Diazepines. Part 23.[1] The Formation and Structure of 1,5-Diaza- and 5-Aza-1-oxa-pentadienium Salts and their Use in the Preparation of 2,3-Dihydro-1,4-diazepinium Salts

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1,5-Diaza- and 5-aza-1-oxa-pentadienium salts serve as excellent precursors for the preparation of 2,3-dihydro-1,4-diazepinium salts, including some that are not readily obtained by other methods. Sometimes imidazolinium rings are formed instead of or in addition to the desired product. The preparation of these precursors is discussed. The shape of diazapentadienium salts is considered, based on spectroscopic evidence. The formation of fourteen-membered rings from azaoxapentadienium salts is also mentioned.

2,3-DIHYDRO-1,4-DIAZEPINES and their salts (I) have most commonly been prepared by the reactions of 1,2-diamines with β-diketones.[2] The method is generally inefficient for the preparation of 5,7-unsubstituted derivatives, possibly because such derivatives are unstable to solvolysis under the conditions which thermodynamically favour their formation.[3,4] Thus a method of preparation involving neutral conditions in preferably non-aqueous media offers advantages. The preparation of (I) [5] and of its 1,4-dimethyl derivative [6] in very good yield from diamines and 1,5-diazapentadienium salts (II) in high dilution conditions has been reported. The present paper considers the use of diazapentadienium salts such as (II) and of 5-aza-1-oxa-pentadienium salts (III) in the preparation of dihydrodiazepinium salts.

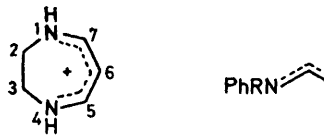
The diazapentadienium salt (II; R = Me) has been prepared from propynal.[7] Salts (II; R = H or Ph) are prepared much more simply by direct acid-catalysed reaction of aniline or diphenylamine with 1,1,3,3-tetraethoxypropane.[5] The 2-methyl analogue of (II; R = H) could be made similarly, and the 2,4-dimethyl analogue was prepared as described [8] from acetylacetone. The 3-phenyl derivative (IV) is readily obtained from

[1] Part 22, D. Lloyd, R. K. Mackie, H. McNab, K. S. Tucker, and D. R. Marshall, *Tetrahedron*, 1976, **32**, 2339.
[2] See D. Lloyd, H. P. Cleghorn, and D. R. Marshall, *Adv. Heterocyclic Chem.*, 1974, **17**, 1.
[3] C. Barnett, H. P. Cleghorn, G. E. Cross, D. Lloyd, and D. R. Marshall, *J. Chem. Soc.* (*C*), 1966, 93.
[4] C. Barnett, D. R. Marshall, and D. Lloyd, *J. Chem. Soc.* (*B*), 1968, 1536.
[5] D. Lloyd, H. McNab, and D. R. Marshall, *Synthesis*, 1973, 791.
[6] G. Scheibe, J. Heiss, and K. Feldmann, *Angew. Chem.*, 1965, **77**, 545; *Angew. Chem. Internat. Edn.*, 1965, **4**, 525.
[7] S. S. Malhotra and M. C. Whiting, *J. Chem. Soc.*, 1960, 3812.
[8] G. Scheibe, *Ber.*, 1923, **56**, 137.

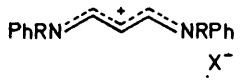
phenylacetic acid, phosphoryl chloride, and dimethylformamide.[9]

5-Aza-1-oxapentadienium salts (III) are prepared by alkylation of oxoenamines, which in turn are obtained from β-diketones and amines.[10] Ethoxy derivatives (III; R^1 = Et) were prepared using triethyloxonium tetrafluoroborate,[11] but the preferred technique was to prepare methoxy derivatives (III; R^1 = Me) by the action of methyl fluorosulphonate in methylene chloride at room temperature. Reaction was rapid and exothermic and high yields were obtained.

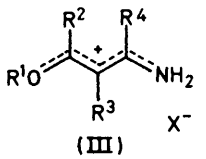
Open-chain diazapentadienium salts exist in the all-*trans* form (II).[11] The electronic spectra of (II; R = H and Ph) are almost identical, indicating that the second phenyl groups on each nitrogen atom in (II; R = Ph) have little conjugative interaction with the diazapentadienium chain. ^{1}H N.m.r. spectra confirm that these phenyl groups are twisted out of the plane of the remainder of the molecule and are *trans* to the 2,4-hydrogen atoms, for the 3-H signal of (II; R = Ph) appears more than 1 p.p.m. upfield from the corresponding signal of (II; R = H).



(I)



(II)



(III)

(where unspecified R^n = H)

a; R^1 = Et, R^2 = R^4 = Me, X = BF_4

b; R^1 = R^2 = R^4 = Me, X = FSO_3

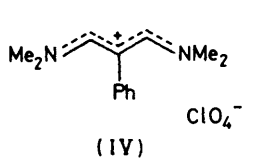
c; R^1 = R^4 = Me, R^2 = Ph, X = FSO_3

Similar shielding effects are evident when the spectra of the 2-methyl (V) and 2,4-dimethyl derivatives (VI) of (II; R = H) are compared. The vicinal coupling constants ($J_{3,4;\ 4,5}$ *ca.* 12 Hz) in (V) confirm the *trans*-geometry of the PhNH·CH·CH portion of the molecule. The chemical shifts observed for the methyl groups in both molecules suggest that they have similar environments. The two methyl groups of (VI) give one sharp singlet, precluding a *cis,trans* geometry for the chain. The 3-H signal of (V) is deshielded by 0.36 p.p.m. relative to the corresponding signal of (VI). Of the two possible all-*trans* structures for each of these molecules, these observations are consistent only with (V) and (VI) in which the methyl groups are *trans* to the neighbouring phenyl groups, which are twisted out of plane, thus causing shielding of 3-H. The resultant inefficient conjugation of the phenyl groups with the chain in (VI) is evident from the similarity of its electronic spectrum, $\lambda_{max.}$ 346 nm, with that of the 1,1,2,4,6,6-tetramethyl analogue, $\lambda_{max.}$ 345 nm.[12]

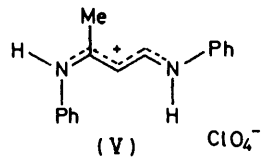
^{13}C N.m.r. spectra of 1,5-diazapentadienium salts [δ (p.p.m. downfield from Me_4Si)]

Salt	δ(C-3)	δ(C-2,-4)	Substituent Ph group δ(*ipso*)	δ(*o*)	δ(*m*)	δ(*p*)	δ(*m*) − δ(*p*)	δ (Others)
(II; R = H)	98.89	158.50	138.72	117.98	130.39	126.64	3.75	
(VI)	*ca.* 93.2br	*ca.* 170.8br	137.02	125.57	129.96	127.97	1.99	22.25 (2,4-Me)
1,5-Dipiperidino	88.51	160.78						22.91, 24.98, 26.27, 46.70, 55.48 (pentamethylene)
1-Phenyl-5-piperidino	94.07	156.91 162.58	139.31	117.36	130.28	125.63	4.65	23.17, 25.56, 26.68, 48.00, 56.86 (pentamethylene)

