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STUDIES ON THE 1*H*-1-PYRINDINE SYSTEM[1]

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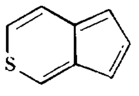
Abstract—The NMR spectrum of 1-pyrindine (3) indicates the presence of the 5*H* and 7*H* tautomers in solution. Reaction of 3 with methyl iodide followed by extractive basification afforded mainly a dimeric species (**10**) plus a small amount of the new 1-methyl-1*H*-1-pyrindine (**5**). Similar treatment of a methochloride obtained from 3, however gave 40% of 5, and this was formed also in low yield from the reaction of the conjugate base of 1-pyrindine with methyl iodide, or of the conjugate acid of 1-pyrindine with diazomethane. The UV and visible absorption of **5** are very similar to those of analogous heteroanalogs of azulene and confirm the presence of the 1*H*-tautomer in pure 3. The properties and possible structures of the intermediate methiodide and methochloride compounds formed from 3 are discussed.

THE FINDING[3,4] that the pi-excessive heteroanalogs of azulene, cyclopenta[c]-thiapyran (**1**) and 2-phenyl-2-pyrindine (**2**) showed a marked resemblance to the parent non-alternant hydrocarbon, including characteristic absorption in the visible region, let to the postulation[3] that the colour of freshly distilled 1-pyrindine (**3**) observed by Robinson[5] was due to the presence of the 1*H*-tautomer (**3c**). As a part of our research in this area, efforts to achieve the otherwise unknown 1*H*-1-pyrindine structure were subsequently initiated.



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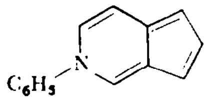

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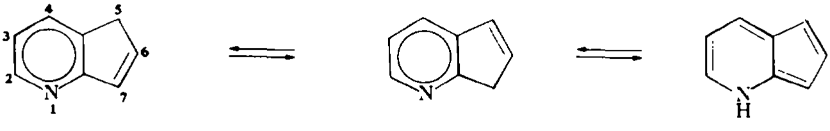

3a **3b** **3c**

The IR and NMR spectra of 1-pyrindine (assumed to be a mixture of **3a** and **3b**[5]) have been discussed in a previous communication[6] and are consistent with the postulated presence of the tautomer **3c**. An UV spectrum, which has appreciably more detail

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[3] A. G. Anderson, Jr., W. F. Harrison, R. G. Anderson and A. G. Osborne, *J. Am. Chem. Soc.* **81**, 1255 (1959).

[4] A. G. Anderson, Jr., W. F. Harrison and R. G. Anderson, *J. Am. Chem. Soc.* **85**, 3448 (1963); A. G. Anderson, Jr., and W. F. Harrison, *J. Am. Chem. Soc.* **86**, 708 (1964).

[5] M. M. Robison, *J. Am. Chem. Soc.* **80**, 6254 (1958).

than that originally reported by Robinson[5] was obtained; the spectrum of the conjugate acid, which proved to be more important to the present study, is given in Fig. 1.

A route to the desired 1-methyl-1*H*-1-pyrindine (**5**) which seemed simple and straightforward, the quaternization of 1-pyrindine to form salt (**4**) and subsequent reaction of this with base, was the first studied.[7] Robison and Robison[9] had found that the methotosylate of 7-azaindole could be purified readily whereas the methiodide could not and, in the present work, it was observed that the product from the reaction of 1-pyrindane (6,7-dihydro-5*H* or 5,6-dihydro-7*H*-1-pyrindine) and methyl iodide decomposed extensively on attempted recrystallization. Treatment of 1-pyrindine with methyl tosylate, however, gave an ether insoluble, water soluble, orange gum which could not be crystallized. The addition of base to an aqueous solution of the gum yielded a very small amount of an unstable orange–red oil. The UV and visible spectra of this product were qualitatively the same as those found later for **5**.[6] The

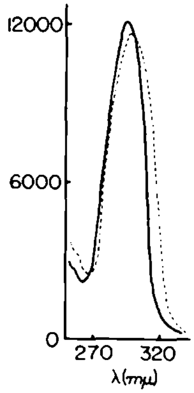

FIG. 1 UV spectra of 1-pyrindine (——) and 1-methyl-1*H*-1-pyrindine (---) in methanol made acidic (0·005N) with hydroiodic acid.

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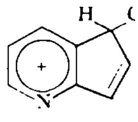
[6] A. G. Anderson, Jr., and H. L. Ammon, *Tetrahedron Letters* 2579 (1966).

[7] The possibility of quaternization of the 1*H*-isomer (**3c**) to give the tautomeric ions **6** and/or **7** was considered, but the small amount of **3c** indicated to be present made it seem unlikely that appreciable quantities of these products would be formed. Subsequent conversion of the methiodide, in good yield, to a compound (**10**, $X = I$) of known structure[8] served to verify that quaternization had occurred extensively on nitrogen.



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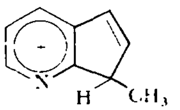

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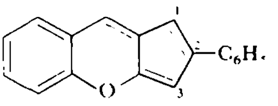


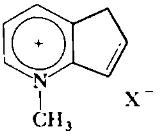
8

For convenience, only one tautomeric structure is shown for **4**, **6**, **7**, etc. G. V. Boyd and A. W. Ellis (*J. Chem. Soc.* [*B*], 349 (1966)) have found the position of protonation of **8** to be C(1) and have calculated that protonation of 1*H*-1-pyrindine (**3c**) would occur at C(5).

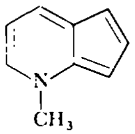
[8] H. L. Ammon and L. H. Jensen, *J. Am. Chem. Soc.* **88**, 681 (1966).

