The Preparation and Properties of a Series of 1,2,5-Triazapentadienium Salts

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A series of 1,2,5-triazapentadienium salts has been made by the condensation of ammonium salts with monohydrazones of 1,2-dicarbonyl compounds. Their u.v., ^1H, ^{13}C, and variable-temperature n.m.r. spectra are compared with those of some related salts. These studies indicate that the interaction of *N*-phenyl substituents with the conjugated system is more efficient at the 1- than at the 5-position. Deuterium exchange occurs at the 3-position, but attempts to observe substitution reactions with other electrophiles failed. Displacement of the terminal amino-function takes place by reaction of *N*-nucleophiles at the 4-position.

THE properties of 1,5-diazapentadienium or vinamidinium cations (1) have been extensively studied over the past 10 years.[1] In general, their chemical reactions are dependent on the pronounced charge alternation in the system, which renders their 2(4) positions open to nucleophilic attack and the 3-position to reaction with electrophiles. The former mode of reaction is especially important, since derivatives have been used as three-carbon synthons for the preparation of a variety of cyclic compounds.[1] Alternatively, reaction with electrophiles is of theoretical interest, since many classic aromatic-type substitution reactions may be carried out.[2,3] For this reason, vinamidines have been cited as examples of ' quasi-aromatic '[4] or ' medeidic '[5] compounds, the latter term emphasising the particular stability of the system.

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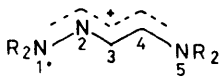

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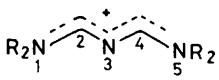
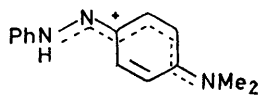


(3)

In this context, the two possible azavinamidinium cations (2) and (3) represent quasi-aromatic analogues of pyridine and it is of some interest to consider the effect of the replacement of CH by N on the properties of the system.

Simple 1,3,5-triazapentadienium salts (3) were first prepared by Gold,[6] and have since been isolated as side products in certain vinamidine reactions.[7,8] They have found some application in synthesis,[9,10] and the ^1H n.m.r. spectrum of one derivative has been discussed in detail.[11] However, prior to this study, only one simple



(4)

example of the isomeric 1,2,5-triazapentadienium system (2) had been isolated,[12] despite the fact that heavily substituted derivatives have been known since last century,[13] and that vinylogues include the well characterised azacyanines,[14] and even the acid form of Methylene Blue (4). This paper describes an easy synthesis of a series of salts (2), and discusses their spectroscopic and chemical properties with particular reference to those of the related compounds (1) and (3).

2-Azavinamidines are effectively mixed hydrazone-imines of α-dicarbonyl compounds. Consequently, the salts (7)—(11) were readily prepared in high yield by the action of the appropriate ammonium salt on the glyoxal monohydrazone. The 1,1-dimethyl compounds (7)—(9) were made in a ' one-pot ' reaction without isolation of the intermediate monohydrazone, but reaction of the monohydrazone of biacetyl with anilinium perchlorate under conditions which led to the successful isolation of the glyoxal derivative (11) gave only 10—15% conversion into the salt (12) despite extended reaction times. The condensation proceeded smoothly in acetic acid solution, however, and this provides evidence for

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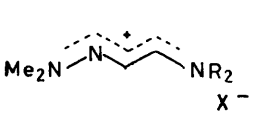
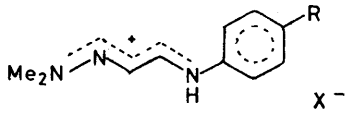
[1] D. Lloyd and H. McNab, *Angew. Chem.*, 1976, **88**, 496; *Angew. Chem. Internat. Edn.*, 1976, **15**, 459.
[2] J. Kůcera and Z. Arnold, *Coll. Czech. Chem. Comm.*, 1967, **32**, 1704.
[3] D. Lloyd, H. P. Cleghorn, and D. R. Marshall, *Adv. Heterocyclic Chem.*, 1974, **17**, 1.
[4] D. Lloyd and D. R. Marshall, *Chem. and Ind.*, 1964, 1760.
[5] D. Lloyd and D. R. Marshall, *Angew. Chem.*, 1972, **84**, 447; *Angew. Chem. Internat. Edn.*, 1972, **11**, 404.
[6] H. Gold, *Angew. Chem.*, 1960, **72**, 956.
[7] V. Krchňák and Z. Arnold, *Coll. Czech. Chem. Comm.*, 1974, **39**, 3327.
[8] V. Krchňák and Z. Arnold, *Coll. Czech. Chem. Comm.*, 1975, **40**, 1384.
[9] R. Kirchlechner and C. Jutz, *Angew. Chem.*, 1968, **80**, 367; *Angew. Chem. Internat. Edn.*, 1968, **7**, 376.
[10] C. Jutz, R. M. Wagner, and H. G. Löbering, *Angew. Chem.*, 1974, **86**, 781; *Angew. Chem. Internat. Edn.*, 1974, **13**, 737.
[11] G. Scheibe, W. Seiffert, H. Wengenmayr, and C. Jutz, *Ber. Bunsengesellschaft Phys. Chem.*, 1963, **67**, 560.
[12] (*a*) T. Severin, R. Adam, and H. Lerche, *Chem. Ber.*, 1975, **108**, 1756; (*b*) T. Severin and H. Lerche, *Chem. Ber.*, 1976, **109**, 1171; (*c*) see, however, R. Brehme and H. E. Nikolajewski, *Z. Chem.*, 1968, **8**, 226.
[13] (*a*) E. von Meyer, *J. prakt. Chem.*, 1895, **52**, 81; (*b*) E. von Meyer, *J. prakt. Chem.*, 1908, **78**, 497.
[14] F. M. Hamer, ' Cyanine Dyes and Related Compounds,' Wiley–Interscience, New York, ch. 12, 1964.