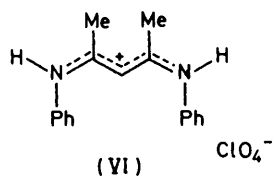
The ^{13}C n.m.r. spectra of the diazapentadienium salts (see Table) are consistent with these structures. The alternating polarity along the chain, characteristic of such systems, is especially evident. The rigidity of the chain at room temperature is shown by the five distinct peaks due to the pentamethylene carbon atoms in *NN'*- and *NNN'N'*-bispentamethylene derivatives. The inefficiency of the conjugation with the phenyl groups in (VI) compared with (II; R = H) is also evident from the δ(*m*) − δ(*p*) values. It is also seen that introduction of methyl groups vicinal to *N*-phenyl groups causes an upfield shift of the C-3 signal, because of the change of geometry, whereas in the necessarily all-*cis* dihydrodiazepinium salts introduction of 5,7-methyl groups next



(IV)



(V)



(VI)

[9] C. Jutz, R. Kirchlechner, and H.-J. Seidel, *Chem. Ber.*, 1969, **102**, 2301.

[10] *Inter alia* (*a*) L. Claisen, *Ber.*, 1891, **24**, 3900; A. Combes and C. Combes, *Bull. Soc. chim. France*, 1892, **7**, 779; E. Knoevenagel, *Ber.*, 1903, **36**, 2180; (*b*) W. Koenigs and A. Mengel, *ibid.*, 1904, **37**, 1322; (*c*) R. D. Archer, *Inorg. Chem.*, 1963, **2**, 292.

[11] S. Dähne and J. Ranft, *Z. Phys. Chem.*, 1963, **224**, 65; K. Feldmann, E. Daltrozzo, and G. Scheibe, *Z. Naturforsch.*, 1967 **22b**, 722; C. P. Richards and G. A. Webb, *Org. Magnetic Resonance*, 1975, **7**, 401.

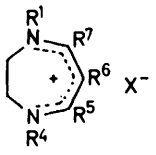
[12] J. Kučera and Z. Arnold, *Coll. Czech. Chem. Comm.*, 1967, **32**, 1704.

to the *N*-phenyl groups causes a downfield shift of the C-6 signal (corresponding to C-3 in the open-chain compounds).

In contrast, the n.m.r. spectra of the azaoxapentadienium salts indicate that they exist in a variety of configurations. An interesting point is that introduction of a formal positive charge onto an oxoenamine by alkylation causes an *upfield* shift of at least 10 p.p.m. of the signal due to the carbonyl carbon atom. Clearly the electron-withdrawing effect of the carbonyl group has been replaced by an electron-donating conjugative effect in the alkylated compound.

The preparation of dihydrodiazepinium salts from diazapentadienium salts is effectively a transamination reaction. Although it becomes part of a ring system, the diazapentadienium system is retained in the reaction, in accord with its meneidic character.[13] As previously reported [5] the unsubstituted dihydrodiazepinium cation (I) is conveniently prepared in high yield in this way. Using similar conditions 1-methyl- and 2-methyl-dihydrodiazepinium perchlorates were prepared, which completes the series of possible monomethyl derivatives, and also the 1,4-dimethyl and 1,4-dibenzyl derivatives. The ready formation of the latter compound is of interest since attempts to make it from malondialdehyde gave instead an imidazolinium salt.[3] The 5-methyldihydrodiazepinium picrate (VIIe; X = picrate) was prepared similarly from 2-methyl-1,4-diphenyl-1,4-diazapentadienium picrate.

Attempted reaction of (II; R = H) with *NN'*-diphenylethylenediamine gave no diazepine, presumably



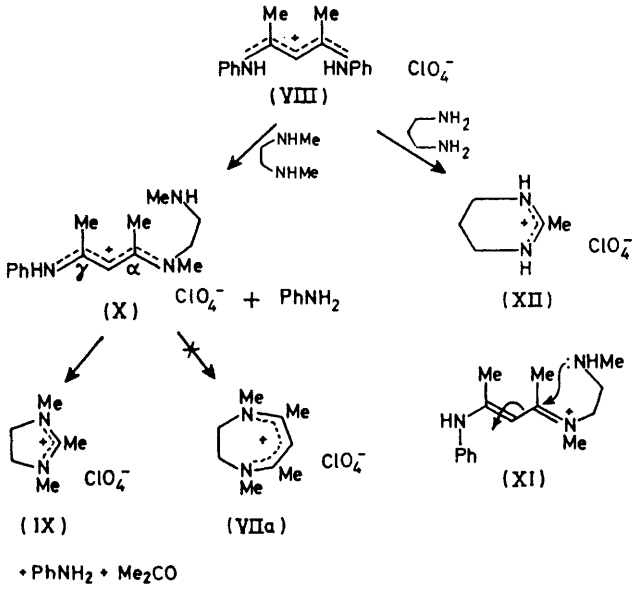
(VII)

(where unspecified R^n = H)

a; $R^1 = R^4 = R^5 = R^7$ = Me
b; R^6 = Ph
c; R^n = H
d; $R^1 = R^4$ = Me
e; R^5 = Me
f; $R^5 = R^7$ = Me
g; R^5 = Me, R^7 = Ph
h; $R^1 = R^4 = R^5$ = Me, R^7 = Ph
i; $R^5 = R^6 = R^7$ = Me
j; $R^1 = R^5$ = Me, R^7 = Ph
k; $R^1 = R^7$ = Me, R^5 = Ph

because of the low nucleophilicity of this amine. The success of the method appears to depend, at least partially, on the reactant diamine being a significantly better nucleophile than the amine which is the leaving group.

An attempted preparation of the 1,4,5,7-tetramethyl derivative (VIIa) by this method from the diazapentadienium salt (VIII) gave instead the imidazolinium salt (IX) in good yield. A likely mechanism for this reaction is shown in the Scheme. In this case the terminal amine group (MeHN) in the intermediate (X) attacks the α-position of the diazapentadienium chain to provide a five-membered ring whereas reaction to give a seven-membered ring entails attack at the γ-position. Attack at the γ-position is disfavoured by the steric effects of the methyl group and the adjacent phenyl group, and attack at the α-position is substantially less hindered, while formation of the linear S_Ni transition state (XI) may be facilitated by the adjacent methyl group. Attempted



SCHEME

preparations of 1,5,7-trimethyl- and 2,2,5,7-tetramethyl-dihydrodiazepinium salts also provided imidazolinium salts instead. In the last case the u.v. spectrum of the crude product showed a small peak at 325 nm, consistent with the formation of a small quantity of dihydrodiazepinium salt.

A similar reaction ensues between (VIII) and 1,3-diaminopropane to give the tetrahydropyrimidinium salt (XII) rather than a diazocine derivative; entropy considerations presumably weigh against formation of an eight-membered ring.