[9] M. M. Robison and B. L. Robison, *J. Am. Chem. Soc.* **77**, 6554 (1955).

inability to purify the methotosylate and the low yield of the oil product led to the trial of methyl iodide. From the latter and 1-pyrindine was obtained a tan solid, having the expected composition, which formed stable solutions in acetonitrile and could be purified from this solvent.[6, 10] This substance reacted slowly with even weakly basic solvents. Thus the UV spectrum in methanol was originally quite similar to that in water but changed markedly with time and absorption in the visible appeared.[11]



4a, X = I
4b, X = Cl



5

The addition of sodium carbonate to an aqueous solution of the methiodide with simultaneous extraction with dichloromethane afforded a purple, crystalline substance (78%) and a very small quantity of an unstable red oil. Efforts to increase the yield of the latter, which had properties more like those expected for **5** and was subsequently found to be this compound, were unsuccessful. The crystalline material was shown by X-ray diffraction to have a molecular weight of 386·4, and the elemental analysis plus a complete structure determination by X-ray[8] have established the formula for this compound as **10** ($X = I$).

These results with the methiodide led to the preparation by ion exchange of the corresponding methochloride. In contrast to the reaction with the methiodide, basification of an aqueous solution of the latter with simultaneous extraction at 0° under an inert atmosphere gave no dimeric product but 40% of **5** as a deep red oil which was stable at −70° under nitrogen but unstable at higher temperatures and quite unstable in the presence of oxygen. The spectra of **5** were qualitatively like those of the small quantities of material previously obtained from the methotosylate and from the methiodide. A less pure sample was also isolated from the reaction of 1-pyrindinium fluoroborate with diazomethane. The identity of the red oil was consistent with the elemental analysis of a stable picrate, neutralization equivalent and its the UV and visible spectra,[6] which were strikingly similar to those of the analogous cyclopenta[c]thiapyran[4] and 1-methyl-7-aza-1*H*-1-pyrindine[9] structures. The IR spectrum showed no absorption for N–H. The NMR spectrum between 2·5 and 8 ppm (chemical shift relative to tetramethylsilane as internal standard) had area ratios corresponding to 6 hydrogens in addition to the methyl group, but was otherwise very complex. The spectrum of an acidic methanol solution (which would have the conjugate acid, **4**, as the species present) corresponded very closely to that of the structurally similar conjugate acid of 1-pyrindine in this medium (Fig. 1). That only

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[10] After the greater part of our studies had been completed, C. B. Reese, *J Am. Chem. Soc.* **84**, 3979 (1962), reported results of the same reaction, and of the conversion of an aqueous solution of the methiodide product to a solution of the corresponding chloride. He was not able to isolate and characterize the material obtained by treating the methiodide with alkali but reported the spectrum of the basified (0·1 N sodium hydroxide) solution of the chloride as that of **5** in this medium.

[11] The use of methanol for purification gave balls which formed a tan powder when crushed but had a reddish outer coating. Reese[10] reported recrystallization from methanol with no mention of color formation or other spectral change.

simple protonation of **5** and **3** has occurred was shown by the immediate regeneration of the spectra of the free bases on neutralization with base.

The visible absorption found for **5** confirms the earlier postulate that the presence (ca. 0·1%) of the 1*H*-tautomer is responsible for the orange–red colour of pure 1-pyrindine.

The observation that the spectra of the conjugate acids of **5** and **3** were very similar, as expected, brought attention to the fact that the spectrum of the methiodide formed by the reaction of **3** with methyl iodide was distinctly different (Fig. 2). The disparity between these spectra was sufficient to indicate that the methiodide in solution could not be **4a**. Further, since the spectrum of the methochloride was the same as that of the methiodide except that the absence of iodide ion absorption revealed a peak at 232 mμ,[12] the cation portions of these two salts appeared to be the same. Efforts to ascertain the structures of these species led to further studies.

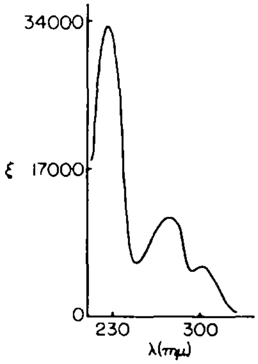

Fig. 2 UV spectrum of the methiodide in water.

In view of the formation of **10** by such a simple process under mild conditions, the properties and relationship of the methiodide, methochloride and the dimer were examined more closely. The UV and visible spectra of **10** (Fig. 3) in acetonitrile

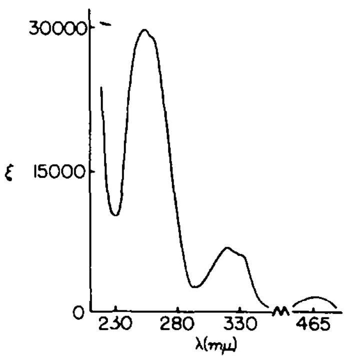

Fig. 3 UV and visible spectra of 1-methyl-6-[5-(1-methyl-1*H*-1-pyrindinyl)]-1-azoniaindane iodide (**10**) in acetonitrile.

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[12] This maximum corresponds to that observed at 235 mμ for 2-vinylpyridine by P. W. Adamson, P. A. Barrett, J. W. Billinghurst and T. S. G. Jones, *J. Chem. Soc.* 2315 (1957).

were unlike those of 1-pyrindine or the methiodide, but the spectra of **10** in dilute base were the same as those of the methiodide in this medium (Fig. 4) and the prompt acidification of the basic solution of **10** generated the spectrum of the methiodide. Also, the direct acidification of an aqueous solution of **10** gave the spectrum of the methiodide in the same solution. The spectral changes resulting from basification and then reacidification were found to be rapidly reversible for both the methiodide and **10**. The spectral behaviour of solutions of the methochloride under these conditions was found to be the same as that of the methiodide. These data strongly suggest a close structural relationship between the methiodide, the methochloride and **10**. Additional evidence to this effect was the observation that the basic solutions of methiodide and **10**, which gave the same spectra, were both unstable on standing and underwent parallel changes.

