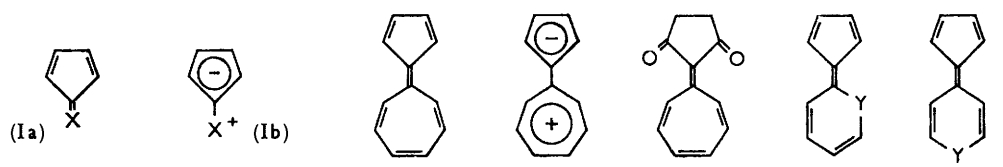
86. *Heterocyclic Analogues of Cyclopentadienylidenecyclo-heptatriene.*

By G. V. Boyd and L. M. Jackman.

A number of 4-cyclopentadienylidene-pyrans and -dihydropyridines related to cyclopentadienylidenecycloheptatriene have been synthesised. The nuclear magnetic resonance and electronic spectra of the pyridine bases and their conjugate acids have been determined. The site of protonation is discussed.

The aromaticity of the cyclopentadienide anion accounts for the existence and stability of many cyclopentadiene derivatives (I) containing an electron-donating atom or group X. The fulvenes (X = C<), diazocyclopentadiene [1] (X = N_2), cyclopentadienylidene-triphenylphosphorane [2] (X = PPh_3), and 9-dimethylsulphonium fluorenide [3] are resonance hybrids of the covalent form (Ia) and the dipolar aromatic form (Ib); the covalent structure of the last-mentioned compounds involves the *d*-orbitals of phosphorus and sulphur. Trimethylammonium [4] and 1-pyridinium cyclopentadienide [5] are aromatic betaines (Ib; X = $^-$N<). An interesting compound of this type is cyclopentadienylidenecycloheptatriene, "sesquifulvalene" [6] (II), first considered by Brown [7] and Tinker.[8] Molecular orbital calculations by Pullman and his colleagues [9] predict a large contribution of the dipolar canonical form (IIb) which consists of the aromatic cyclopentadienide and tropylium ions.* Sesquifulvalene has not yet been synthesised, but a tetrabenzo-derivative is known.[9] Recently, Prinzbach reported the synthesis of tetraphenylcyclopentadienylidenecycloheptatriene [10a] and 3-benzyl-1-indenylidenecycloheptatriene.[10b] Sesquifulvalene does not appear to be highly stabilised, since Kitahara *et al.*[11] found that derivatives of the diketone (III) did not exist in the di-enolic form.



The heterocyclic systems (IV) and (V) (Y = >NR, O, or S) are expected to show some similarity to sesquifulvalene with which they are iso-π-electronic. This paper describes several compounds of type (V).

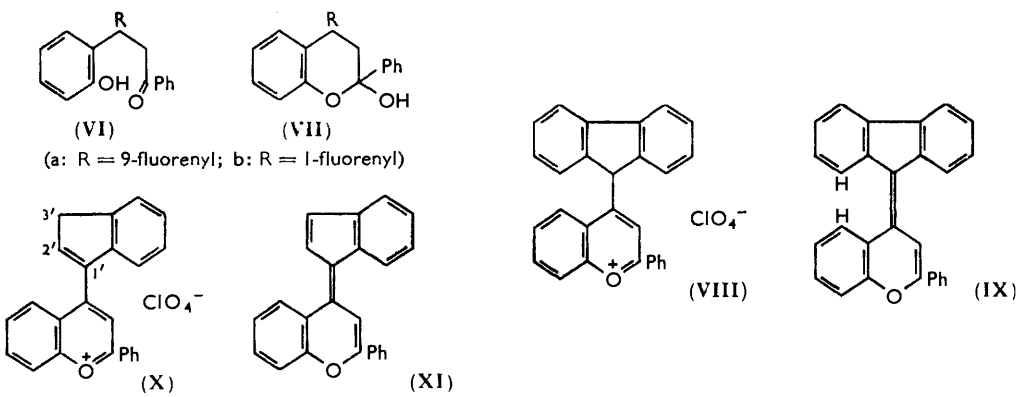
At the beginning of this work only two simple such compounds were known, namely the 4-cyclopentadienylidenedihydropyridines (V; Y = >N·CH_2·$C_6H_3Cl_2$-2,6) [12] and

* These calculations employ simple Hückel orbitals and it is probable that the self-consistent field method would predict a substantially lower degree of charge separation.