These results prompted an examination of the reaction of the salt (VIII) with ethylenediamine itself. N.m.r. spectra of the crude products showed that both five- and seven-membered rings were formed. In refluxing propan-2-ol formation of the imidazolinium salt predominated (60% of the product) but the dihydrodiazepinium salt was the major product in propan-2-ol at 59° (60%) or in refluxing methanol (70%). It thus appears that at least one contributing factor may be the temperature of the reaction mixture.

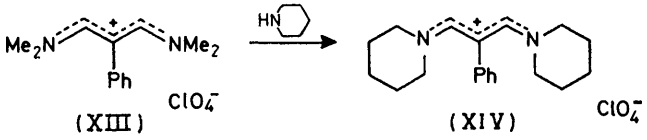
The reactions so far described of diazapentadienium salts with diamines to give dihydrodiazepinium salts require high dilution conditions to obtain good yields, which is surprising for the formation of seven-membered rings. An investigation of the reactions of the salts (II) with monoamines showed that there is a considerable difference in the rates of replacement of the first and second arylamine groups. When the salts (II; R = H

[13] D. Lloyd and D. R. Marshall, *Angew. Chem.*, 1972, **84**, 447; *Angew. Chem. Internat. Edn.*, 1972, **11**, 404.

and Ph) are treated with two equivalents of piperidine either under high dilution conditions or in normal concentrations at ambient temperature only monosubstitution takes place. Similar results were obtained using cyclohexylamine. Disubstitution could be achieved by the use of excess of piperidine. A kinetic investigation of the reaction between (II; R = Ph) and piperidine showed that the first substitution is 570 times faster than the second. The rate difference is possibly due to the increase in electron density in the diazapentadienium chain brought about by substitution of the diarylamine group by an aliphatic amine group, which in turn decreases the electrophilicity of the molecule. This difference in reaction rates causes polymerisation rather than cyclisation to be kinetically favoured in reactions involving diamines in solutions of normal concentration.

The reaction rates are also affected by small steric changes in the vicinity of the reactive site. Thus 2-methylpiperidine reacts with (II; R = Ph) at about one-fifteenth the rate that piperidine reacts. Cyclisations involving unsymmetrical reactants proceed less readily and this may be associated with similar rate differences for the two steps leading to cyclisation, which will promote polymerisation at the expense of cyclisation.

The driving force for the formation of dihydrodiazepinium salts from diazapentadienium salts is thermodynamic, employing the good leaving tendencies of the arylamines. An alternative physical driving force could be provided in such reactions by utilising the selective removal of a volatile amine, which could be boiled out of the reaction mixture. To investigate this possibility the readily prepared diazapentadienium salt (XIII) [9] was treated with excess of piperidine and was

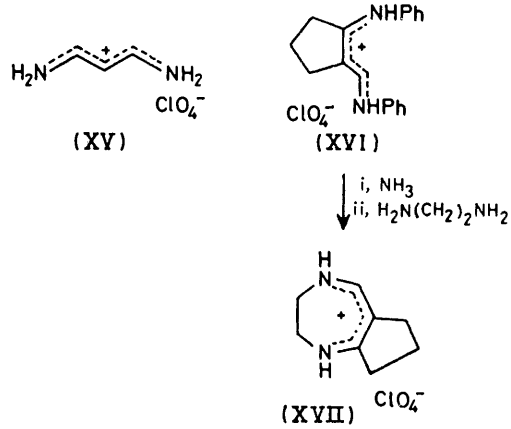


(XIII) (XIV)

rapidly converted into the bispiperidino derivative (XIV). Similarly treatment of (XIII) with ethylenediamine readily provided the 6-phenyldihydrodiazepinium salt (VIIb; X = ClO_4).

The best physical leaving group for this purpose should be ammonia, which might be displaced from the parent diazapentadienium salt (XV). When ammonia was passed through a solution of the dianil salt (II; R = H), $\lambda_{max.}$ 380 nm, an intermediate was first formed, $\lambda_{max.}$ 352 nm, probably with one aniline group displaced by ammonia, which reacted further to give a product, $\lambda_{max.}$ 286 nm, thought to be the salt (XV). This salt could not be isolated satisfactorily; addition of ether to the solution precipitated a solid which was apparently mostly inorganic but whose ^1H n.m.r. spectrum, τ([$^2H_6$]DMSO) 2.2 (d, J 12 Hz) and 4.5 (t), was consistent with the proposed structure. If this solution of (XV) was heated without ammonia being passed through it, the intermediate with $\lambda_{max.}$ 352 nm was reformed, showing the transamination reaction to be reversible.

Reaction of salt (XV), prepared *in situ*, with ethylenediamine gives the parent dihydrodiazepinium salt (VIIc) in high yield without recourse to high dilution methods and provides the most convenient method for its preparation. Similarly *NN'*-dimethylethylenediamine gave



(XV) (XVI) (XVII)

the 1,4-dimethyldihydrodiazepinium salt (VIId), which confirms the proposed course of the reaction. The same method was used to prepare other dihydrodiazepinium salts, including the 2,2-dimethyl and 2,3-cyclohexano derivatives of (VIIc), hitherto unobtainable by reaction of the diamines with either malonaldehyde or its bisanil salts (II). Both of these products were highly soluble and required careful manipulation (see Experimental section) in their purification. When ammonia was passed through a solution of the diazapentadienium salt (V) a product with $\lambda_{max.}$ 297 nm was formed, which, on treatment with ethylenediamine, gave a product with $\lambda_{max.}$ 325 nm, which was probably the 5-methyldihydrodiazepinium salt (VIIe; X = ClO_4) but, apparently because of its hygroscopicity, it could not be isolated satisfactorily. However the picrate (VIIe; X = picrate) was formed in good yield from the picrate analogue of (V).

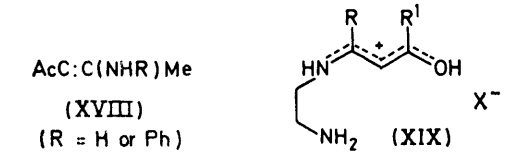
Diazapentadienium salts are also readily obtained from β-chlorovinylaldehydes,[14] and this provides another route to dihydrodiazepinium salts. Thus 2-chlorocyclopent-1-enecarbaldehyde [15] was converted into the salt (XVI) which by successive treatment with ammonia and ethylenediamine gave the dihydrodiazepinium salt (XVII).

5-Aza-1-oxapentadienium salts (III) also react with 1,2-diamines to provide dihydrodiazepinium salts, as do the related oxoenamine bases (XVIII) [16] in acid solution; presumably in the latter case the base is protonated to give (III; $R^1 = R^3 = H$, $R^2 = R^4 = Me$) as the reactant. When dihydrodiazepinium salts are formed

[14] J. M. F. Gagan and D. Lloyd, *J. Chem. Soc.* (*C*), 1970, 2488.
[15] J. M. F. Gagan, A. G. Lane, and D. Lloyd, *J. Chem. Soc.* (*C*), 1970, 2484.
[16] W. Koenigs and A. Mengel, *Ber. Deutsch Chem. Gesellschaft*, 1904, **37**, 1322; G. L. Nelson, G. C. Levy, and J. D. Cargill, *J. Amer. Chem. Soc.*, 1972, **94**, 3089.

from β-dicarbonyl compounds and diamines under the usual acid catalysed conditions an azaoxapentadienium salt (XIX) is a probable intermediate.