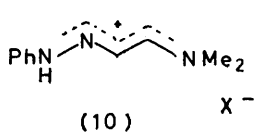
the pH-dependence of the reaction equilibria, a phenomenon which is common in related condensations.[15] Attempted extension of this principle to the benzil series was unsuccessful. The 1,1,5,5-tetra-alkyl derivatives



(5) R = Me
(6) R = $-(CH_2)_5-$



(7) R = H
(8) R = Me
(9) R = NO_2



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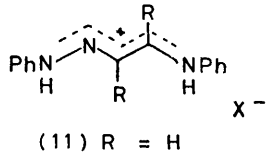
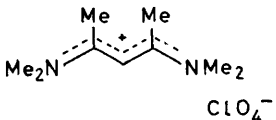


(11) R = H
(12) R = Me

X = ClO_4 and/or picrate

(5) and (6) were prepared from the 5-phenyl derivative (7) through displacement of aniline by the action of the appropriate alkylamine.

In their u.v. spectra, the 2-azavinamidinium salt (5) ($\lambda_{max.}$ 329 nm) shows a bathochromic shift, and the 3-azavinamidinium salt (3; R= Me) ($\lambda_{max.}$ 268 nm [6]) shows a hypsochromic shift relative to the 'parent' system (1; R = Me) ($\lambda_{max.}$ 310 nm [2]). Such behaviour on 'substitution' at sites of varying electron density is consistent with previously reported effects in the spectra of related compounds.[16] Regular shifts are also found within the series of 2-azavinamidinium salts itself. For example, from the values of the bathochromic shifts in the spectra of the *N*-phenyl derivatives (7) and (10) it is possible to estimate the maximum of the 1,5-diphenyl compound (11) [$\lambda_{max.}$ 450 nm; $\lambda_{max.}$(calc.) 453 nm]. However, the spectrum of the 3,4-dimethyl-1,5-diphenyl compound (12) is anomalous on this basis since the maximum is little shifted from that of the 1-phenyl derivative (10). It is probable that the 5-phenyl substituent in (12) is twisted out of plane by the adjacent methyl group, so destroying its conjugative interaction with the chromophore. Similar phenomena have been observed most spectacularly in the spectra of the vinamidinium salts (13) and (14), which have maxima at 345 [2] and 346 nm [17] respectively.



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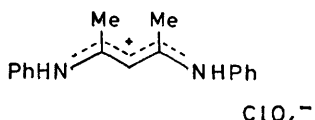


(14)

I.r. spectroscopy is of little diagnostic value in these series. All the 2-azavinamidinium salts had absorptions in the range 1 620—1 650 cm^{-1}, as found in vinamidinium spectra. Those compounds with NH groups gave peaks in the range 3 000—3 300 cm^{-1}, usually showing multiple absorptions.

In contrast, ^1H and ^{13}C n.m.r. spectroscopy have been used extensively in vinamidine chemistry, as probes both of the electronic structure and of the configuration of the system,[18,19] and the techniques also provide valuable information in the azavinamidine series. As expected, the nuclear positions of both 2- and 3-azavinamidinium salts resonate at lower field than in the corresponding vinamidinium compound, although the effects are less dramatic for the 2(4)-positions, especially in the ^{13}C n.m.r. spectra (Table 1). The downfield shift of the 3-position in the 2-azavinamidinium salt (5) is quantitatively similar to the deshielding of the pyridine α-position, relative to benzene.

TABLE 1

^{13}C N.m.r. spectra of 2-azavinamidinium salts [a]

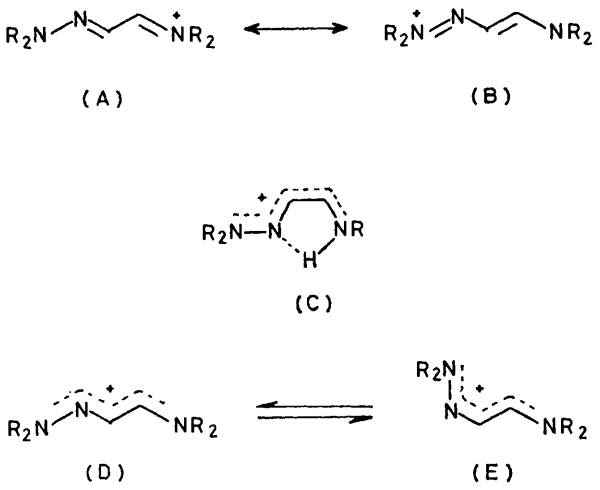
Compound	δ(3)	δ(4)	δ(α)	δ(o)	δ(m)	δ(p)	δ(*N*–Me)
(5)	118.09	162.67					49.26
							46.88
							[b]
(7)	120.14	156.95	136.64	118.22	129.17	126.99	*ca.* 45.9 (br)
(10)	125.37	163.32	140.50	114.69	128.93	124.29	40.71
							47.77
(11)	127.93	157.95	140.47	115.15	129.06	124.83	
			136.94	118.00	129.22	127.20	

[a] Recorded for solutions in [$^2H_6$]dimethyl sulphoxide. [b] Other *N*-methyl signals not apparent.