[1] Doering and dePuy, *J. Amer. Chem. Soc.*, 1953, **75**, 5955.
[2] Ramirez and Levy, *J. Org. Chem.*, 1956, **21**, 488.
[3] Ingold and Jessop, *J.*, 1930, 713.
[4] Spooncer, *Diss. Abs.*, 1956, **16**, 458.
[5] Lloyd and Sneezum, *Tetrahedron*, 1958, **3**, 334.
[6] Doering, in I.U.P.A.C. Kekulé Symposium, Butterworths, London, 1958, p. 35.
[7] Brown, *Trans. Faraday Soc.*, 1949, **45**, 296; 1950, **46**, 146.
[8] Tinker, *J. Chem. Phys.*, 1951, **19**, 981.
[9] Pullman, Pullman, Bergmann, Berthod, Fischer, Hirshberg, Lavie, and Mayot, *Bull. Soc. chim. France*, 1952, **19**, 73.
[10] (*a*) Prinzbach, *Angew. Chem.*, 1961, **73**, 169; (*b*) Prinzbach and Seip, *ibid.*, 169.
[11] Kitahara, Murata, and Asano, *Bull. Chem. Soc. Japan*, 1961, **34**, 589.
[12] Kröhnke, Ellegast, and Bertram, *Annalen*, 1956, **600**, 176.

(V; Y = >N·CH_2Ph),[13a,b] both made by the dehydrogenative addition of cyclopentadiene to the appropriate pyridinium salt. The orientation of the benzyl compound has been established by degradation [13c] and by an unambiguous synthesis [14a] from sodium cyclopentadienide and 1-benzyl-4-bromopyridinium bromide. Essentially the same method was used by one of us [15] to prepare a number of derivatives of the dihydropyridine (V; Y = >NR) (see below). In the 2-pyridine series, the parent compound (IV; Y = >NMe) [14b] and a number of polycyclic derivatives have recently been reported.[14c,16] No representatives of the oxygen and the sulphur system (IV; Y = O or S) are known, but several 4-9′-fluorenylidene-pyrans and -thiopyrans, cf. (V; Y = O or S), have been prepared.[17]

We first investigated the synthesis of pyrans (V; Y = O). The potassium hydroxide-catalysed addition of fluorene to salicylideneacetophenone in pyridine [18] afforded a colourless adduct which gave no colour with ferric chloride, was insoluble in aqueous alkali, and did not react with 2,4-dinitrophenylhydrazine under the usual conditions. However, as previously found in analogous systems,[19–21] its intense absorption at 1670 cm.$^{-1}$ showed it to be the keto-phenol (VIa) rather than the isomeric hemiketal (VIIa). Perchloric acid [22] converted the adduct into the flavylium perchlorate (VIII) which lost the elements of perchloric acid on treatment with cold aqueous sodium carbonate or warm water to yield the deep purple 4-9′-fluorenylideneflav-2-ene (IX). Addition of perchloric acid regenerated the salt. When the fluorene adduct (VIIa) was boiled for a short time with chloranil in xylene it underwent cyclisation, dehydration, and dehydrogenation and gave the flavene quantitatively. This compound (IX) cannot be planar because of the severe steric clash of the hydrogen atoms marked in the formula.



In the indene series, the adduct (VIb) was easily obtained from indene and salicylideneacetophenone. Conversion into the flavylium salt (X) with perchloric acid was unsatisfactory and irreproducible: the yield in some thirty experiments varied from 5 to 0%.

[13] (*a*) Kursanov, Baranetskaya, and Setkina, *Doklady Akad. Nauk. S.S.S.R.*, 1957, **113**, 116; (*b*) Kursanov and Baranetskaya, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1958, 362; (*c*) *ibid.*, 1961, 1703.

[14] (*a*) Berson and Evleth, *Chem. and Ind.*, 1961, 1362; (*b*) Berson, Evleth, and Hamlet, *J. Amer. Chem. Soc.*, 1960, **82**, 3793; (*c*) Berson and Evleth, *Chem. and Ind.*, 1959, 901.