Alkylated azaoxapentadienium salts (III; R^1 = Me or Et), prepared as described, react with ethylenediamine in ethanol in normal concentrations at room temperature to give dihydrodiazepinium salts in high yield. Conditions are neutral and mild and reaction is rapid. In this

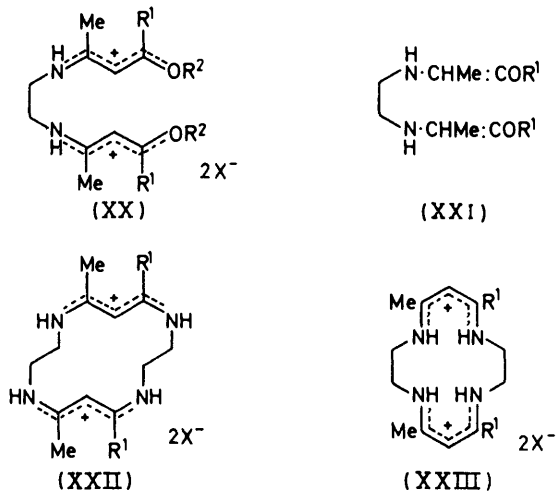


way were prepared 5,7-dimethyl- (VIIf), 5-methyl-7-phenyl- (XIIg), 1,4,5,7-tetramethyl- (VIIa) (which is difficult to prepare by a condensation reaction from a diketone), and the hitherto unreported 1,4,5-trimethyl-7-phenyldihydrodiazepinium (VIIh) salts. The 5,6,7-trimethyl salt (VIIi), which requires a modified procedure for its preparation from 3-methylacetylacetone,[4,17] was also prepared but was contaminated with 2-methylimidazolinium fluorosulphonate, and, because of their similar properties, it proved impossible to remove this impurity completely. Likewise reaction of the azaoxapentadienium salts (IIIa and b) with *NN'*-dibenzylethylenediamine gave mixtures of dihydrodiazepinium and imidazolinium salts. The five-membered rings are presumably formed in an analogous manner to that shown in the Scheme.

The reaction between an unsymmetric diamine and an azaoxapentadienium salt with different substituents R^2 and R^4 was of interest. Previous work [18] indicated that the alkoxy group of a salt (III) was the better leaving group, so that the more nucleophilic amino group should attack preferentially at that site, thus providing selectivity by the reagent. In accord with this, *N*-methylethylenediamine reacted with the salt (IIIc) to give a mixture containing 85% of the expected isomer (VIIj). With benzoylacetone this diamine gives predominantly (78%) the alternative isomer (VIIk),[19] so that either isomer is accessible by suitable choice of the mode of preparation. The preferential formation of (VIIj) from the salt (IIIc) arises because the masked benzoyl group ($MeO\overset{+}{=}CPh$) of this salt has been made more reactive than the masked acetyl group ($CMe=\overset{+}{N}H_2$) by different derivitisation of the two ketone groups, achieved in a two-step preparation of (IIIc) from benzoylacetone; the normal relative carbonyl reactivity in this diketone is in this way reversed in its derivative (IIIc). This principle could well be applied to the regiospecific synthesis of other non-symmetric heterocycles by use of the suitable diketone derivatives.

[17] D. Lloyd, R. H. McDougall, and D. R. Marshall, *J. Chem. Soc.* (*C*), 1966, 780.
[18] T. J. Truex and R. H. Holm, *J. Amer. Chem. Soc.*, 1971, **93**, 285; 1972, **94**, 4529.
[19] A. M. Gorringe, D. Lloyd, and D. R. Marshall, *J. Chem. Soc.* (*C*), 1969, 1081.

Azaoxapentadienium salts are also useful in the preparation of fourteen-membered ring compounds.[20] Thus reaction of ethylenediamine with the bisazaoxapentadienium salts (XX), obtained by alkylation of the bisoxoenamines (XXI),[17,21] provide the macrocyclic salts (XXII). It seems likely that these salts have the transoid structure shown in (XXII) instead of the cisoid form (XXIII) in which they have usually been represented and which is the form of the corresponding bases. This follows from the very high value reported [22] for $J_{6,7}$ of an analogous dication, which is incompatible with a cisoid structure for these portions of the ring, and also from the upfield shift of the NH signal on going from the chelated base to the dication,[22] whereas a dication of similar structure to the base would be expected to show a downfield shift. The huge difference



a; R^1 = Me, R^2 = Et, X = BF_4
b; R^1 = R^2 = Me, X = FSO_3
c; R^1 = Ph, R^2 = Me, X = FSO_3

in the coupling constants $J_{6,7}$ for the base (2.5 Hz) and dication (20 Hz) [22] also infers a fundamentally different stereochemistry for the two species. A number of different conformations for structure (XXIII) are possible, depending upon the orientation of the ethylene bridges but all have the conjugated portions of the ring in planar transoid forms.

EXPERIMENTAL

Electronic spectra were recorded for methanolic solutions and i.r. spectra for Nujol mulls unless otherwise stated. N.m.r. spectra were recorded using 10% solutions, ^{13}C n.m.r. spectra at 20 MHz, ^1H n.m.r. spectra at 100 MHz.

1,5-*Diazapentadienium Salts*.—Salts (II; R = H or Ph), (IV), and (VI) were prepared as previously reported.[5,8,9]

2-*Methyl*-1,5-*diphenyl*-1H-1,5-*diazapentadienium Per-*

[20] S. C. Tang, S. Koch, G. N. Winstein, R. W. Lane, and R. H. Holm, *Inorg. Chem.*, 1973, **12**, 2589.
[21] A. Combes, *Compt. rend.*, 1889, **108**, 1252; A. Combes and C. Combes, *Bull. Soc. chim. France*, 1892, **7**, 788; L. Rügheimer, *Ber.*, 1914, **47**, 2759.
[22] D. P. Riley, J. A. Stone, and D. H. Busch, *J. Amer. Chem. Soc.*, 1976, **98**, 1752.

chlorate (V) *and Picrate.*—Perchloric acid (60%, 20 ml) was added to a solution of 3-oxobutyraldehyde 1-(dimethyl acetal) (13 g, 0.1 mol) and aniline (18.8 g, 0.2 mol) in methanol (10 ml), and the solution was heated to *ca.* 60° for 1 h. Addition of ether to the cooled solution caused the *perchlorate* (V) to crystallise (19.5 g, 58%), m.p. 185—187° (from propan-2-ol), $\lambda_{max.}$ 238 and 367 nm (ε 9 400 and 37 700), $\nu_{max.}$ 3 300, 1 640, 1 560, 1 490, 1 330, 1 260, 1 100, and 770 cm^{-1}, τ[$(CD_3)_2CO$] −0.46br (d), 1.28 (1 H, q), 2.4—2.8 (10 H, complex), 3.90 (1 H, d), and 7.24 (3 H, s) (Found: C, 56.9; H, 5.05; N, 8.4. $C_{16}H_{17}ClN_2O_4$ requires C, 57.05; H, 5.05; N, 8.3%). Use of picric acid (wet; *ca.* 60 g) in place of perchloric acid and of ethanol (100 ml)–acetone (100 ml) as solvent gave the *picrate* (67%), m.p. 149—150° (from ethanol) (Found: C, 56.55; H, 4.2; N, 14.75. $C_{22}H_{19}N_5O_7$ requires C, 56.75; H, 4.1; N, 15.05%).