The effect of *N*-phenyl groups on the n.m.r. spectra of the vinamidinium systems is of particular interest, since it is well known that these substituents can interact conjugatively only by electron-withdrawal.[18,19] The shift to lower field of the signals due to the 3-position in these salts is consistent with this picture, as is the relatively high field position of the *p*-carbon resonances

[15] D. Lloyd and D. R. Marshall, *J. Chem. Soc.*, 1956, 2597.
[16] C. Barnett, D. R. Marshall, and D. Lloyd, *J. Chem. Soc.* (*B*), 1968, 1536.
[17] D. Lloyd and H. McNab, unpublished work.
[18] D. Lloyd, R. K. Mackie, H. McNab, and D. R. Marshall, *J.C.S. Perkin II*, 1973, 1729.
[19] D. Lloyd, R. K. Mackie, H. McNab, K. S. Tucker, and D. R. Marshall, *Tetrahedron*, 1976, **32**, 2339.

of compounds (7) and (10). As in the u.v. spectra, these effects are additive, and calculated values for the 1,5-diphenyl derivative (11) are in good agreement with experiment. It is also clear that the electron-withdrawing effect is much more pronounced in the 1-phenyl derivative (10) than the 5-phenyl isomer (7) (see Table 1),



which suggests that conjugation is more efficient in the former case. Although this may simply reflect the relative planarity of the aryl groups of the two compounds, a more probable explanation is that the π-electron density itself is greater at the 1- than at the 5-position, *i.e.* that the hydrazone hybrid (A) is preferred over the azonium hybrid (B). This might be expected intuitively, since in the unfavoured form (B), the positive charge is carried by the atom adjacent to the aza-nitrogen.

One consequence of this picture is that the (*N*,*N*)-1,2-bond in the 2-azavinamidinium salts would have less double-bond character than the 4,5-bond, and so there might be indication of a specific exchange phenomenon. There is some preliminary evidence of this from the ^{1}H n.m.r. spectra of the isomers (7) and (10), since the former shows a single broad peak for the *N*-methyl groups (τ 6.34), while these appear as discrete singlets (τ 6.16 and 6.34) in the spectrum of the latter compound. However, a more general picture of the phenomenon is available from a study of the temperature dependence of these signals, and the data are summarised in Table 2. Thus, the tetramethyl derivative (5) shows four *N*-methyl singlets at room temperature in [$^2H_6$]acetone, but two of these (at τ 6.30 and 6.57) are considerably broadened at 55 °C. These are assigned as the 1,1-dimethyl groups, by analogy both with the above spectra of the *N*-phenyl derivatives, and with the spectrum of the 5,5-pentamethylene salt (6). At higher temperatures, in [$^2H_6$]dimethyl sulphoxide, the broadened peaks of (5) reappear as a singlet indicating that rotation around the 1,2-bond is now fast on the n.m.r. time scale. Unfortunately, the corresponding rotation about the 4,5-bond could not be observed in the same compound because of its complete decomposition above 120 °C, but the available data may be compared with those for the analogous process in the vinamidinium salt (1; R = Me) ($\Delta G^{\ddagger}$ 90 kJ mol^{-1} [20]), and the 3-azavinamidinium (3; R = Me), for which no coalescence behaviour was observed at temperatures up to 160 °C, equivalent to $\Delta G^{\ddagger} \gg 95$ kJ mol^{-1}. Substitution by a phenyl group at the 1- or 5-position causes a general [20] reduction in the activation energy for rotation. This result is surprising, since conjugation with the phenyl group would tend to favour the ' non-rotating ' canonical forms (B) in the case of (7) and (A) in the case of (10), but it is possible that the reduction in the overall electron density in the pentadienium system due to the phenyl group is sufficient to cause this effect. In addition to $\Delta G^{\ddagger}$, the following parameters were calculated for the 5-phenyl derivative (7), from line-width measurements in the range T_c to (T_c + 20) °C: $\Delta H^{\ddagger}$ 28.6 kJ mol^{-1}, $\Delta S^{\ddagger}$ −88 J mol^{-1} K^{-1}, E_a 30.6 kJ mol^{-1}. The magnitude of $\Delta S^{\ddagger}$ is unexpectedly large and may be due to systematic errors, but its sign is consistent with extensive charge localisation in the transition state. The effect of substituents within the 5-aryl ring was also briefly investigated. In particular, the dramatic increase in $\Delta G^{\ddagger}$ for the *p*-nitro-compound (9) may be correlated with the increased importance of the resonance form (B)

TABLE 2

Variable-temperature ^{1}H n.m.r. spectra of 2-azavinamidinium salts [a]

Compound	T_c/°C	$\Delta G^{\ddagger}$/kJ mol^{-1}
(5) [b]	68	71.9
	>120	>86.2
(7)	−27	50.3
(8)	−35	49.3
(9)	>60	>70.2
(10) [b]	66	73.3

[a] Recorded for solutions in [$^2H_6$]acetone unless stated otherwise. [b] [$^2H_6$]Dimethyl sulphoxide solution.