[15] Boyd, *Proc. Chem. Soc.*, 1960, 253.

[16] Meerwein, Florian, Schön, and Stopp, *Annalen*, 1961, **641**, 19.

[17] (*a*) Schönberg, Elkaschef, Nosseir, and Sidky, *J. Amer. Chem. Soc.*, 1958, **80**, 6312; (*b*) Schönberg and Sidky, *ibid.*, 1959, **81**, 2259.

[18] Pinck and Hilbert, *J. Amer. Chem. Soc.*, 1946, **68**, 2014.

[19] Löwenbein, Pongrácz, and Spiess, *Ber.*, 1924, **57**, 1517.

[20] Geissman, *J. Amer. Chem. Soc.*, 1940, **62**, 1363.

[21] Hall and Howe, *J.*, 1959, 2886.

[22] Allen and Sallans, *Canad. J. Res.*, 1933, **9**, 578.

Ferric chloride, a common reagent for pyrylium syntheses, failed completely. The indenylflavylium salt is assigned the more conjugated 3′*H*-structure (X) in preference to the less conjugated tautomeric 1′*H*-structure by analogy with the corresponding pyridinium salts (see below).

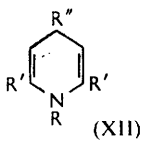
The flavylium perchlorate (X) afforded the red anhydro-base (XI) [23] on treatment with base; perchloric acid regenerated the salt. Scale models of the anhydro-base indicate that the *trans*-form (XI) can achieve coplanarity, and this configuration is assigned to it. The base was chromatographically homogeneous; there was no evidence for the existence of the overcrowded *cis*-form.

Attempts to cyclise and dehydrogenate the ketone (VIb) to the flavene directly failed with chloranil, lead tetra-acetate, sulphur, selenium, and palladium. The ketone lost one molecule of water in boiling benzene in the presence of a catalytic amount of oxalic acid; but the resulting 4-1′-indenylflav-2-ene could not be dehydrogenated with these reagents, or with iodine or triphenylmethyl perchlorate.[24] The flavenes (IX) and (XI) could not be obtained from flavone and fluorenyl-lithium and indenylmagnesium bromide, respectively.

Both flavenes are stable in air; they resist alkaline hydrolysis and the action of boiling acetic acid. They dissolve in mineral acids to give yellow solutions of the flavylium salts.

The difficulties encountered in the synthesis of the indenylflavylium perchlorate discouraged us from attempting the preparation of the Michael adduct of cyclopentadiene and salicylideneacetophenone and submitting it to the action of acidic oxidising agents; but experiments designed to produce 4-cyclopentadienylidenepyrans (V; Y = O) under neutral or alkaline conditions from precursors in the proper oxidation state were unsuccessful. The action of Grignard reagents on 2,6-dimethyl-4-pyrone [25] and xanthone [26] results, ultimately, in the formation of pyrylium salts. However no basic products could be isolated from the attempted reaction of metal cyclopentadienides with these pyrones, or with flavone. Potassium cyclopentadienide attacked 4-methoxy-2,6-dimethylpyrylium perchlorate at C-2 to afford 6-methoxy-4,8-dimethylazulene [27] rather than at C-4 to give the desired pyran.

However, this type of reaction was successfully applied to analogous pyridinium salts, which are less prone to ring-opening, affording 4-cyclopentadienylidene-1,4-dihydropyridines in high yields (Table 1).



