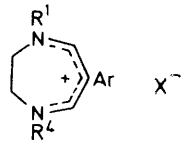
Diazepines. Part 25.[1] Preparation and Properties of 6-Aryl-2,3-dihydro-1,4-diazepinium Salts. Electronic Interaction between the Rings and Steric Inhibition thereof

By **Douglas Lloyd** * and **Kanwaljit S. Tucker**, Department of Chemistry, Purdie Building, University of St. Andrews, St. Andrews, Fife KY16 9ST
Donald R. Marshall, School of Physical and Molecular Sciences, University College of North Wales, Bangor, Gwynedd LL57 2UW

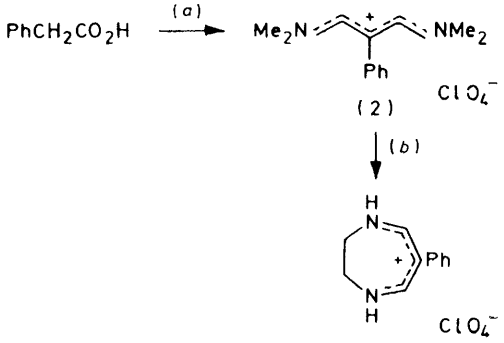
A variety of 6-aryldihydrodiazepinium salts (including also 6-biphenyl-4-yl, 6-α-naphthyl, and 6-*N*-pyridyl) has been prepared, mostly by reactions of 1,2-diamines with 3-aryl-1,5-diazapentadienium salts. The electron-rich dihydrodiazepinium cation activates the 6-aryl substituent towards electrophilic attack, and halogenation and nitration take place at the *p*-position. Substituents vicinal to the ring junction in either the six- or seven-membered rings inhibit this reactivity, presumably by preventing coplanarity of the two rings; the ^{13}C n.m.r. spectra of these vicinally substituted compounds also show the lowered electronic interactions between the rings. *NN'*-Diphenyl and *NN'*-dibenzyl substituents also inhibit electrophilic substitution in the 6-phenyl ring. Solution in deuteriosulphuric acid generates a stable radical species. Nucleophiles (monoamines, diamines, sodium hydroxide) attack the 5- and 7-positions of the diazepine ring. The ^{13}C n.m.r. and mass spectra of these compounds are discussed.

2,3-DIHYDRO-1,4-DIAZEPINIUM salts commonly undergo a variety of reactions, with electrophiles and nucleophiles, at the 6-position.[2] 6-Aryldihydrodiazepinium salts (1) have been little studied and it seemed worthwhile to investigate the interactions between the dihydrodiazepinium ring and attached aryl groups.



(1) Ar = Aryl

Preparation.—The most usual method of preparation, exemplified in the Scheme, started from an arylacetic acid, which was first converted into a 3-arylvinamidinium salt,[3] *e.g.* (2), by means of a Vilsmeier reaction; this salt in turn reacted with ethylenediamine, or derivatives thereof, to provide a dihydrodiazepinium salt. By this method a variety of 6-aryl derivatives was obtained, for the most part in high yield. (For a detailed list see the Experimental section.) The method was also extended to provide a number of 6-biphenyl-4-yl, 6-α-naphthyl, 6-β-naphthyl, and 6-*N*-pyridyl derivatives.



(*a*) (i) $POCl_3$, $HCONMe_2$; (ii) H_2O; (iii) $NaClO_4$
(*b*) $H_2N[CH_2]_2NH_2$

SCHEME

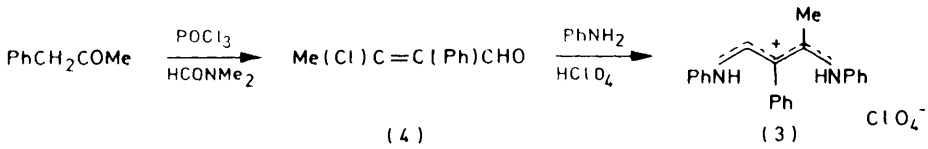
Preparation of dihydrodiazepinium salts from *NN'*-diphenylvinamidinium salts required high-dilution conditions[4] but when dimethylamine replaced aniline or diphenylamine as the leaving group, as in the Scheme, no such conditions were necessary. The necessity for high-dilution conditions was attributed to the large difference in the rates of substitution of the first and second arylamine groups from *NN'*-diphenylvinamidinium salts.[4] Despite the ease of cyclisation with the present tetramethylvinamidinium salts, there still remains a difference in the ease of substitution of the first and second amine groups. When the 3-phenylvinamidinium salt (2) or its 3-*p*-tolyl analogue was treated with two equivalents of piperidine in methanol only one piperidine group was introduced. Displacement of both dimethylamine groups by piperidine in methanol required a large excess of piperidine and a long period of heating. Even under these conditions the 3-*o*-tolyl analogue underwent only monosubstitution by piperidine, possibly for steric reasons. Replacement of methanol by acetonitrile as solvent enabled both dimethylamine groups of (2) and of its 3-α- or 3-β-naphthyl analogues to be substituted by using only two equivalents of piperidine, but prolonged heating was again required.