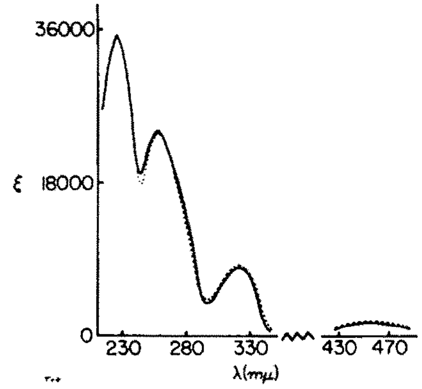
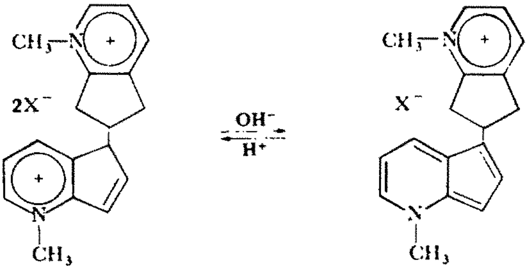


FIG. 4 UV and visible spectra of the methiodide (——) and of 1-methyl-6-[5-(1-methyl-1*H*-1-pyrindinyl)]-1-azoniaindane iodide (**10**) (- - -) in 0·01N aqueous sodium hydroxide.

The simplest interpretation which would account for these spectral correlations was that the methiodide and methochloride were also dimeric and had structure **9**. This postulate accounted for the facile interconversion of **9** and **10** *via* a simple acid–base reaction and brought the comparable extinction coefficients into agreement. The finding, mentioned earlier, that the methiodide reacted slowly with methanol and a colour was produced could be attributed to the action of methanol as a weak base.



9 **10**

It was also observed that the spectrum of **10** in water was dependent on its initial concentration; this was consistent with an equilibrium reaction of **10** with water to form **9**. The UV spectrum of the most dilute solution bore a closer resemblance to that of the methiodide. The basic portion of **10** would be the heteroaromatic ring and, since this had the structure of **5**, the basicity of this system to water was tested with the latter compound. The basicity of **5** was appreciable; its spectrum in water was distinctly shifted toward that in dilute aqueous acid, whereas the spectrum in dilute aqueous base was very similar to that in methanol. Attempts to confirm the dimeric nature of **9** by molecular weight determinations were unsuccessful. The NMR spectrum of an aqueous solution, however, had the general pattern expected from **9** and the correct area ratios. A multiplet for 6 protons in the region 8·35–8·87 ppm (chemical shift relative to 3-trimethylsilylpropanesulfonate as internal reference) was assigned to the hydrogens on the two positively charged 6-membered rings. The two vinyl protons fit a quartet of area two at 7·75 and 8·2 ppm and a singlet of unit area at 6·95 ppm was assigned to the allylic proton on the same ring. This low field portion of the spectrum was similar to those previously found for the conjugate acids of azulene and cyclopenta[c]thiapyran[4] except that the position of the allylic proton in the present case was appreciably further (2·6–3 ppm) downfield. A molecular model of **9** shows this hydrogen to be projected directly toward the positively charged ring of the other half of the dimer at an angle of about 60° to the plane of the ring. Possibly this molecular environment could account for the additional deshielding observed. The water proton was found at 4·6 ppm; two sharp singlets at 4·45 and 4·36 ppm, each representing three hydrogens, correlated with the presence of two methyl groups, each in a slightly different environment (pyridinium vs. 2-vinylpyridinium cation). The shifts observed for these pyridinium methyl hydrogens are in general agreement with those of 4·6–4·7 ppm found by Lyle and co-workers for a series of 1-methyl-pyridinium ions (which, however, had an electron withdrawing substituent at the 3-position).[13] The absorption for the remaining 5 hydrogens was assigned to a complex multiplet in the region 3·4–4·2 ppm. Values of 2·74–2·76 ppm have been found[13] for methyl in the 5-position of 3-cyanopyridinium ions. Again, the spatial orientation of the single beta hydrogen which projects at an angle toward the positively charged other portion of the molecule might account for the apparent unusual deshielding of this hydrogen.

The wavelength values for the absorption in the UV of aqueous solutions of the methiodide (and methochloride) were compared with those of compounds corresponding to the moieties of structure **9**. The position of the maximum at 275 mμ was in good agreement with those found for 1-methylpyrindanium iodide (274 mμ in methanol) and for the conjugate acids of 1-pyrindane[5] (275 mμ), 7-acetoxypyrindane[5] (273 mμ), 7-hydroxypyrindane[5] (275 mμ), and 7-methylpyrindane (276 mμ). The maximum at 302 mμ, in turn, fit with the values of 295 mμ and 297 mμ, respectively, for the structurally analogous conjugate acids of 1-pyrindine and 1-methyl-1H̲-1-pyrindine if the small difference was attributed to the presence of the substituent in the 5-position. The peak at 233 mμ observed for the methochloride also corresponded to the absorption at 231 mμ for the conjugate acid chloride of **5**. The intensities of the maxima of the methiodide and methochloride, however, did not uniformly

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[13] The authors wish to thank Prof. Robert E. Lyle for making this data (with DOH as internal standard at 4·75 ppm relative to tetramethylsilane) available to us prior to publication.

correspond to those of the analogous component monomers of known structure. Thus ε at 233 mμ was about twice as great as that for the protonated ion from **5**. The intensity (log ε 4–4·1) of the peak at 275 mμ was explicable since it would contain components of log ε 3·9 and ca. 3·6 from the two parts of the molecule. The height of the absorption at 302 mμ (log ε 3·75), however, was markedly less than could be accounted for from the sum of the spectra of analogous monomeric species. A considerable range (log ε 4·08–4·13) of intensities at ca. 297 mμ was found for the 1-pyrindinium ion, depending on the solvent and the gegenion, and it is thus possible that the intensity of this absorption could be depressed further by the environment in solutions of **9**. It was also noted that there was not an exact correlation of the intensities found for the known dimeric structure, **10**, with those of its moieties,[14] but the deviations were not so large.