(XII)

a: R = R′ = Me; R″ = cyclopentadienylidene
b: R = R′ = Me; R″ = 1-indenylidene
c: R = R′ = Me; R″ = 9-fluorenylidene
d: R = Bu^n; R′ = Me; R″ = cyclopentadienylidene
e: R = Bu^n; R′ = Me; R″ = 1-indenylidene
f: R = Bu^n; R′ = Me; R″ = 9-fluorenylidene
g: R = Me; R′ = H; R″ = cyclopentadienylidene
h: R = Me; R′ = H; R″ = 1-indenylidene
i: R = Me; R′ = H; R″ = 9-fluorenylidene

Fluorene condensed with 4-methoxy-1,2,6-trimethylpyridinium iodide in t-butyl alcohol in the presence of potassium t-butoxide to give the orange anhydro-base (XIIc) in 32% yield. Orange anhydro-bases were also obtained under these conditions from cyclopentadiene and indene and the above pyridinium salt. The unsubstituted anhydro-bases (XIIg) [14a] and (XIIh) could not be prepared from 1-methyl-4-phenoxypyridinium iodide; dark intractable tars resulted. However, 4-9′-fluorenylidene-1,4-dihydro-1-methylpyridine (XIIi) was readily isolated.

The structure of the products follows from the method of synthesis, analysis, the proton magnetic resonance spectra of the corresponding *N*-butyl compounds (see below),

[23] Boyd, *Proc. Chem. Soc.*, 1959, 93.
[24] Reid, *J.*, 1959, 2773.
[25] Baeyer and Piccard, *Annalen*, 1911, **384**, 208.
[26] Bünzly and Decker, *Ber.*, 1904, **37**, 2933.
[27] Hafner and Kaiser, *Annalen*, 1958, **618**, 140.

TABLE 1.

Condensation of 4-pyridinium ethers with cyclopentadiene hydrocarbons.

Pyridinium iodide	Hydrocarbon	Product	M. p.
4-Methoxy-1,2,6-trimethyl-	Cyclopentadiene	(XIIa) [a]	>170° (decomp.)
,,	Indene	(XIIb) [b]	>200 (decomp.)
,,	Fluorene	(XIIc) [c]	>220 (decomp.)
1-Butyl-4-methoxy-2,6-dimethyl-	Cyclopentadiene	(XIId) [d]	160—161 (decomp.) [e]
,,	Indene	(XIIe)	162·5—163 (decomp.) [e]
,,	Fluorene	(XIIf)	182 (decomp.) [e]
1-Methyl-4-phenoxy-	Cyclopentadiene	(XIIg) [f]	—
,,	Indene	(XIIh) [f]	—
,,	Fluorene	(XIIi)	178·5—179 [g]

			Found (%)				Required (%)		
Product	Colour	Yield (%)	C	H	N	Formula	C	H	N
(XIIa) [a]	Yellow	75	—	—	7·3	$C_{13}H_{15}N$	—	—	7·55
(XIIb) [b]	Orange	84	86·45	7·3	5·7	$C_{17}H_{17}N$	86·75	7·3	5·95
(XIIc) [c]	Orange	81	88·1	6·8	5·0	$C_{21}H_{19}N$	88·35	6·7	4·9
(XIId) [d]	Yellow	90	84·75	9·35	6·0	$C_{16}H_{21}N$	84·5	9·35	6·2
(XIIe)	Orange	86	86·5	8·4	5·2	$C_{20}H_{23}N$	86·6	8·35	5·05
(XIIf)	Red	85	88·0	7·8	4·1	$C_{24}H_{25}N$	88·0	7·7	4·3
(XIIg) [f]	—	—	—	—	—	—	—	—	—
(XIIh) [f]	—	—	—	—	—	—	—	—	—
(XIIi)	Red	80	88·4	5·95	5·75	$C_{19}H_{15}N$	88·7	5·9	5·45

[a] *Picrate*, yellow, m. p. 148—148·5° (decomp.) (from aqueous acetic acid) (Found: C, 55·1; H, 4·6; N, 13·45. $C_{19}H_{18}N_4O_7$ requires C, 55·05; H, 4·4; N, 13·5%). [b] *Perchlorate*, colourless, m. p. 226·5—228° (from acetone–acetic acid) (Found: C, 60·55; H, 5·5; N, 4·3. $C_{17}H_{16}ClNO_4$ requires C, 60·8; H, 5·4; N, 4·15%). [c] *Perchlorate*, colourless, m. p. 218—219° (from acetic acid) (Found: C, 65·65; H, 5·5; N, 3·3. $C_{21}H_{20}ClNO_4$ requires C, 65·35; H, 5·25; N, 3·65%). [d] *Perchlorate*, colourless, m. p. >127° (decomp.) (from acetic acid) (Found: C, 58·35; H, 6·55; N, 4·0. $C_{16}H_{22}ClNO_4$ requires C, 58·6; H, 6·8; N, 4·25%). [e] From aqueous acetone. [f] Not isolated. [g] From benzene.

and their behaviour as anhydro-bases; they dissolve in acids to give colourless solutions containing the derived pyridinium ions and are regenerated on basification.