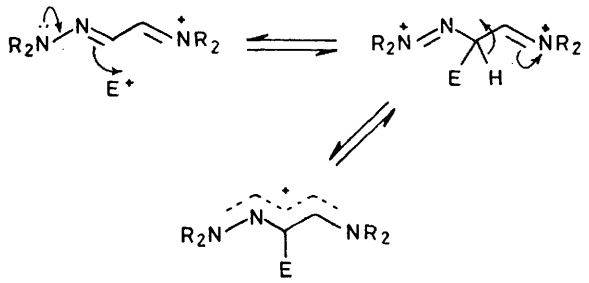
relative to the 5-phenyl derivative itself. This example excludes the possibility of a slow nitrogen inversion at the 2-position as an alternative explanation of these exchange processes. It is also relevant to note that similar exchange phenomena have been observed in the linear triazene series,[21] of which the present salts are vinylogues.

Throughout this discussion, an all-*trans*-structure has been tacitly assumed for the 2-azavinamidinium salts, by analogy with the well documented vinamidinium series,[1,22] for which J_{vic} is generally *ca.* 8 Hz and *ca.* 13 Hz for *cis*- and *trans*-systems respectively.[18,23] The observation of $J_{4,5}$ (where possible) in the 2-azavinamidinium series under mildly [18] acidic conditions confirms both the relative assignment of the 3- and 4-protons, and, from

[20] M. L. Filleux-Blanchard, D. le Botlan, A. Reliquet, and F. Reliquet-Clesse, *Org. Magnetic Resonance*, 1974, **6**, 471.
[21] N. P. Marullo, C. B. Mayfield, and E. H. Wagener, *J. Amer. Chem. Soc.*, 1968, **90**, 510.
[22] B. W. Matthews, R. E. Steinkamp, and P. M. Colman, *Acta Cryst.*, 1973, **B29**, 449.
[23] S. Dähne and J. Ranft, *Z. Phys. Chem.*, 1963, **224**, 65.

the size of the coupling constant ($J_{4,5}$ *ca.* 15 Hz) that the stereochemistry about this bond is indeed *trans*. However, the much lower value of $J_{3,4}$ (*ca.* 10 Hz) might be indicative of a *cis*-arrangement, a situation which would be especially favourable in the cases of the 5*H* compounds, due to possible hydrogen bonding (structure C) (*cf.* refs. 24 and 25). However, since $J_{3,4}$ is unchanged throughout the series, even for 5,5-disubstituted examples where there is no possibility of such energetic advantage, it seems more likely that a *trans*-geometry is favoured, but that the magnitude of $J_{3,4}$ is smaller than expected due to the well known [26] effect of an adjacent electronegative substituent. Nothing can be deduced about the arrangement of the 1,2-bond, and in any case nitrogen inversion would interconvert the two possibilities (D) and (E).

In general, the 3- and 4-proton resonances of the 2-azavinamidinium salts are shifted upfield by 0.2—0.5 p.p.m. in trifluoroacetic acid solution by comparison with their positions in [$^2H_6$]acetone and so substantial protonation of the system may be ruled out under these conditions. However, slow deuterium exchange at the



SCHEME

3-position does take place in [^{2}H]trifluoroacetic acid, by a mechanism presumably parallel to that of the vinamidine series (Scheme). Semi-quantitative studies using [$^2H_2$]sulphuric acid indicated that the exchange reaction for the tetramethyl compound (5) was slower by a factor of *ca.* 10^4 than that for the vinamidinium salt (1; R = Me).[27] These results also contrast with deuterium exchange processes in the pyridine series, which take place exclusively at the β-position: indeed there was no evidence of reaction at the 4 (β)-position of the salt (5), even after four weeks in 50% [$^2H_2$]sulphuric acid, an experiment which incidentally shows the high stability of this derivative towards acid hydrolysis.

For reasons of solubility, [^{2}H]trifluoroacetic acid was used as the solvent in a qualitative study of the deuterium exchange reaction in the 2-azavinamidinium salts (5), (7), and (10). As expected, the electron-withdrawing nature of the *N*-phenyl groups caused a reduction in rate, with the effect being greater for the 1-phenyl substituent. Thus the reaction, which was essentially complete in <12 h for the tetramethyl compound (5) only approached completion after *ca.* 300 h in the 5-phenyl case (7), while >1 200 h were required for the 1-phenyl isomer (10).

A number of reactions with other electrophiles were carried out in an attempt to prepare 3-bromo- or 3-nitro-derivatives of 2-azavinamidines, but none were successful (see Experimental section). In particular, the 5-phenyl derivative (7) gave only tars on attempted nitration even though one of the possible products of this reaction [*viz.* the *p*-nitro-derivative (9)] is well characterised and highly crystalline.

Both the 2-aza- and 3-aza-vinamidinium salts (5) and (3; R = Me) were unaffected by neat methyl fluorosulphonate, which confirms the low reactivity of the free lone-pairs in these systems.

By analogy with vinamidine chemistry [1] the 2-azavinamidinium salts would be expected to react with nucleophiles at the 4- and 2-positions (although the latter is inherently unlikely in view of the paucity of reactions in which such attack occurs at a nitrogen atom). Indeed, the only reported reactions of the 2-azavinamidinium system involve its susceptibility to *C*-nucleophilic attack [12a,b] and to *in situ* hydrolysis [12c] at the 4-position, while reaction of *N*-nucleophiles in this way was implicit in the formation of the 1,1,5,5-tetraalkyl derivatives (5) and (6) from the 5-phenyl compound (7). Treatment of the tetramethyl derivative (5) with piperidine also generated the monopiperidino-compound (6): that this compound was recovered unchanged after treatment with further piperidine confirms that the 2-position is inert towards nucleophilic attack.