Preparation of Dihydrodiazepinium Salts directly from NN′*-Diphenyldiazapentadienium Salts.*—Solutions of ethylenediamine (or other 1,2-diamines) (3 mmol) in methanol (100 ml) and the diazapentadienium perchlorate (3 mmol) in methanol (100 ml) were added severally over *ca.* 3 h to boiling methanol (500 ml). Evaporation of the solvent *in vacuo* followed by addition of ether promoted the crystallisation of the dihydrodiazepinium perchlorate. In this way were prepared the unsubstituted salt (VIIc) (69%),[5] and the 2-*methyl* (16%), m.p. 182—184° (carefully precipitated from methanol by ether), $\lambda_{max.}$ 330 nm (ε 13 400), $\nu_{max.}$ 3 300, 1 640, 1 570, 1 320, 1 100, and 740 cm^{-1}, τ[$(CD_3)_2CO$] 0.6br, 2.14 (t) and 2.27 (t) (2 H), 4.72 (1 H, t), 5.80br (1 H), 6.26 (2 H, s), and 8.66 (3 H, d) (Found: C, 34.25; H, 5.3; N, 13.1. $C_6H_{11}ClN_2O_4$ requires C, 34.2; H, 5.25; N, 13.3%), 1,4-*dibenzyl* (48%), m.p. 107.5—108.5° (from ethanol), $\lambda_{max.}$ 347 nm (ε 22 800), $\nu_{max.}$ 1 640, 1 570, 1 240, 1 100, 760, and 710 cm^{-1}, τ[$(CD_3)_2CO$] 2.02 (2 H, d), 2.63 (10 H, s), 4.74 (1 H, t), 5.10 (4 H, s, benzyl), and 6.33 (4 H, s) (Found: C, 60.45; H, 5.4; N, 7.45. $C_{19}H_{21}ClN_2O_4$ requires C, 60.55; H, 5.6; N, 7.45%), 1-methyl (48%),[1] 1,4-dimethyl [3] (80%), 5,7-dimethyl [23] (53%), and 2,3-cyclohexano-5,7-dimethyl [17] (33%) perchlorates. The 5-methyl picrate [24] (46%) was prepared similarly from the diazapentadienium picrate.

1H-*Imidazolinium Perchlorates.*—Reaction of the diazapentadienium salt (VIII) with *NN′*-dimethylethylenediamine, *N*-methylethylenediamine, or 1,2-diamino-2-methylpropane as described in the previous section gave, respectively, 1,2,3-*trimethyl-* (IX) (68%), m.p. 242—244° (from ethanol), $\lambda_{max.}$ 235 nm (ε 7 500), $\nu_{max.}$ 1 640, 1 310, 1 100, and 625 cm^{-1}, τ(D_2O) 6.21 (4 H, s), 6.96 (6 H, s), and 7.84 (3 H, s) (Found: C, 34.0; H, 6.5; N, 13.05. $C_6H_{13}ClN_2O_4$ requires C, 33.9; H, 6.1; N, 13.2%), 1,2-*dimethyl-* (53%), m.p. 135.5—136.5° (from propan-2-ol), $\lambda_{max.}$ 226 nm (ε 5 400), $\nu_{max.}$ 3 350, 1 650, 1 600, 1 300, 1 100, and 625 cm^{-1}, τ(D_2O) 6.17 (4 H, s), 6.96 (3 H, s), and 7.83 (3 H, s) (Found: C, 30.1; H, 5.85; N, 14.25. $C_5H_{11}ClN_2O_4$ requires C, 30.25; H, 5.55; N, 14.1%), and 2,4,4-*trimethyl-imidazolinium perchlorates* (80%), m.p. 119—119.5° (from propan-2-ol), $\lambda_{max.}$ 216 nm (ε 6 700), $\nu_{max.}$ 3 300, 1 610, 1 340, 1 100, and 670 cm^{-1}, τ(D_2O) 6.35 (2 H, s), 7.82 (3 H, s), and 8.61 (6 H, s) (Found: C, 33.9; H, 6.2; N, 12.95. $C_6H_{13}ClN_2O_4$ requires C, 33.9; H, 6.1; N, 13.2%).

3,4,5,6-*Tetrahydro-2-methyl-*1H-*pyrimidinium Perchlorate* (XII).—When the diazapentadienium salt (VIII) reacted with 1,3-diaminopropane as described in the previous sections the product (33%) crystallised only with difficulty when cooled to −78°. This *pyrimidinium salt* had m.p. 78—79° (from methanol–ether at −78°), $\lambda_{max.}$ *ca.* 208 nm (ε *ca.* 5 200), $\nu_{max.}$ 3 340, 1 670, 1 630, 1 320, and 1 100 cm^{-1}, τ(D_2O) 6.63 (4 H, t), 7.87 (3 H, s), and 8.06 (2 H, m) (Found: C, 30.45; H, 5.65; N, 13.6%; M^+, 198.084. $C_5H_{11}{}^{35}ClN_2O_4$ requires C, 30.25; H, 5.55; N, 14.1%; *M*, 198.084).