The trimethyl-bases (XIIa, b, c) charred when heated and could not be recrystallised; they were characterised as crystalline salts. The indenylidene and fluorenylidene compounds are stable as solids but decompose slowly in solution; the cyclopentadienylidene compound could be kept for only a few hours, even in a nitrogen atmosphere. The low solubilities of the *N*-methyl compounds precluded determination of their nuclear magnetic resonance spectra; we therefore prepared the corresponding *N*-butyl bases (XIId, e, f), which were readily soluble in organic solvents, and, unexpectedly, much more stable than the *N*-methyl analogues. Their proton magnetic resonance spectra (Table 2) confirm the assigned structures.

TABLE 2.

The chemical shifts (τ-values) of protons of compounds (XII).

	2(6)-Me	*N*-CH_2	3(5)-H	R″
(XIId)	7·83	6·49	3·35	3·84, 3·62 [a]
(XIIe)	8·08	7·07	3·47, 2·99 [b]	3·5—2·4 [c]
(XIIf)	8·09	7·01	3·02	3·0—2·0 [c]

[a] A_2B_2 system. [b] The 2·99 signal arises from the proton on the same side as the benzene ring of the indenylidene residue. [c] Complex band.

The spectrum of compound (XIId) is particularly simple and shows that the molecule possesses an axis of symmetry. Thus the resonances of the 2- and the 6-methyl group and of the 3- and the 5-proton are coincident. Furthermore, the four protons of the five-membered ring absorb as an A_2B_2 system. The same symmetry (C_{2v}) applies to compound (XIIf) and is reflected by its spectrum, although the absorptions of the fluorenylidene protons are too complex to analyse. The indenylidene derivative (XIIe) is unsymmetrical,

and the chemical shifts of the 3- and the 5-proton are quite different since one of them is close to, and in the plane of, the benzene ring, and is accordingly deshielded. The chemical shifts of the *N*-methylene groups, 3(5)-protons, and the 2(6)-methyl groups indicate that the pyridine ring in these structures is not highly aromatic.[28] A quantitative investigation of aromaticity in these and related systems will be reported later.

TABLE 3.

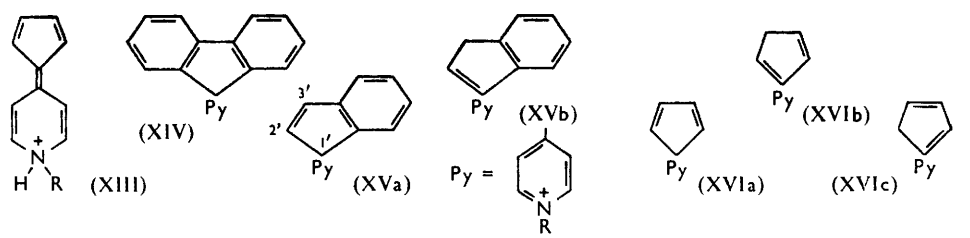
Electronic spectra of 4-cyclopentadienylidene-1,4-dihydropyridines and their conjugate acids.

Compound	Solvent	$\lambda_{max.}$ (mμ) and log ε (in parentheses)	
(XIId)	Dioxan	242 (3·96)	335 (3·58)
		428 (4·69)	440 * (4·68)
,,	Ethanol + $HClO_4$	249 (3·65)	300 * (3·88)
		348 (4·40)	
(XIIe)	Dioxan	294 (4·00)	458 (4·62)
		480 * (4·53)	
,,	Ethanol + $HClO_4$	246 (4·33)	288 (3·85)
		325 (3·74)	
(XIIf) †	Dioxan	252 (4·54)	258 (4·47)
		296 (3·87)	448 (4·45)
		468 (4·51)	
,,	Ethanol + $HClO_4$	266 (4·43)	302 (3·82)
Equimolecular mixture of fluorene and 1,2,4,6-tetramethylpyridinium perchlorate	Ethanol	264 (4·43)	300 (3·99)

* Inflexion. † The spectrum of compound (XIIi) is virtually the same.