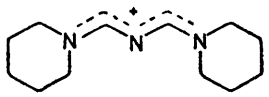
Alternatively, reactions in which amines act simply as bases may take place with 2-azavinamidinium salts in which all conjugated components of the equilibria retain an NH. Thus treatment of the 1-phenyl or 1,5-diphenyl derivatives (10) or (11) with an excess of dimethylamine gave predominantly the 2-azavinamidine free base, although in the latter case, a small amount (15%) of the 5,5-dimethyl derivative (10) was also isolated.

Although nucleophilic attack at the 3-position is not normally [1,3] observed in vinamidinium salt chemistry, because of its high electron density, it was thought that the electronic effect of the adjacent nitrogen might favour this mode in the 2-azavinamidine series. However, the reaction of the tetramethyl derivative (5) with an excess of cyclohexylamine gave the amine hydroperchlorate as the only ether-insoluble product, while an examination of the basic fraction showed at most only traces of the well characterised [24] dicyclohexylimine of glyoxal.

Surprisingly, the reaction of the 3-azavinamidinium salt (3; R = Me) with simple amines does not appear to have been studied. As expected, the bis-replacement product (15) is formed on reaction with piperidine in chloroform, but in 98% ethanol solution, complete

[24] J. M. Kliegman and R. K. Barnes, *Tetrahedron*, 1970, **26**, 2555.
[25] J. M. Kliegman and R. K. Barnes, *Tetrahedron Letters*, 1970, 1859.
[26] L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon, London, 1969, p. 302.
[27] G. Scheibe, C. Jutz, W. Seiffert, and D. Grosse, *Angew. Chem.*, 1964, **76**, 270; *Angew. Chem. Internat. Edn.*, 1964, **3**, 306.

destruction of the system ensues with the ultimate production of *N*-formylpiperidine and piperidinium picrate. The detailed mechanism of this retro-Vilsmeier reaction is obscure, but presumably involves successive *O*-nucleophile attacks (either H_2O or EtOH) at the 2(4) position, followed by displacement of the stable amidine



(15) (picrate)$^-$

system (itself open to attack in a similar manner) and consolidation of these intermediate acetals to give the observed products.

EXPERIMENTAL

Unless otherwise stated, i.r. spectra were recorded for Nujol mulls, and n.m.r. spectra at 100 MHz for solutions in [$^2H_6$]acetone.

1,5-*Diphenyl*-1H-1,2,5-*triazapentadienium Perchlorate* (11).—A solution of glyoxal monophenylhydrazone [12] (0.84 g, 6 mmol) and anilinium perchlorate [28] (1.16 g, 6 mmol) in ethanol (5 ml) was allowed to react at room temperature for 10 min. Addition of ether completed the crystallisation of the *pentadienium perchlorate* (1.73 g, 89%) as a dark red solid. It had m.p. 197 °C (decomp.) (reprecipitated by ether from methanol), $\nu_{max.}$ 3 200, 1 650, 1 590, 1 550, 1 510, 1 490, 1 350, 1 300, 1 230, 1 190, 1 100, and 750 cm^{-1}; $\lambda_{max.}$($CHCl_3$) 450 nm (ε 43 500); τ −2.3v.br, 0.81 (1 H, d, $J_{3,4}$ 9.2 Hz), 1.86 (1 H, d, $J_{3,4}$ 9.2 Hz), 2.0—2.8 (10 H, complex) and $J_{4,5}$ ([$^2H_6$]acetone–trifluoroacetic acid) 14.2 Hz (Found: C, 52.1; H, 4.6; N, 12.8. $C_{14}H_{14}ClN_3O_4$ requires C, 51.95; H, 4.35; N, 13.0%).

5,5-*Dimethyl*-1-*phenyl*-1H-1,2,5-*triazapentadienium Perchlorate* (10).—A solution of glyoxal monophenylhydrazone (0.42 g, 3 mmol) and dimethylammonium perchlorate [28] (0.44 g, 3 mmol) in ethanol (5 ml) was boiled for 1 min. The solvent was partially evaporated and ether was added to give the *perchlorate* (0.55 g, 67%) as a mass of orange needles; recrystallised from ethanol, it had m.p. 187—188 °C; $\nu_{max.}$ 3 240, 1 660, 1 600, 1 550, 1 290, 1 210, 1 100, 880, and 760 cm^{-1}; $\lambda_{max.}$($CHCl_3$) 405 nm (ε 34 600); τ 1.40 (1 H, d, $J_{3,4}$ 9.5 Hz), 1.91 (1 H, d, $J_{3,4}$ 9.5 Hz), 2.4—2.6 (5 H, complex), 6.16 (3 H, s), and 6.34 (3 H, s) (*NH* not apparent) (Found: C, 43.75; H, 5.4; N, 15.1. $C_{10}H_{14}ClN_3O_4$ requires C, 43.55; H, 5.1; N, 15.25%).