Thus a major part of the total data on the properties of the methiodide (and methochloride) and of compounds related to them is in agreement with their representation as **9**. Some uncertainty remains, however, primarily arising from the deviations from expected intensities in the UV absorption and the unusual deshielding of two hydrogens required in the interpretation of the NMR spectrum. However, all other structures for the methiodide and methochloride which were envisioned were definitely less satisfactory.[15]

An important point for consideration would be that quaternization of 1-pyrindine proceeded in a normal fashion to give a "monomeric" methiodide (i.e. structure **4a**) and that "dimerization" to form the monoiodide (**10**) occurred on basification of **4a**. There is a great similarity in the ultraviolet spectra of the methiodide and **10** in acidic and in basic media; the reversibility of these changes has been demonstrated. The concentrations utilized in these spectral measurements, ca. 10^{-4}M would make rapid dimerization and dissociation reactions improbable. Further consideration should be given to the spectral similarity of the conjugate acids of 1-pyrindine (**3**) and 1-methyl-1*H*-1-pyrindine (**5**)[16] and the differences between the spectra of these conjugate acids and that of the methiodide.

With **9** as the best structure that was formulated, it was necessary to advance a reasonable scheme by which **9** could be formed from the reaction of 1-pyrindine with methyl iodide. The series of reactions (a–d) is proposed. The first (a) is the normal quaternization, in (b) an unreacted 1-pyrindine molecule abstracts a proton from the acidic methylpyrindinium ion to form **5**, in (c) the azulene-like **5** reacts with an electrophilic methylpyrindinium ion,[17] and in (d) the dimeric intermediate abstracts a proton (e.g. from a pyrindinium ion) to form the more stable **9**.

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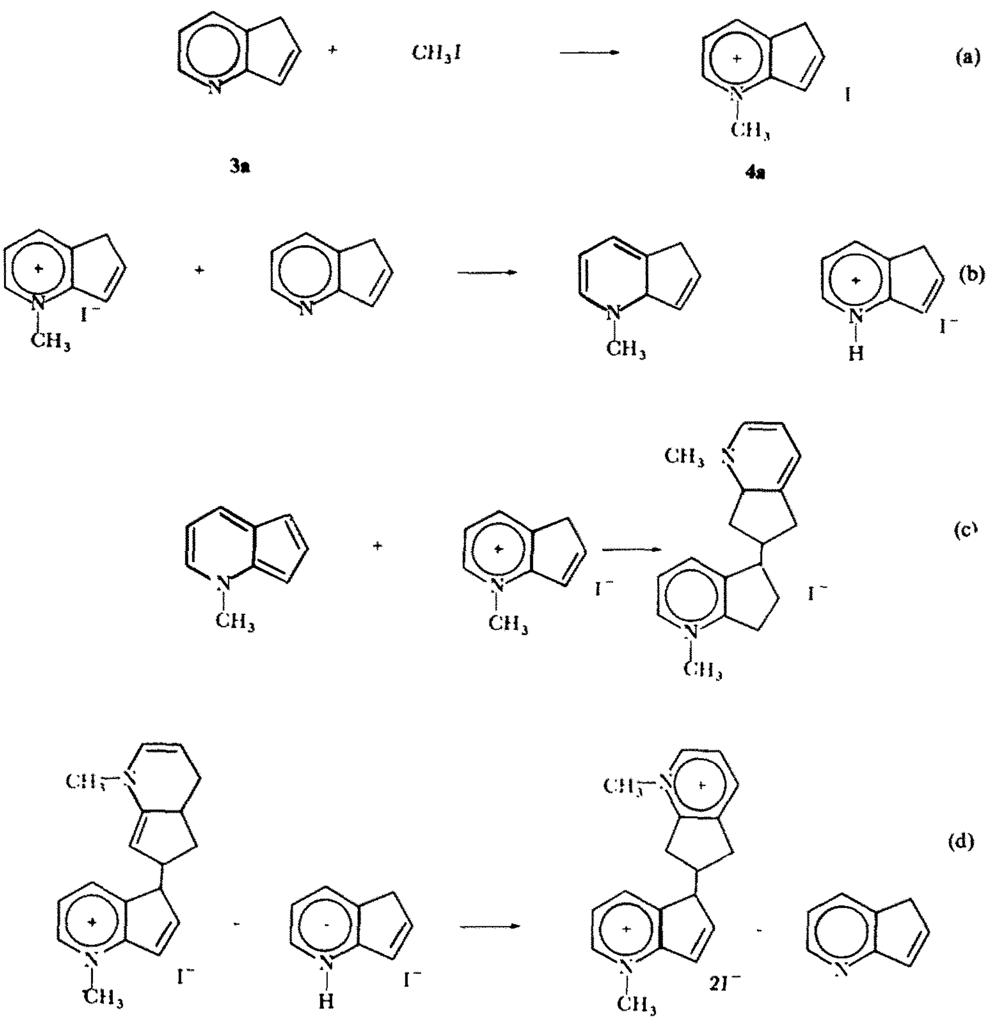
[14] λ_{max} in mμ (log ε) values (methanol solutions) for **10** were 263 (4·42), 321 (3·9) and 469 (3·22), whereas for **5** they were 256 (4·35), 318 (3·86) and 460 (2·95), and for the 1-methylpyrindanium ion 277 (3·88). The 263 mμ peak of **10** thus represents the combination of the 256 mμ peak of **5** and the 277 mμ peak of the 1-methylpyrindanium species.