Reaction of Diazapentadienium Salts (II) *with Monoamines.*—Solutions of the amine (6 mmol) in methanol (100 ml) and of the diazapentadienium perchlorate (II) (3 mmol) in methanol (100 ml) were run severally during 3 h into boiling methanol (500 ml). Solvent was then removed *in vacuo*. Addition of ether promoted crystallisation of the product. In this way salt (II; R = H, X = ClO_4) and piperidine gave 5,5-*pentamethylene-*1-*phenyl-*1H-1,5-*diazapentadienium perchlorate* (47%), m.p. 186—187° (from ethanol), $\lambda_{max.}$ 234 and 348 nm (ε 7 600 and 43 200), $\nu_{max.}$ 3 300, 1 630, 1 590, 1 250, 1 100, 1 030, 850, and 770 cm^{-1}, τ(CF_3CO_2H) 1.10br (1 H), 1.94 (1 H, t), 2.31 (1 H, d), 2.5—2.9 (5 H, complex), 4.04 (1 H, t), 6.35br (4 H), and 8.18br (6 H, s) (Found: C, 53.45; H, 5.95; N, 8.8. $C_{14}H_{19}ClN_2O_4$ requires C, 53.4; H, 6.05; N, 8.9%); salt (II; R = Ph, X = ClO_4) and cyclohexylamine gave 5-*cyclohexyl-*1,1-*diphenyl-*1H-1,5-*diazapentadienium perchlorate* (80%), m.p. 217—219° (from propan-2-ol), $\lambda_{max.}$ 230 and 342 nm (ε 16 200 and 58 800), $\nu_{max.}$ 3 200, 1 650, 1 620, 1 580, 1 490, 1 250, 1 220, 1 100, and 710 cm^{-1}, τ(CF_3CO_2H) 1.81 (1 H, m), 2.11 (1 H, d), 2.2—2.9 (10 H, complex), 4.43 (1 H, t), 6.52br (1 H, s), and 7.8—8.8br (10 H, complex) (Found: C, 62.1; H, 6.2; N, 6.7. $C_{21}H_{25}ClN_2O_4$ requires C, 62.3; H, 6.2; N, 6.9%); salt (II; R = Ph, X = ClO_4) and piperidine gave 5,5-*pentamethylene-*1,1-*diphenyl-*1H-1,5-*diazapentadienium perchlorate* (86%), m.p. 207—208° (from ethanol), $\lambda_{max.}$ 230 and 344 nm (ε 11 700 and 44 800), $\nu_{max.}$ 1 630, 1 570, 1 250, 1 100, 1 010, 780, and 710 cm^{-1}, τ(CF_3CO_2H) 1.80 (1 H, d), 2.18 (1 H, d), 2.4—2.9 (10 H, complex), 4.51 (1 H, t), 6.28br and 6.56br (4 H, s), 8.22br (6 H, s) (Found: C, 58.6; H, 5.85; N, 6.7. $C_{20}H_{23}ClN_2O_4,H_2O$ requires C, 58.75; H, 6.1; N, 6.85%). The latter compound was also prepared without recourse to high dilution techniques by addition of a solution of piperidine (0.51 g, 6 mmol) in methanol (20 ml) to a solution of the salt (II) (1.43 g, 3 mmol) in methanol (100 ml). Evaporation of solvent, followed by addition of ether, provided the product (1.1 g, 95%).

1,1;5,5-*Bispentamethylene-*1H-1,5-*diazapentadienium Perchlorate.*—A solution of 5,5-pentamethylene-1,1-diphenyl-1*H*-1,5-diazapentadienium perchlorate (0.20 g, 0.5 mmol) and piperidine (0.25 g, 3 mmol) in methanol (10 ml) was heated under reflux for 20 min. Solvent was evaporated *in vacuo* and addition of ether caused crystallisation of the perchlorate (0.14 g, 92%), m.p. 131—132.5° (from ethanol) (lit.,[25] 130—131°), $\lambda_{max.}$ 315 nm (ε 60 900), τ[$(CD_3)_2CO$] 2.21 (2 H, d), 4.21 (1 H, t), 6.34br (8 H, s), and 8.27br (12 H, d).

Kinetic Studies of Reactions of Salts (II) *with Piperidine.*—Reactions were carried out in methanol (AnalaR grade) at 25°. Reactions of salt (II; R = Ph, X = ClO_4) were followed at 390 nm on solutions which were 2.1×10^{-5}M in salt, and 2.5×10^{-3} and 2.0×10^{-2}M in piperidine and 2-methylpiperidine, respectively. Reactions of the salt (II; R = H, X = ClO_4) were followed at 340 nm on solutions which were 2.4×10^{-5}M in salt and 0.25M in piperidine.

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The reactions obeyed first-order kinetics for at least three half-lives.

1,1;5,5-Bispentamethylene-3-phenyl-1H-1,5-diazapentadienium Perchlorate (XIV).—Piperidine (1.7 g, 20 mmol) was added to a solution of 1,1,5,5-tetramethyl-3-phenyl-1*H*-1,5-diazapentadienium perchlorate (XIII) [9] (0.91 g, 3 mmol) in methanol (20 ml), and the mixture was heated under reflux for 30 min. Solvent was evaporated *in vacuo* and ether was added. The *perchlorate* (XIV) (1.00 g, 87%) had m.p. 231—232° (decomp.) (from methanol), $\lambda_{max.}$ 315 nm (ε 21 100), $\nu_{max.}$ 1 590, 1 470, 1 300, 1 280, 1 220, 1 100, 1 020, 760, and 730 cm^{-1}, τ[$(CD_3)_2SO$] 2.31 (2 H, s), 2.4—2.8 (5 H, complex), 6.42br (4 H, s), 7.19br (4 H, s), and 8.1—8.9br (12 H, complex) (Found: C, 59.55; H, 7.25; N, 7.3. $C_{19}H_{27}ClN_2O_4$ requires C, 59.6; H, 7.05; N, 7.3%).

2,3-Dihydro-6-phenyl-1,4-diazepinium Perchlorate (VIIb).—A solution of ethylenediamine (0.18 g, 3 mmol) and the diazapentadienium salt (XIII) [9] (0.91 g, 3 mmol) in methanol (20 ml) was heated under reflux for 20 min. Solvent was evaporated *in vacuo* and ether was added. The perchlorate (0.79 g, 96%) had m.p. 179—180° (from ethanol), $\lambda_{max.}$ 246 and 352 nm (ε 10 900 and 7 400), $\nu_{max.}$ 3 300, 1 650, 1 600, 1 550, 1 320, 1 100, 770, and 710 cm^{-1}, τ[$(CD_3)_2CO$] 0.7br, 1.93 (2 H, s), 2.66 (5 H, complex), and 6.04 (4 H, s), $J_{1.7}$ [$(CD_3)_2CO$–CF_3CO_2H] 7.8 Hz (Found: C, 48.4; H, 4.9; N, 10.2. $C_{11}H_{13}ClN_2O_4$ requires C, 48.45; H, 4.75; N, 10.3%).

Preparation of Dihydrodiazepinium Perchlorates via the 1,5-Diazapentadienium Salt (XV).—The *NN'*-diphenyldiazapentadienium salt (II; R = H, X = ClO_4) (0.32 g, 1 mmol) was dissolved in methanol (15 ml). The solution was heated under reflux and ammonia was passed through it for 30 min. A solution of ethylenediamine (0.06 g, 1 mmol) in methanol (5 ml) was then added in one portion and heating was continued for 5 min. Addition of ether to the cooled solution precipitated 2,3-dihydrodiazepinium perchlorate (0.12 g, 61%), m.p. 265° (decomp.) [lit.,[5] 250° (decomp.)], $\lambda_{max.}$ 330 nm (lit.,[5] 331 nm), i.r. spectrum identical with that of an authentic sample. In similar fashion were prepared the following derivatives: 1,4-*dimethyl* (76%), m.p. and mixed m.p. 95—97° (lit.,[3] 98—99°); 2,3-*cyclohexano* (56%), m.p. 136—138° (reprecipitated from methanol by ether), $\lambda_{max.}$ 330 nm (ε 12 800), $\nu_{max.}$ 3 300, 1 640, 1 590, 1 550, 1 280, 1 260, and 1 100 cm^{-1}, τ[$(CD_3)_2CO$] 0.95br, 2.32 (2 H, d), 4.77 (1 H, t), 6.70 (2 H, complex), 8.0—8.8 (8 H, complex), $J_{5.6}$ 7.8 Hz, $J_{1.7}$ [$(CD_3)_2CO$–CF_3CO_2H] *ca.* 7.6 Hz (Found: C, 43.2; H, 6.2; N, 11.2. $C_9H_{15}ClN_2O_4$ requires C, 43.1; H, 6.0; N, 11.2%); 2,2-*dimethyl* (53%) (initially separates as an oil which slowly solidifies), m.p. 84—87° (reprecipitated from acetone by ether), $\lambda_{max.}$ 327 nm, $\nu_{max.}$ 3 300, 1 640, 1 580, 1 550, 1 320, and 1 100 cm^{-1}, τ[$(CD_3)_2CO$] 2.13 (1 H, d), 2.38 (1 H, d), 4.70 (1 H, t), 6.42br (2 H, s), 8.61br (6 H, s), $J_{5.6}$ 8.2 Hz, $J_{5.7}$ *ca.* 1 Hz (Found: C, 36.9; H, 6.0; N, 12.65. $C_7H_{13}ClN_2O_4$ requires C, 37.4; H, 5.8; N, 12.45%). The two latter salts were highly soluble and their purification was difficult; the following method was moderately satisfactory. The crude product was dissolved in a small quantity of methanol, and about three times the volume of ether was added. The liquors were decanted from precipitated tar and swamped with ether, whereupon the dihydrodiazepinium salts solidified.