1,1-*Dimethyl*-5-*phenyl*-1H-1,2,5-*triazapentadienium Salts* (7).—*NN*-Dimethylhydrazine (1.95 g, 32 mmol) was added dropwise to an excess of aqueous glyoxal (30%, 10 ml), and the solution was set aside for 10 min. Addition of a solution of anilinium perchlorate (6.3 g, 32 mmol) in water (15 ml) caused the immediate precipitation of the *pentadienium perchlorate* (7.89 g, 89%) as an oil which soon crystallised. It had m.p. 162—163 °C (reprecipitated by ether from methanol), $\nu_{max.}$ 3 200, 1 650, 1 590, 1 500, 1 250, 1 100, 980, 850, and 760 cm^{-1}; $\lambda_{max.}$($CHCl_3$) 377 nm (ε 33 000); τ 1.13 (1 H, d, $J_{3,4}$ 9.5 Hz), 2.2—2.7 (6 H complex), 6.34br (6 H, s) (NH not apparent), and $J_{4,5}$ ([$^2H_6$]acetone–trifluoroacetic acid) 15.5 Hz (Found: C, 43.5; H, 4.95; N, 15.05. $C_{10}H_{14}ClN_3O_4$ requires C, 43.55; H, 5.1; N, 15.25%).

The *picrate* was prepared in 81% yield by a slightly modified procedure. Aniline (3.0 g, 32 mmol), followed immediately by a solution of picric acid (wet, *ca.* 12.5 g) in the minimum quantity of acetone was added to the solution of glyoxal dimethylhydrazone. The *pentadienium picrate*, which crystallised immediately, had m.p. 212—214 °C (decomp.) (from acetonitrile) (Found: C, 47.8; H, 4.1; N, 20.7. $C_{16}H_{16}N_6O_7$ requires C, 47.5; H, 3.95; N, 20.8%).

1,1-*Dimethyl*-5-p-*tolyl*-1H-1,2,5-*triazapentadienium Perchlorate* (8).—Prepared in quantitative yield by the same method as described for the above *picrate*, from *NN*-dimethylhydrazine (0.39 g, 6.5 mmol), glyoxal (30%, 2 ml), *p*-toluidine (0.70 g, 6.5 mmol), and perchloric acid (70%, 1 ml); this *perchlorate* had m.p. 169—170 °C (reprecipitated by ether from methanol), τ 1.24 (1 H, d, $J_{3,4}$ 9.1 Hz), 2.46 (1 H, d, $J_{3,4}$ 9.1 Hz), 2.59 (4 H, dd), 6.39 (6 H, s), and 7.64 (3 H, s) (*NH* not apparent) (Found: C, 45.9; H, 5.3; N, 14.65. $C_{11}H_{16}ClN_3O_4$ requires C, 45.6; H, 5.55; N, 14.5%).

1,1-*Dimethyl*-5-p-*nitrophenyl*-1H-1,2,5-*triazapentadienium Perchlorate* (9).—Also available in quantitative yield by the method described for the *p*-tolyl derivative, this *perchlorate* had m.p. 205—207 °C (decomp.) (from ethanol), τ([$^2H_6$]-DMSO) 0.90 (1 H, d, $J_{3,4}$ 9.1 Hz), 1.62 (2 H, d), 2.18 (2 H, d), 2.67 (1 H, d, $J_{3,4}$ 9.1 Hz), 6.30 (6 H, s), and $J_{4,5}$ (trifluoroacetic acid) 15.5 Hz (Found: C, 37.5; H, 3.9; N, 17.35. $C_{10}H_{13}ClN_4O_6$ requires C, 37.45; H, 4.05; N, 17.45%).

1,1,5,5-*Tetramethyl*-1H-1,2,5-*triazapentadienium Salts* (5).—Ethanolic dimethylamine (30%, 4 ml, *ca.* 2.5 times excess) was added to a suspension of the 5-phenylpentadienium perchlorate (7) (2.6 g, 10 mmol) in methanol (10 ml) and the mixture was kept for 10 min. Addition of ether gave the required *perchlorate* (1.98 g, 87%), m.p. 87.5—88 °C (reprecipitated by ether from methanol), $\nu_{max.}$ 1 650, 1 510, 1 230, 1 100, and 830 cm^{-1}; $\lambda_{max.}$($CHCl_3$) 329 nm (ε 36 000); τ 1.78 (1 H, d, $J_{3,4}$ 9.5 Hz), 2.74 (1 H, d, $J_{3,4}$ 9.5 Hz), 6.30 and 6.32 (6 H, 2s), 6.49 (3 H, s), and 6.57 (3 H, s) (Found: C, 31.95; H, 6.25; N, 18.55. $C_6H_{14}ClN_3O_4$ requires C, 31.65; H, 6.15; N, 18.45%).

The same procedure, using the 5-phenylpentadienium picrate (7) in place of the perchlorate salt, gave the 1,1,5,5-*tetramethylpentadienium picrate*, m.p. 91—94 °C (reprecipitated by ether from ethanol), in 46% yield (Found: C, 40.25; H, 4.6; N, 23.5. $C_{12}H_{16}N_6O_7$ requires C, 40.45; H, 4.5; N, 23.6%).