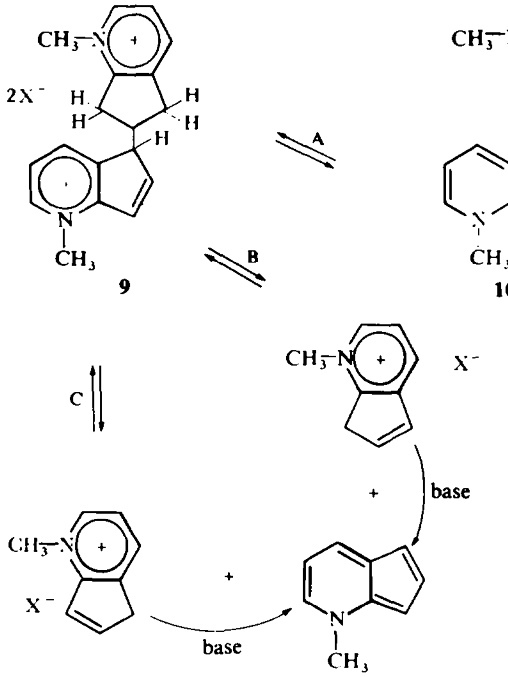
[15] The assumptions by Reese[10] that the methiodide and methochloride were the simple monomers, and that the colour observed on basification of an aqueous solution of the latter was due to **5** are probably incorrect. The present data point to the chloride of **10** (formed reversibly even in very dilute solutions) as the coloured species.

[16] 2-Methyl-6-vinylpyridine shows λ_{max} in mμ (log ε) in acidic media at 292 (4·06) (G. B. Gechele and S. Pietra, *J. Org. Chem.* **26**, 4412 (1961)); 1-pyrindine and 1-methyl-1*H*-1-pyrindine show absorption at 295 (4·08), and at 297 (4·02), respectively, in acidic methanol.

[17] Reaction at the 5-position of the methylpyrindine and at the 6-position of the methylpyrindinium ion, as shown, would be expected.



Finally, an explanation was needed for the difference in behaviour of the methiodide (which gave 78% of **10** and a small amount of **5**) and the methochloride (which gave 40% of **5** with no dimer observed) on extractive basification. It had been demonstrated that the reaction of **9** with aqueous base to form **10** was reversible. The fact that **10** ($X = I$) was only slightly soluble in water but was quite soluble in dichloromethane indicated that, for the iodide, this product would be readily extracted into the organic layer (and removed from further reaction) as it was formed. The positive organic ion in **9** has hydrogens at three locations which would be expetced to be acidic. The abstraction of the proton at the allylic position by the base represents the reversible process (path A) which produces **10**. Removal of a proton from either of the other two positions (paths B and C) represents the reverse of the reaction proposed (see above) for the formation of **9**, and results in the formation of **5** plus its conjugate acid. Further reaction of the latter with base would give a second molecule of **5**. Thus, if the solubility of **10** as the chloride were such that this remained in the aqueous phase while **5** would be removed by extraction into the dichloromethane, essentially only **5** would be found in the organic layer.



The reaction of **5** with methyl iodide gave a low yield of a purple–red solid, m.p. 250–253° (dec.) along with a considerable amount of purple–red gum. The UV spectrum of an aqueous solution of the solid changed with time. The spectrum of a basic solution resembled that of **10**, but acidification did not regenerate the spectrum of an acidic solution. There was not sufficient material for further characterization.

EXPERIMENTAL

M.ps are uncorrected. UV spectra were recorded on a Cary Model 14 Recording Spectrophotometer using cells with path lengths ranging from 0·05 to 10·0 cm. Infrared spectra were recorded with a Perkin Elmer Model 21 Spectrophotometer fitted with a sodium chloride prism. NMR spectra were recorded by Mr. B. J. Nist on a Varian Model V-K 3507, 60 Mc/s spectrometer. Elemental analyses were performed by Dr. A. Bernhardt, Max Planck Institute, Mulheim, Germany.

1-Pyrindine (**3**). This compound was prepared by procedures given in the literature. The synthesis of the intermediate 2,4-dihydroxy-1-pyrindane from adiponitrile by the route of Schroeder and Rigby[18] was used to prepare most of the compound. This procedure was found to be more amenable to the handling of quantities in excess of 100 g than the method of Prelog and Szpilfogel[19] which employed 2-carbethoxycyclopentanone as the starting material. Difficulty was experienced in the removal of acetic anhydride from 2-acetyliminocyclopentane-carbonitrile by recrystallization from ligroin as described by Schroeder and Rigby;[18] this was satisfactorily accomplished by sublimation of the crude product at 0·1 mm and 80°. The yield thus obtained was ca. 95%; m.p. 121–125° (lit.[18] 127°).

The route of Robison[5, 20] for the conversion of 2,4-dihydroxy-1-pyrindane to 1-pyrindine was used

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[18] H. E. Schroeder and G. W. Rigby, *J. Am. Chem. Soc.* **72**, 2205 (1949).

[19] V. Prelog and S. Szpilfogel, *Helv. Chim. Acta*, **28**, 1684 (1945).

