer. Samples were prepared in 10.0-ml. volumetric flasks and diluted to the appropriate concentration with purified solvents. The spectra were measured in 1.00-cm. square quartz cells (Beckman). A preliminary base line was determined for each spectrum. The optical density and peak position were recorded at a scan rate of 5 $\text{\AA}/\text{sec}$.

The oscillator strength (f) was computed by graphical integration of the band envelope from the relationship

$$f = 4.31 \times 10^{-9} \int \epsilon d\nu$$

where the integral is evaluated by the area under the band envelope on a plot of molar extinction coefficient (ϵ) vs. frequency in cm^{-1} (ν). In those situations in which two maxima were present in the same band envelope, the whole envelope was integrated and the components were separated visually by assuming an approximate gaussian distribution. The literature values were estimated from the band width at one-half the ϵ_{max} .