The electronic spectra of the three *N*-butyl-bases (Table 3) show that anellation of the cyclopentadiene ring produces a bathochromic shift in the long-wavelength maximum (the indene compound has an inflexion beyond the absorption maximum of the fluorene compound). Berson's [14b] 2-cyclopentadienylidenedihydro-1-methylpyridines (IV; Y = >NMe) absorb in the same sequence, and so do arylfulvenes.[29] The opposite effect of anellation is observed in simple alkylfulvenes and is predicted for the series: fulvene, benzofulvene, dibenzofulvene.[29]

The Protonated Bases.—All the dihydropyridines give colourless solutions in acids, including acetic acid, from which they are regenerated on basification. The lack of visible-light absorption by the acidic solutions requires the bases to be protonated on the five-membered ring, since a cation such as (XIII) represents a fulvene and would be coloured. Indeed, the isolated perchlorates of (XIIb), (XIIc), and (XIId), and the picrate of (XIIa) have no infrared absorption in the >NH^+ region.



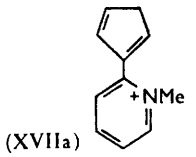
In the case of the fluorenylidene compounds only the 9'-position is a likely site of protonation (XIV), and this was confirmed spectroscopically for the *N*-butyl base (XIIf). The ultraviolet spectrum of a solution of this compound in ethanol containing perchloric acid is almost superimposable on that of an equimolecular mixture of fluorene and 1,2,4,6-tetramethylpyridinium perchlorate (Table 3). The protonated indenylidene compounds

[28] Elvidge and Jackman, *J.*, 1961, 859.
[29] Bergmann, *Progr. Org. Chem.*, 1955, **3**, 102, 103.

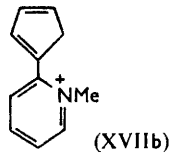
may reasonably be represented as (XVa) or (XVb); protonation at position 2′ would involve an *o*-quinonoid form. Since the long-wave absorption band in the spectrum of the perchlorate of the base (XIIe) at 325 mμ is situated beyond that of either tetramethylpyridinium perchlorate (270 mμ) or indene (292 mμ),[30] the cation must possess more extended conjugation than is expressed in the formula (XVa) and we therefore prefer structure (XVb).

For the protonated cyclopentadienylidene compounds the three tautomeric forms (XVIa), (XVIb), and (XVIc) must be considered. Of these, form (XVIc) is the most conjugated and this structure was originally assigned to the cation since there is a bathochromic shift of 23 mμ in the ultraviolet absorption maximum between the perchlorate of the indene base (XIIe) and that of the cyclopentadiene base (XIId). The extended conjugated structure (XVIc) accounts better for this shift than the cross-conjugated structure (XVIb). However, examination of the nuclear magnetic resonance spectrum of 1-butyl-4-cyclopentadienylidene-1,4-dihydro-2,6-dimethylpyridine perchlorate in trifluoroacetic acid indicates the presence of at least two conjugate acids. The methylene protons of one of these give rise to absorption at τ 6·47 which is equivalent to 0·7 of a proton or a proportion of 35% of the corresponding conjugate acid. The analogous absorption of the other protonated species is assumed to be part of a complex band near τ 7·1, which is equivalent to 7·3 protons, six of which are the protons of the 2- and 6-methyl groups. These observations are similar in many respects to those of Berson and Evleth [14a] for the protonated 2-cyclopentadienylidene-1,2-dihydro-1-methylpyridine (IV; Y = >NMe).