[20] M. M. Robinson, *J. Am. Chem. Soc.* **80**, 5481 (1958).

without modification. It was found that 1-pyrindine could be stored for long periods (i.e. months) under nitrogen at Dry Ice temperatures with only slight decomposition. A neat sample showed λ_{max} at 466 mμ (ε 0·68).[21] λ_{max} in mμ (log ε) were shown by a cyclohexane solution at 247 (3·91), 276 (3·68), 281 (3·74), 285 (3·73) and 291 (3·70), by a methanol solution at 244 (3·87), 278 (3·73, shoulder), 283 (3·78), and 292 (3·68), and by an acidic (0·005N hydroiodic acid) methanol solution at 256 (3·45, shoulder) and 295 (4·08). The NMR and IR spectra have been described elsewhere.[6]

Reaction of 1-*pyrindine with methyl iodide.* The dissolution of 3·7 g (31·6 mmole) of 1-pyrindine in ca. 30 ml of methyl iodide (freshly shaken with basic alumina) gave an immediate orange colour, followed by the evolution of heat and the formation of a dark, red–brown gum on the walls of the flask.[22] After ca. 2 hr, the excess methyl iodide was removed in a rotary evaporator under reduced pressure (aspirator); an extremely viscous red–brown glass remained in the flask. Trituration of the glass with a small volume of acetonitrile formed a light orange–tan solid and the solvent became red–brown in colour. The solid material was heated with 30 ml of acetonitrile under reflux with vigorous stirring for 30 min. After cooling, the solid was separated by filtration and dried. The yield of light tan or cream coloured powder was 3·84 g (47%), m.p. 238–241° (dec.). The analytical sample was obtained by recrystallization from the same solvent (a relatively large volume was required to give complete solution and then concentration was necessary) and was in the form of a slightly tan powder, m.p. 240–241·5° (dec.) (lit.[10] 248–250°). λ_{max} in mμ (log ε) were displayed by an acetonitrile solution at 250 (4·52), 272 (4·11, shoulder), and 300 (3·78), by an aqueous solution at 227 (4·53),[23] 275 (4·07), and 302 (3·75), by a 0·018N hydroiodic acid solution at 276 (4·08) and 301 (3·77), by a methanolic 0·005N hydroiodic acid solution at 277 (4·06) and 303 (3·75), and by a 0·01N sodium hydroxide solution at 223 (4·55),[22] 257 (4·39), 321 (3·90), and 455 (3·13).[24] (Found: C, 41·71; H, 3·94; N, 5·60. $C_{18}H_{20}N_2I_2$[23] requires: C, 41·72; H, 3·89; N, 5·41%.)

Attempts to determine molecular weight by measurements of the vapour pressure of 0·01 to 0·1 M aqueous solutions (the substance was not sufficiently soluble in other suitable solvents) on a Mechrolab osmometer were unsuccessful owing to decomposition of the compound in this medium.

Recrystallization from methanol gave the material in the form of small, reddish balls which became a tan powder when crushed.[25] The discovery (see discussion section) that the compound reacted with methanol made the use of the latter as a solvent undesirable.

1-*Methyl*-6-[5-(1-*methyl*-1*H*-1-*pyrindinyl*)]-1-*azoniaindane Iodide* (**10**, X = I). Solid sodium carbonate (2 g) was slowly added to a vigorously stirred mixture of the product from the reaction of 1-pyrindine and methyl iodide (0·97 g, 1·87 mmole) in 20 ml of water and 50 ml of dichloromethane under a nitrogen atmosphere. A red colour appeared immediately in the aqueous layer and then in the dichloromethane. When about one-half of the base had been added, the deep red organic layer was separated and replaced by a fresh portion of dichloromethane. Very little coloured material was taken up by the second portion of solvent as the remainder of the base was added (or by extraction with further portions). Removal of the solvent at aspirator pressure with a rotatory evaporator gave a mixture of a deep red–black solid and a small quantity of red oil. Trituration of the mixture with ether readily dissolved the oil and left a red–purple solid.

The red, ethereal solution was placed in a small sublimation apparatus and the solvent removed by a stream of nitrogen. Distillation, at 0·5 mm and 60–100°, of the residual dark red oil gave one drop of red liquid which was collected on the cold finger. The UV and visible spectra (cyclohexane) of this material corresponded to those of 1-methyl-1*H*-1-pyrindine (see below). Maxima in mμ (D) were recorded in the UV at 260 (0·703), 268 (0·603, shoulder), 315 (0·164, shoulder), 321 (0·216), 327 (0·202) and 335 (0·209), and in the visible for a separate solution at 458 (0·752, shoulder), 472 (0·834), 488 (0·860), 503 (0·779), 523 (0·650), 542 (0·425, shoulder), 568 (0·259), and at ca 610 (0·05, plateau).

The dried, red–purple solid, m.p. ca. 200° (dec.) amounted to 0·57 g (78%). Recrystallization from aceto-

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[21] The density of the substance was measured and the concentration determined from this was used for calculation of ε.

[22] C. B. Reese[10] also used methyl iodide as both reactant and solvent.

[23] This maximum was attributed to absorption by iodide ion and the extinction coefficient was calculated on the basis of the molar concentration of a dimeric methiodide.

[24] The major part of the data are in agreement with a dimeric structure (e.g. 1-methyl-5[6-(1-methyl-1-azoniaindanyl)]-5*H*-1-azoniaindene diiodide (**9**)) for this substance and the extinction coefficients and analytical data are calculated on this basis.