2,3-Dihydro-5-methyl-1,4-diazepinium Picrate (VIIe; X = *picrate*).—Ammonia was passed through a solution of 2-methyl-1,5-diphenyl-1*H*-1,5-diazapentadienium picrate (0.47 g, 1 mmol) in boiling methanol (15 ml) for 45 min. A solution of ethylenediamine (0.06 g, 1 mmol) in methanol (5 ml) was then added in one portion, and the mixture was heated under reflux for 1 h. Solvent was then partially evaporated and addition of ether to the residue gave the diazepinium picrate (0.26 g, 77%), m.p. 144—145° (from ethanol).

Preparation of a Dihydrodiazepinium Salt from a β-Chlorovinylaldehyde.—2-Chlorocyclopent-1-enecarbaldehyde [15] was converted into a diazapentadienium chloride by treatment with aniline.[14] This chloride (1.0 g) was covered with perchloric acid (70%) and the resultant sludge was recrystallised from ethanol to give the *diazapentadienium perchlorate* (XVI) (0.96 g, 83%), m.p. 209—210° (decomp.) (Found: C, 59.5; H, 5.5; N, 7.6. $C_{18}H_{19}ClN_2O_4$ requires C, 59.6; H, 5.25; N, 7.7%). Ammonia was passed through a solution of this perchlorate (XVI) (0.36 g, 1 mmol) in methanol (25 ml), heated under reflux, for 30 min. Ethylenediamine (0.06 g, 1 mmol) in methanol (5 ml) was then added and heating was continued for 30 min. The hot solution was then shaken with activated charcoal, and filtered. Solvent was removed *in vacuo*. Addition of ether to the residue gave an oil which was washed twice with ether. Overnight the *perchlorate* (XVII) crystallised (0.20 g, 84%) and had m.p. 80—82° (carefully reprecipitated from methanol by ether), $\lambda_{max.}$ 348 nm (ε 12 000), $\nu_{max.}$ 3 300, 1 650, 1 550, 1 500, 1 300, 1 250, and 1 100 cm^{-1}, τ[$(CD_3)_2CO$] 2.25 (1 H, s), 6.19 (4 H, s), 7.10 and 7.23 (4 H, 2t), 8.03 (2 H, m), $J_{1.7}$ [$(CD_3)_2CO$–CF_3CO_2H] 7.8 Hz (Found: C, 39.85; H, 5.85; N, 12.05. $C_8H_{13}ClN_2O_4$ requires C, 40.6; H, 5.5; N, 11.85. $C_8H_{13}ClN_2O_4,\frac{1}{4}H_2O$ requires C, 39.85; H, 5.6; N, 11.6%).

Dihydrodiazepinium Salts from Oxoenamines.—Solutions of ethylene diamine (0.6 g, 10 mmol) and the oxoenamines (XVIIIa) [10c] (1.02 g, 10 mmol) or (XVIIIb) [16] (1.75 g, 10 mmol) in acetic acid (1 ml) were heated to *ca.* 120° for 15 min. Addition of perchloric acid to the cooled solution gave, respectively 59 and 68% of the dimethyldihydrodiazepinium salt (VIIf),[23] m.p. and mixed m.p. 141—142°.

Methylation of Oxoenamines.—A molar equivalent of methyl fluorosulphonate was added to a solution of the oxoenamine in methylene chloride. In most cases a vigorous reaction ensued. The mixture was kept at room temperature for 30 min. Addition of ether completed the crystallisation of the products. By this means the following azaoxapentadienium fluorosulphonates were prepared: 2,4-*dimethyl* (IIIb) (90%), m.p. 101—103° (from propan-2-ol), $\lambda_{max.}$ 290 nm (ε 19 200), $\nu_{max.}$ 3 350, 3 150, 1 600, 1 300, 1 070, 830, and 720 cm^{-1}, τ[$(CD_3)_2SO$] −0.58br, 0.00br, 4.49 (1 H, s), 5.94 (3 H, s), 7.68 (6 H, s), δ_C 19.48 (R^2), 23.33 (R^4), 57.99 (R^1), 98.05 (C-3), 177.04, and 181.04 (C-2, -4) (Found: C, 34.05; H, 5.75; N, 6.5. $C_6H_{12}FNO_4S$ requires C, 33.8; H, 5.65; N, 6.55%); 2-*phenyl*-4-*methyl* (IIIc) (84%; reaction was slower and the mixture was kept overnight before work-up), m.p. 97—99° (reprecipitated from acetone by ether), $\lambda_{max.}$ 303 nm (ε 21 200), $\nu_{max.}$ 3 340, 3 100, 1 570, 1 300, 1 270, 1 070, and 730 cm^{-1}, ^1H n.m.r. [$(CD_3)_2SO$] shows two configurations (a) τ −0.9br, 2.3—2.6 (5 H, complex), 3.83 (1 H, s), 6.02 (3 H, s), and 8.18 (3 H, s) and (b) τ −0.9br, 2.3—2.6 (5 H, complex), 4.17 (1 H, s), 6.11 (3 H, s), and 7.47 (3 H, s), δ_C 21.98, 23.56 (R^4), 58.37, 60.71 (R^1), 98.76, 102.41 (C-3), 128.43, 128.97, 129.13, 131.71, 131.95, 132.03, 133.81 (Ph), 176.93, 178.19, 179.26, and 181.68 (C-2, -4) (Found: C, 48.05; H, 5.1; N, 5.05. $C_{11}H_{14}FNO_4S$ requires C, 48.0; H, 5.1; N, 5.1%); and 2,3,4-*trimethyl* (90%), m.p. 99—101° (from propan-2-ol),

$\lambda_{max.}$ 305 nm (ε 15 900), $\nu_{max.}$ 3 340, 3 160, 1 570, 1 520, 1 290, 1 220, 1 180, 1 170, and 720 cm^{-1}, τ[$(CD_3)_2SO$] −0.77br, −0.03br, 5.98 (3 H, s), 7.61 (3 H, s), 7.68 (3 H, s), and 8.16 (3 H, s) (Found: C, 37.15; H, 6.4; N, 6.15. $C_7H_{14}FNO_4S$ requires C, 37.0; H, 6.15; N, 6.15%).