The question now arises as to the structures of the conjugate acids in both the 2- and the 4-cyclopentadienylidene series. In the 2-series, Berson [14a] observed two signals assignable to the methylene protons of the five-membered ring. That at higher field (τ 6·78) was approximately half as intense as the low-field (6·48) band and was attributed to 32% of the conjugate acid (XVIIa) on the grounds that the methylene group in (XVIIb) would be preferentially deshielded by the ring current in the pyridine ring. In the 4-series, it is evident from the above results that the methylene absorption of the minor constituent [only two conjugate acids (XVIb) and (XVIc) being assumed to exist] is at a lower field than that of its tautomer. This difference in behaviour can be attributed either to different proportions of conjugated and cross-conjugated tautomers in the two series or to different shielding considerations in the two systems. We believe that it is difficult to assign structures to the conjugate acids on the basis of the chemical shifts of



(XVIIa)



(XVIIb)

their methylene protons. Thus, in the 2-series the *N*-methyl group will force the five-membered ring out of the plane of the pyridine ring to an unknown extent, so that the shielding contribution of the latter cannot be predicted. Furthermore, the local diamagnetic shielding of the methylene protons will be influenced by the charge distribution in the five-membered ring in a way which cannot yet be assessed for any of the conjugate acids discussed. The methylene protons of the conjugate acid (XVIIb) could be deshielded by the positive pole on nitrogen, which it can approach closely. Finally, in neither series has it been established that the bases are reversibly protonated under the conditions employed. Further study of the structures of these conjugate acids is in progress.

[30] Morton and de Gouveia, *J.*, 1934, 911.

Experimental

Nuclear magnetic resonance spectra were determined at 56·4 Mc./sec. with a Varian V 4300 and A 60 spectrometer. The free bases were examined in deuterochloroform, tetramethylsilane (0·5%) being used as internal reference.

ω-9′-*Fluorenyl*-ω-o-*hydroxyphenylpropiophenone* (VIa).—A solution of fluorene (36·1 g.) and salicylidenacetophenone (42·4 g.) in pyridine (200 ml.) was treated with a solution of potassium hydroxide (36 g.) in water (24 ml.). When the initial red precipitate had disappeared (6—8 days), the mixture was poured into dilute hydrochloric acid, and the resulting solid was filtered off and dissolved in a hot solution of potassium hydroxide (16 g.) in methanol (300 ml.). The cooled, filtered, solution was acidified with acetic acid, and the precipitated *propiophenone* recrystallised from benzene; it had m. p. 165·5—166·5° (48 g., 65%) (Found: C, 86·1; H, 5·8. $C_{28}H_{22}O_2$ requires C, 86·1; H, 5·7%), and exhibited a band at 1670 cm.$^{-1}$ (Nujol).

4-9′-*Fluorenylflavylium Perchlorate* (VIII).—An ice-cold solution of the above adduct (1·95 g.) in ether (20 ml.) and acetic anhydride (10 ml.) was slowly treated with 72% perchloric acid (1·6 ml.) and then left overnight. The orange *perchlorate* (0·63 g., 26·8%), m. p. 241—242° (decomp.), separated (Found: C, 71·2; H, 4·3. $C_{28}H_{19}ClO_5$ requires C, 71·4; H, 4·1%).

4-9′-*Fluorenylideneflav*-2-*ene* (IX).—(*a*) The above perchlorate (0·32 g.) was stirred with aqueous sodium carbonate; the resulting *flavene* (0·20 g., 82%) crystallised from ethanol–acetone as nearly black prisms with a green reflex, m. p. 162·5—163·5° (Found: C, 90·85; H, 4·95. $C_{28}H_{18}O$ requires C, 90·75; H, 4·9%); $\lambda_{max.}$ (in cyclohexane), 254 (4·74), 314 (infl.) (4·20), 474 mμ (log ε 4·42).

(*b*) ω-9′-Fluorenyl-ω-*o*-hydroxyphenylpropiophenone (9·2 g.) and chloranil (5·8 g., 1 mol.) in xylene (100 ml.) were heated under reflux for 20 min. The solution was cooled, filtered from the precipitated tetrachloroquinol, and washed with 5% aqueous sodium hydroxide. The solvent was removed in steam, and the residue (8·6 g., 98·5%), after recrystallisation, had m. p. and mixed m. p. 162·5—163·5°. A solution of the flavene in chloroform–ether deposited 4-9′-fluorenylflavylium perchlorate on treatment with 72% perchloric acid.