1,1-*Dimethyl*-5,5-*pentamethylene*-1H-1,2,5-*triazapentadienium Picrate* (6).—Addition of piperidine (0.17 g, 2 mmol) to a suspension of the 5-phenylpentadienium picrate (7) (0.40 g, 1 mmol) in methanol (1 ml) gave the required *picrate* (0.30 g, 76%) on addition of ether; it had m.p. 137—138 °C (from ethanol), τ([$^2H_6$]DMSO) 1.32 (2 H, s), 1.69 (1 H, d), 2.68 (1 H, d), 6.14br (4 H, s), 6.41 (3 H, s), 6.71 (3 H, s), and 8.27br (6 H, s) (Found: C, 45.65; H, 5.2; N, 21.3. $C_{15}H_{20}N_6O_7$ requires C, 45.45; H, 5.05; N, 21.2%).

3,4-*Dimethyl*-1,5-*diphenyl*-1H-1,2,5-*triazapentadienium Perchlorate* (12).—A solution of biacetyl monophenylhydrazone [29] (0.70 g, 4 mmol) and anilinium perchlorate (0.76 g, 4 mmol) was heated under reflux in acetic acid (2 ml) for 10 min. Addition of ether to the cooled solution gave the *perchlorate* (0.40 g, 29%), m.p. 198—200 °C (decomp.) (from acetic acid), $\nu_{max.}$ 3 250, 1 600, 1 540, 1 250,

[28] D. Lloyd and H. McNab, *Synthesis*, 1977, 258.

[29] H. von Pechmann, *Ber.*, 1888, **21**, 1411.

1 100, 760, and 740 cm^{-1}, $\lambda_{max.}(CHCl_3)$ 409 nm (ε 18 000); τ −0.80br, 2.2—3.0 (10 H, complex), 7.24 (3 H, s), and 7.50 (3 H, s) (Found: C, 54.8; H, 5.0; N, 11.7. $C_{16}H_{18}ClN_3O_4$ requires C, 54.6; H, 5.1; N, 11.95%).

A similar reaction carried out in ethanol as solvent gave a mixture of recovered anilinium perchlorate (85—90%) and the 2-azapentadienium perchlorate (10—15%) after being heated for 5 min under reflux. The position of the equilibrium was essentially unchanged after 2 h under reflux. Work-up of the ethereal mother liquors gave recovered biacetyl monophenylhydrazone (80%), m.p. 135—137 °C, mixed m.p. 136—138 °C (lit.,[29] m.p. 134 °C).

Attempted Preparation of 1,3,4,5-*Tetraphenyl*-1H-*triazapentadienium Perchlorate*.—A solution of benzil monophenylhydrazone [30] (1.20 g, 4 mmol) and anilinium perchlorate (0.76 g, 4 mmol) in acetic acid (5 ml) was heated under reflux for 2 h. The crude crystals (0.30 g) which slowly formed on cooling the dark solution, did not depress the melting point of benzil monophenylhydrazone (25% recovery).

Attempted Bromination of 1,1,5,5-*Tetramethyl*-1H-1,2,5-*triazapentadienium Perchlorate* (5).—Preliminary experiments were carried out in deuteriated solvents using molecular bromine as the electrophile. The course of the reaction was followed by ^1H n.m.r. spectroscopy. In a typical experiment, the pentadienium salt (23 mg, 0.1 mmol) was dissolved in [$^2H_4$]methanol (0.5 ml) and a solution of bromine (50 mg, 0.3 mmol) in [$^2H_4$]methanol (0.3 ml) was added in 0.1-ml portions over a period of days. Unchanged pentadienium salt was still present after this period, although it was clear from the spectrum that extensive reaction had taken place.

A similar experiment in [$^2H_4$]acetic acid solution gave an instantaneous precipitate of a black oil after 1 equivalent of bromine had been added, although again starting material remained. This had disappeared after *ca.* 6 h, but the complexity of the reaction is indicated by the number of peaks in the *N*-methyl region of the spectrum (>10).

Reaction of the pentadienium salt with *N*-bromosuccinimide in acetic acid was followed by u.v. spectroscopy. Starting material still remained after 100 min heating under reflux, in the presence of 5 equivalents of brominating agent. A repeat of this experiment in chloroform solution was similarly unpromising.

Attempted Nitration Reactions.—The 1,1,5,5-tetramethyl- or 1,1-dimethyl-5-phenyl-pentadienium salt (1 mmol) was dissolved in acetic anhydride (2 ml), and the solution was cooled to 0 °C. Nitric acid (conc.; 0.2 ml) was added, and the solution was stirred for 2 h. No product precipitated during this time, and attempted work-up yielded only tars.

Action of Piperidine on 1,1,5,5-*Tetramethyl*-1H-1,2,5-*triazapentadienium Picrate* (5).—The pentadienium picrate (0.36 g, 1 mmol) and piperidine (0.17 g, 2 mmol) were heated to boiling in ethanol (2 ml) for 1 min. Addition of ether to the cooled solution gave 1,1-dimethyl-5,5-pentamethylene-1*H*-1,2,5-triazapentadienium picrate (0.24 g, 60%), m.p. 134—135 °C (from ethanol), mixed m.p. 135—136 °C.

Action of Piperidine on 1,1-*Dimethyl*-5,5-*pentamethylene*-1H-1,2,5-*triazapentadienium Picrate* (6).—The pentadienium picrate (0.20 g, 0.5 mmol) in ethanol (5 ml) containing a 5-fold excess of piperidine (0.21 g), was heated under reflux for 1 h. The cooled solution crystallised on seeding with starting material. The recovery was 0.09 g (45%), m.p. 135—136 °C, mixed m.p. 136—137 °C.