6-Aza-3,5-dimethyl-6-phenyl-2-oxahexa-2,4-dienium Fluorosulphonate.—Prepared as described in the previous paragraph from 4-anilinopent-3-en-2-one [10b] this salt (80%) had a complex n.m.r. spectrum indicating a variety of configurations, m.p. 92—94° (reprecipitated from propan-2-ol by ether), $\lambda_{max.}$ 310 nm, $\nu_{max.}$ 3 240, 3 050, 1 610, 1 570, 1 390, 1 310, 1 260, 1 070, 1 040, and 720 cm^{-1} (Found: C, 49.35; H, 5.55; N, 4.95. $C_{12}H_{16}FNO_4S$ requires C, 49.85; H, 5.55; N, 4.85%).

Preparation of Dihydrodiazepinium Salts from Azaoxapentadienium Salts.—A molar equivalent of diamine was added to a solution of the azaoxapentadienium salt in ethanol. After 5 min ether was added to complete the precipitation of the dihydrodiazepinium salt, as follows: 5,7-dimethyl tetrafluoroborate (VIIf; X = BF_4) [from (IIIa), 81%]; *5,7-dimethyl fluorosulphonate* (VIIf; X = FSO_3) [from (IIIb), 78%, from the *N*-phenyl derivative of (IIIb), 76%], m.p. 133—135° (from propan-2-ol) (Found: C, 37.65; H, 5.8; N, 12.6. $C_7H_{13}FN_2O_3S$ requires C, 37.5; H, 5.8; N, 12.5%); *5-methyl-7-phenyl fluorosulphonate* (VIIg; X = FSO_4) [from (IIIc), the reaction mixture being boiled for 2 min and then filtered through Hyflo Supercel, 68%], m.p. 137—139° (Found: C, 50.55; H, 5.35; N, 9.7. $C_{12}H_{15}FN_2O_3S$ requires C, 50.35; H, 5.25; N, 9.8%); 1,4,5,7-tetramethyl tetrafluoroborate (VIIa; X = BF_4) [from (IIIa), 38%]; *1,4,5,7-tetramethyl fluorosulphonate* (VIIa; X = FSO_3) [from (IIIb), 87%], m.p. 109—110° (from propan-2-ol) (Found: C, 42.95; H, 7.0; N, 11.35. $C_9H_{17}FN_2O_3S$ requires C, 42.85; H, 6.75; N, 11.1%); *1,4,5-trimethyl-7-phenyl fluorosulphonate* (VIIh; X = FSO_3), m.p. 96—97° (from propan-2-ol), $\lambda_{max.}$ 256 and 345 nm (ε 5 800 and 20 600), $\nu_{max.}$ 1 590, 1 530, 1 400, 1 290, 1 070, and 710 cm^{-1}, τ[$(CD_3)_2SO$] 2.4—2.6 (5 H, complex), 4.88 (1 H, s), 6.13br (4 H, s), 6.63 (3 H, s, 4-Me), 6.95 (3 H, s, 1-Me), and 7.70 (3 H, s, 5-Me) (Found: C, 53.7; H, 6.15; N, 8.75. $C_{14}H_{19}FN_2O_3S$ requires C, 53.5; H, 6.05; N, 8.9%).

2,3-Dihydro-1,5-dimethyl-7-phenyl-1,4-diazepinium Fluorosulphonate (VIIj).—Reaction of the azaoxapentadienium salt (IIIc) with *N*-methylethylenediamine provided a mixture of the 1,5-dimethyl-7-phenyl (85%) and 1,7-dimethyl-5-phenyl (15%) fluorosulphonates. The minor product had τ[$(CD_3)_2SO$] 0.2br, 2.46 (5 H, complex), 4.58 (1 H, s), 6.26br (4 H, s), 6.62 (3 H, s), and 7.64 (3 H, s). Recrystallisation from propan-2-ol provided the *1,5-dimethyl-7-phenyl* salt (67%), m.p. 157—159°, τ[$(CD_3)_2SO$] 0.2br, 2.46 (5 H, complex), 4.98 (1 H, s), 6.26br (4 H, s), 6.92 (3 H, s), and 7.73 (3 H, s) (Found: C, 52.35; H, 5.85; N, 9.25. $C_{13}H_{17}FN_2O_3S$ requires C, 52.0; H, 5.65; N, 9.35%).

Preparation of Macrocyclic Salts (XXII) (*with* K. S. Tucker).—Ethylenediamine (0.6 g, 10 mmol) was added directly to a solution of the bisazaoxapentadienium salt (XXa) [20] (4.7 g, 10 mmol) in methanol (200 ml), and the mixture was heated briefly to boiling. Addition of ether to the cooled solution completed the separation of *5,7,12,14-tetramethyl-1,4,8,11-tetra-azatetradecadienedi-ium* (XXIIa) 3.19 g, 76%), m.p. 200—203°, $\lambda_{max.}$ 295 nm, $\nu_{max.}$ 3 360, 1 550, 1 300, 1 230, and 1 050 cm^{-1} (Found: M^+, 248.199. $C_{14}H_{24}N_4$ requires *M*, 248.200) (Found: C, 38.9; H, 6.45; N, 12.75. $C_{14}H_{26}B_2F_8N_4,\frac{1}{2}H_2O$ requires C, 38.85; H, 6.25; N, 12.95%). Treatment of the salt (0.5 g) with aqueous sodium hydroxide (4M, 20 ml) and extraction with chloroform (4 × 200 ml), followed by washing the extract with water, drying (Na_2SO_4), and evaporation of solvent, gave the base.[20] Prepared in a similar way were the *salt* (XXIIb) (80%), m.p. 240—244°, τ[$(CD_3)_2SO$] 0.75—0.9br (4 H), 4.10—4.20br (2 H), 6.6—6.7 (8 H, m), and 7.64 (12 H, s) (Found: C, 37.55; H, 6.05; N, 12.65. $C_{19}H_{26}F_2N_4O_6S_2$ requires C, 37.45; H, 5.8; N, 12.95%) and the *salt* (XXIIc) (83%), m.p. 128—130° (from ethanol) (Found: C, 50.35; H, 5.3; N, 9.85. $C_{24}H_{30}F_2N_4O_6S_2$ requires C, 50.3; H, 5.3; N, 9.8%). The bisazaoxapentadienium salts were prepared (in 90—95% yield) by adding two mol. equiv. of methyl fluorosulphonate to a solution of the bisoxoenamine (XXI) in methylene chloride. Compound (XXI; R = Me) reacted exothermically; the mixture from (XXIc) was kept overnight. Addition of ether completed the separation of the methylated products.

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