ω-1′-*Indenyl*-ω-o-*hydroxyphenylpropiophenone* (VIb).—Sodium hydroxide (31 g.) in water (31 ml.) was added to a solution of freshly distilled indene (64 g.) and salicylideneacetophenone (62 g.) in pyridine (140 ml.). After 16 hr. at room temperature the mixture was poured into dilute hydrochloric acid. The resulting moist semi-solid was dissolved in hot benzene (400 ml.), the lower aqueous layer was run off, and the benzene solution was dried and concentrated by distilling off 200 ml. On cooling, the *hydroxy-ketone* (68·4 g., 72·7%) crystallised, m. p. 149—149·5° (from benzene) (C=O band at 1670 cm.$^{-1}$ in Nujol) (Found: C, 84·8; H, 5·8. $C_{24}H_{20}O_2$ requires C, 84·7; H, 5·9%).

4-3′-*Indenylflavylium Perchlorate* (X).—The foregoing adduct (5·1 g.) in ether (40 ml.) and acetic anhydride (30 ml.) was treated at 0° with 72% perchloric acid (5 ml.). When kept in the refrigerator overnight, the dark solution deposited the brown *perchlorate* (0·70 g., 11·1%) which did not melt below 300°. The analytical specimen (yellow) was obtained by adding perchloric acid to a chloroform–ether solution of the indenylideneflavene described below (Found: C, 68·4; H, 4·2. $C_{24}H_{17}ClO_5$ requires C, 68·5; H, 4·1%). This was the most successful preparation of the flavylium salt; in numerous other runs the yield never exceeded 5%.

4-1′-*Indenylideneflav*-2-*ene* (XI).—This was obtained by treating the above salt with warm water; *the product* formed red needles (from acetone), m. p. 157·5° (Found: C, 90·3; H, 5·25. $C_{24}H_{16}O$ requires C, 90·0; H, 5·05%); $\lambda_{max.}$ (in cyclohexane), 234 (4·45); 268 (4·23); 296 (4·56); 345 (3·97); 360 (3·81); 442 (3·89); 450 mμ (log ε 3·89).

1-*Butyl*-4-*methoxy*-2,6-*dimethylpyridinium Perchlorate*.—4-Methoxy-2,6-dimethylpyrylium perchlorate [25] (88·6 g.) was added to a solution of butylamine (108·5 g., 4 mol.) in acetic acid (210 ml.); the mixture was heated under reflux for 1 hr., cooled, and treated with ether to turbidity; the *salt* crystallised (59·3 g., 54·3%) as flat prisms (from methanol–ether), m. p. 99—99·5° (Found: C, 49·1; H, 6·85; N, 4·65. $C_{12}H_{20}ClNO_5$ requires C, 49·05; H, 6·9; N, 4·75%). It was converted into the *iodide*, plates (from methanol–ether), m. p. 119—120° (Found: C, 45·1; H, 6·05; N, 4·1. $C_{12}H_{20}INO$ requires C, 44·85; H, 6·3; N, 4·35%) by adding the calculated amount of methanolic potassium iodide to its solution in methanol, filtering, concentrating, and adding ether.

The *pyridine anhydro-bases* (XII) (Table 1) separated when the appropriate pyridinium salt

was added to a solution of a cyclopentadiene hydrocarbon in t-butyl alcohol in the presence of potassium t-butoxide. A typical preparation is described:

1-*Butyl*-4-*cyclopentadienylidene*-1,4-*dihydro*-2,6-*dimethylpyridine* (XIId).—A solution prepared from potassium (8·35 g.) and t-butyl alcohol (550 ml.) was stirred in an atmosphere of nitrogen, and cyclopentadiene (28 g.) was added, followed by 1-butyl-4-methoxy-2,6-dimethylpyridinium iodide (68·7 g., 1 mol.). Stirring was continued for 30 min. The dihydropyridine (43·74 g., 90%) was collected and washed with water; it formed red crystals, m. p. 154·5—157°. A portion was dissolved in cold acetone, and water was added to incipient cloudiness; the base crystallised as golden-yellow needles, m. p. 160—161° (decomp.) with previous darkening.

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