[25] C. B. Reese[10] reported cream coloured crystals from methanol. No truly crystalline material was observed in our product.

nitrile-benzene afforded the analytical sample of **10** (*X* = *I*) as deep purple needles, m.p. 230–231° (dec.). Measurement of the melting point in the usual way resulted in gradual decomposition over a wide range of temperature. The determination was made by placing a crystal on the block of a Fischer-Johns apparatus which was stabilized at a certain temperature and observing whether melting occurred within ca. 15 sec. This procedure served to bracket the value obtained and was then repeated at 1° intervals from 225 to 235°. (Found: C, 55·31; H, 4·73; N, 6·92; mol. wt. (X-ray), 386·4. $C_{18}H_{19}N_2I$ requires: C, 55·39; H, 5·91; N, 7·18%; mol. wt., 390·3.) λ_{max} in mμ (log ε) were displayed by an acetonitrile solution at 253 (4·47), 321 (3·86), 332 (3·83, shoulder), and 466 (3·21, broad peak), by a methanol solution at 263 (4·42), 321 (3·9), 333 (3·84), and 469 (3·23), by a 0·01N sodium hydroxide solution at 223 (4·33), 257 (4·37), 321 (3·9) and 455 (3·22), by an acidic (0·018N hydroiodic acid) solution at 275 (4·05) and 302 (3·74), and by an acidic (0·005N hydroiodic acid) methanol solution at 275 (4·05), 303 (3·75), 459 (2·68) and 507 (2·68).

1-*Methyl*-1*H*-1-*pyrindine* (**5**). *A*. The passage of 100 ml of an aqueous solution containing 4 g (15·5 mmole) of the product from the reaction of 1-pyrindine with methyl iodide through a 1 × 20 cm column of Dowex 1-X8 anion exchange resin (100 mesh) in the chloride form[26] afforded a solution of the corresponding chloride as indicated by the correspondence of the UV spectrum with that of the solution of the starting compound except for a peak at 233 mμ[12] which had been concealed by the absorption of iodide ion at 225–227 mμ, and the identity of the spectral changes observed when the solution was treated with base with those found when an aqueous solution of the iodide compound was treated with base. λ_{max} in mμ (log ε) were displayed by a water solution at 233 (4·07), 275 (4·1), and 302 (3·79), by 0·01 and 0·019N hydrochloric acid solutions at 232 (4·08), 275 (4·1) and 302 (3·79), and by 0·01N and 0·1N sodium hydroxide solutions at 258 (4·41), 321 (3·94), and 457 (3·2).

The solution thus obtained was stirred rapidly with 100 ml of dichloromethane at 0° under a nitrogen atmosphere while 5 g of sodium carbonate was added. The reaction and work-up were then carried out as described for the preparation of **10**. In the present case removal of the solvent left only a dark red oil which was distilled (molecular still) at 0·5 mm. The temperature was raised slowly from 60 to 130° and the majority of the material was collected at the higher portion of this range. The yield of **5** as a dark red oil was 0·81 g (40%). The substance was decidedly less stable in air than 1-pyrindine but could be stored under nitrogen at Dry Ice temperatures as a red solid for several months. It was handled at room temperature in an inert atmosphere cabinet under nitrogen. Attempts to obtain satisfactory combustion analyses were unsuccessful.

Potentiometric titration of a solution of **5** in acetic acid with perchloric acid gave a titration curve with a single inflection and afforded a value of 131·8 for the neutralization equivalent (C_9H_9N requires: neut. eq., 131·2).

λ_{max} in mμ (log ε) were shown by a cyclohexane solution at 260 (4·38), 268 (4·24, shoulder), 315 (3·79, shoulder), 321 (3·92), 328 (3·87), 335 (3·91), 459 (2·9, shoulder), 472 (2·93), 488 (2·93), 504 (2·86), 525 (2·76), 545 (2·51, shoulder), and 570 (2·26), by a methanol solution at 256 (4·35), 318 (3·86), 324 (3·83, shoulder), 330 (3·76, shoulder), and 459 (2·94), and by a methanolic 0·018N hydroiodic acid solution at 249 (3·57, shoulder), and 297 (4·02), and by a methanolic 0·01N sodium hydroxide solution at 256 (4·42), 320 (3·92), 325 (3·89, shoulder), 331 (3·83), and 462 (3·02). The compound was not sufficiently soluble in aqueous solutions to permit quantitative spectral measurements but λ_{max} in mμ (intensity ratio with one peak as 1·0) were observed for a water solution at 230 (1·2), 251 (1·0), 296 (1·8), and 445 (0·17, broad), for a 0·0195N hydrochloric acid solution at 231 (1·0), 249 (0·7, shoulder), 297 (2·88), for a 0·0195N hydroiodic acid solution (excluding the absorption by iodide ion) at 297, and for a 0·01N sodium hydroxide solution at 252 (2·89), 317 (1·0), and 433 (ca. 0·3, broad).

B. To ca. 40 ml of anhydrous liquid ammonia containing a few crystals of ferric nitrate nonahydrate in a flask fitted with a stirrer, Dry Ice condenser, and dropping funnel was added with stirring 0·4 g (17·4 mmole) of sodium metal.[27] The addition of a solution of 340 mg (2·9 mmole) of 1-pyrindine in 2 ml of dry ether to the rapidly stirred mixture caused a change in the colour from grey to yellow. After 30 min, 2·9 g (20 mmole) of methyl iodide (freshly passed over basic alumina) in 2 ml of ether was introduced and the colour thereupon changed to deep red. The ammonia was allowed to evaporate and the residue was taken up in 30 ml of water. The solution was extracted with ether and the solvent was removed from the combined organic extracts with a rotary evaporator under aspirator pressure. The residue of purple–red oil was distilled in a molecular still at 0·1 mm and a block temperature of 100°. The deep red oil collected amounted to 0·27 g (71%).

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[26] The resin from the bottle was first treated with dilute hydrochloric acid and then washed with distilled water until the washings were neutral.

[27] T. H. Vaughn, R. R. Vogt and J. A. Niewland, *J. Am. Chem. Soc.* **80**, 5481 (1958).