Action of Dimethylamine on 5,5-*Dimethyl*-1-*phenyl*-1H-1,2,5-*triazapentadienium Perchlorate* (10).—A solution of the pentadienium perchlorate (0.01 g) and ethanolic dimethylamine (30%, 0.1 ml, large excess) in methanol (1 ml) was kept overnight, after which time the u.v. spectrum of the mixture remained unchanged. Addition of ether gave a small amount of colourless precipitate, which was filtered off, and the mother liquors were evaporated *in vacuo*. Perchloric acid (70%, 1 drop) was added to the residue, and the crystals which formed were partially recrystallised *in situ* from ethanol. They were identified as the unchanged pentadienium perchlorate by melting point (181—183 °C) and mixed melting point (182—184 °C).

Reaction of 1,5-*Diphenyl*-1H-1,2,5-*triazapentadienium Perchlorate* (11) *with Dimethylamine*.—Ethanolic dimethylamine (30%, 0.2 ml, 1.2 mmol) was added to a suspension of the pentadienium perchlorate (0.32 g, 1 mmol) in methanol (1 ml), and the mixture was boiled for 1 min. The yellow crystals (0.18 g) which formed on cooling were filtered off and recrystallised from methanol. They had m.p. 159—161 °C (decomp.); τ($CDCl_3$) 2.4—3.4 (complex), M^+ 223 (100%) and were identified as the free base of the pentadienium salt, obtained in 81% yield. An analytical sample, recrystallised from methanol, contained *ca.* 5% 5,5-dimethyl-1-phenyl-1*H*-1,2,5-triazapentadienium perchlorate (Found: C, 73.5; H, 5.75; N, 18.5. The proposed mixture requires C, 73.5; H, 5.8; N, 18.6%). Addition of ether to the methanolic mother liquors of the initial reaction gave a further yield of this side-product (0.04 g, 15%), m.p. 184—185 °C (from ethanol), mixed m.p. 183—184 °C.

Action of Cyclohexylamine on 1,1,5,5-*Tetramethyl*-1H-1,2,5-*triazapentadienium Perchlorate* (5).—A solution of the pentadienium perchlorate (0.34 g, 1.5 mmol) and cyclohexylamine (0.5 g, 5 mmol) in ethanol (5 ml) was heated under reflux for 1 h. The solvent was evaporated *in vacuo*, and ether was added to the residue to give a crystalline solid (0.25 g), m.p. 222—224 °C, which was identified as cyclohexylammonium perchlorate (83%) by its n.m.r. spectrum and by comparison with an authentic sample (mixed m.p. 224—225 °C). The ethereal filtrate was concentrated, and the n.m.r. spectrum ($CDCl_3$) of the residue showed, in the region τ 0—5, only the AX pattern due to 3 and 4 protons of the pentadiene system. Even allowing for accidental equivalence, the level of glyoxal di-imines [24] was ⩽10%.

Cyclohexylammonium Perchlorate (*see ref.* 28).—Cyclohexylamine (0.1 g, 1 mmol) was added to a suspension of anilinium perchlorate (0.2 g, 1 mmol) in ethanol (0.5 ml), and the mixture was shaken until all the solid had dissolved. Addition of ether gave the *perchlorate* (0.16 g, 80%), m.p. 224—226 °C.

Reaction of 1,1,5,5-*Tetramethyl*-1H-1,3,5-*triazapentadienium Picrate* (3; R = Me) *with Piperidine*.—(i) *Ethanol solution*. The pentadienium picrate (0.36 g, 1 mmol) and piperidine (0.45 g, 5 mmol) in ethanol (5 ml) were heated under reflux for 1.5 h. The solution was concentrated and ether was added to it, yielding piperidinium picrate (0.28 g, 89%, based on available picrate), m.p. 154—156 °C (from water), mixed m.p. 152—154 °C (lit., 151—152 °C), as sole ether-insoluble product. Concentration of the ethereal mother liquors gave an oil (0.31 g), whose major constituent (g.l.c.) was *N*-formylpiperidine, $\nu_{max.}$ (liquid film) 1 660 cm^{-1};

[30] C. F. H. Allen and J. A. Van Allan, *J. Amer. Chem. Soc.*, 1951, **73**, 5850.

$\tau(CDCl_3)$ 1.94 (1 H, s), 6.2—6.8 (4 H, complex), 8.0—8.6 (6 H, complex); mass spectrum M^+ 113 (100%), isolated by preparative g.l.c. on Carbowax at 190 °C.

(ii) *Chloroform solution.* A solution of piperidine (0.26 g, 3 mmol) and the pentadienium picrate (0.36 g, 1 mmol) was heated under reflux in chloroform (5 ml) for 30 min. Evaporation of the solvent and addition of ether gave 1,1,5,5-bis(pentamethylene)-1*H*-1,3,5-triazapentadienium picrate (0.37 g, effective yield 68%) contaminated with *ca.* 30% piperidinium picrate. One recrystallisation from aqueous ethanol gave the pure pentadienium salt, m.p. 126—128 °C (lit.,[6] 126 °C); $\tau(CDCl_3)$ 0.99 (2 H, s, 2,4-protons), 1.12 (2 H, s, picrate), 6.0—6.4 (8 H, complex), and 7.9—8.4 (12 H, complex).

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