The absorption spectra (cyclohexane) recorded in mμ log ε) of this material corresponded to that of 5 obtained in *A* except that the lower values of ε indicated the material to be less pure: 254 (3·76), 279 (3·58, shoulder), 285 (3·63), 295 (3·47), 314 (2·03), 320 (2·14), 327 (2·11), 335 (2·14), 458 (1·14), 470 (1·17), 487 (1·18), 505 (1·0), 547 (0·7, shoulder), and 568 (0·4).

The product obtained from a duplicate experiment employing 100 mg (0·85 mmole) of 1-pyrindine was added directly to a solution of 0·22 g (0·85 mmole) of picric acid (10% in water) and 3 ml of methanol. The yellow picrate which formed was recrystallized twice from methanol and gave 0·15 g (49%) of fluffy yellow needles which melted at 147–151° (dec.) in a sealed capillary. One further recrystallization afforded the analytical sample, m.p. (sealed capillary) 151–154·5° (dec.). The IR spectrum showed no N–H absorption. (Found: C, 49·75; H, 3·29; N, 15·49%; mol. wt. (spectroscopic[28]), 363. $C_{15}H_{12}N_4O_7$ requires: C, 50·00; H, 3·36; N, 15·55%; mol. wt., 360.)

The reaction of 1-*pyrindinium fluoroborate with diazomethane.* To a solution of 0·3 g (2·5 mmole) of 1-pyrindine and 0·7 g (3·9 mmole) of 48% fluoroboric acid in 10 ml of acetonitrile (purified and freshly passed over basic alumina) at 0° was added slowly, in portions an ethereal solution of diazomethane prepared from 2·1 g (20 mmole) of N-nitroso-N-methylurea. A rapid evolution of nitrogen occurred and the solution became yellow and then red. If the addition was stopped at the first formation of red colour, the latter would fade and be replaced by yellow. The addition of a little more diazomethane reformed the red colour which would again become yellow. This cycle could be repeated several times. (Treatment of a small sample of the yellow solution with aqueous base gave a permanent deep red colour.) When all of the diazomethane had been added the solution became permanently red. The reaction mixture was then added to 30 ml of 5% sodium hydroxide and the whole was extracted with ether. Removal of the solvent with rotary evaporator at reduced pressure (aspirator) left a dark red oil and distillation of this in a molecular still at 0·1 mm and a block temperature of 95° gave 0·21 g (64% of the theoretical for 5) of a red oil. The UV and visible spectra of this material indicated that it contained 5. Maxima in mμ were found for a cyclohexane solution at 259, 313 (shoulder), 320, 327, 334, 456, 470, 485, 502, 521, 546 (shoulder), and 568. The relative intensities of the peaks in the visible region were 0·94, 1·0, 1·0, 0·88, 0·72, 0·44 and 0·29 as compared to 0·93, 1·0, 1·0, 0·85, 0·67, 0·38 and 0·21 for 5.

A red oil product which exhibited UV and visible spectra identical with those of the above material was obtained from the introduction of excess gaseous diazomethane into a solution of 1-pyrindine and fluoroboric acid in acetonitrile.

The reaction of 1-*pyrindine with methyl* p-*toluenesulfonate and then base.* To a solution of 1·0 g (5·4 mmole) of methyl *p*-toluenesulfonate (freshly distilled) in 10 ml of purified (freshly passed over basic alumina and boiled under a dry, oxygen-free nitrogen atmosphere) acetonitrile was added 0·5 g (4·4 mmole) of 1-pyrindine with stirring. The solution became yellow and then red–orange and an orange gum formed on the sides of the flask over a period of ca. 2 hr. The mixture was then heated at 60–80° for 1 hr. The solvent was removed under reduced pressure and the dark red oil which remained was triturated with several portions of ether; the remaining orange–yellow gum could not be crystallized. Solution of the material in 20 ml of water, followed by basification with solid potassium carbonate, produced a dark red solution. Extraction with ether, removal of the ether under reduced pressure yielded a viscous residue which was distilled in a small sublimation apparatus at 0·5 mm and a bath temperature of 120°. Two drops of orange–red oil were collected on the cold finger. A cyclohexane solution showed λ_{max} in mμ in the UV at 255 (shoulder), 259, 261 (shoulder), 267 (shoulder), 314 (shoulder), 321, 327, and 334, and in the visible at 456 (shoulder), 470, 485, 502, 522, 545 (shoulder) and 570.. The ratios of the intensities in the visible were 0·93, 1·0, 1·0, 0·87, 0·69, 0·41, and 0·24, respectively. The appearance of both spectra resembled those of 1-methyl-1*H*-1-pyrindine (5) and indicated the presence of this substance.

1-*methyl*-7-*aza*-1*H*-1-*pyrindine.* This substance was prepared in 91% yield by the treatment of 7-aza-7*H*-1-pyrindine with methyl *p*-toluenesulfonate to form 7-methyl-7-aza-7*H*-1-pyrindinium *p*-toluenesulfonate, and then reaction of the latter with aqueous potassium carbonate as described by Robison.[9] The yellow solid melted at 48–50°.[9] A cyclohexane solution showed λ_{max} in mμ (log ε) at 246 (4·20), 311 (3·94), 323 (3·85), 385 (2·99, shoulder), 391 (3·0), 404 (2·98), 415 (2·91, shoulder), 427 (2·78), 440 (2·55, shoulder), and 459 (2·28). The previous workers[9] reported only the principal maxima at 245 (4·20), 309 (3·94) and 385 (2·99).

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[28] Measurements were made at 380 mμ. A. Gillam and E. S. Stern, *An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry*, p. 290. Arnold, London (1954).