Steric hindrance also apparently prevented formation of either 1,4-diethyl-6-phenyl- or 2,2,3,3-tetramethyl-6-phenyl-dihydrodiazepinium salts from the vinamidinium salt (2).

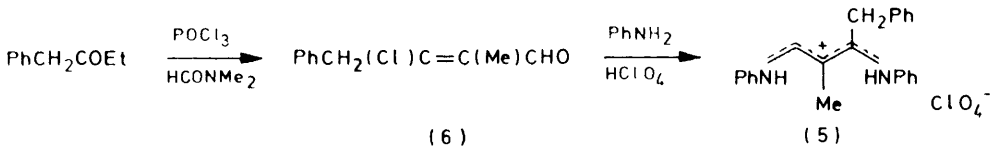
The preparation of dihydrodiazepinium salts from *NN'*-diphenylvinamidinium salts has also been modified by first passing ammonia through a solution of the latter, followed by addition of ethylenediamine or its derivatives.[4] By using this method it proved possible to obtain the 6-*o*-tolyl-, 1,4-diethyl-6-phenyl-, 1,4,5-trimethyl-6-phenyl-, and 2,2,3,3-tetramethyl-6-phenyl-dihydrodiazepinium salts from (2) or its analogues, all being unobtainable from the corresponding vinamidinium salts by the direct route. Also prepared by this method

were 6-phenyl, 5-methyl-6-phenyl, and 1,5-dimethyl-6-phenyl derivatives. The formation of the latter salt, as indicated by the lack of coupling of the 7-H signal with NH in the n.m.r. spectrum, rather than the alternative possibility, the 1,7-dimethyl-6-phenyl derivative, is presumably due to the greater crowding which would be introduced in formation of the 1,7-dimethyl isomer.

The vinamidinium salt (3), from which the 1,5-dimethyl-6-phenyldihydrodiazepinium salt was obtained,



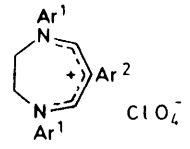
(4) (3)



(6) (5)

was prepared by an alternative method, from the β-chloroacrylaldehyde (4), itself obtained by a Vilsmeier reaction on phenylacetone. An attempted preparation of the 2-ethyl analogue of (3) provided instead a 2-benzyl-3-methylvinamidinium salt (5), indicating that the precursor acrylaldehyde was (6). The latter was obtained by means of a Vilsmeier reaction on 1-phenylbutan-2-one; reaction obviously takes place preferably at the 3-carbon atom of this ketone rather than at the benzyl methylene group, as expected. The salt (5) in turn provided a 5-benzyl-6-methyldihydrodiazepinium salt.

1,4,6-Triaryldihydrodiazepinium salts (7) could not be obtained by reaction of 1,2-diaryldiamines with 3-arylvinamidinium salts either directly, or by the ammonia method. In these cases the salts (7a—f) were prepared from the sodium salts of the appropriate arylmalonaldehydes by addition of methanolic perchloric acid followed by the diamine. 1,6-Diphenyl- and 6-*p*-nitrophenyl-1-phenyl-dihydrodiazepinium salts were also obtained similarly.

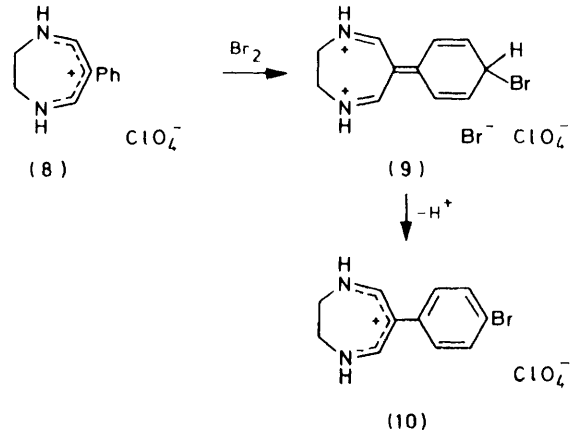


(7)

(a) $Ar^1 = Ar^2 = Ph$
(b) $Ar^1 = p\text{-}MeOC_6H_4$, $Ar^2 = Ph$
(c) $Ar^1 = Ph$, $Ar^2 = p\text{-}MeOC_6H_4$
(d) $Ar^1 = Ar^2 = p\text{-}MeOC_6H_4$
(e) $Ar^1 = Ph$, $Ar^2 = p\text{-}O_2NC_6H_4$
(f) $Ar^1 = Ph$, $Ar^2 = \alpha\text{-}naphthyl$

A series of 1,4-dimethyl-6-aryldihydrodiazepinium salts (aryl = phenyl, *p*-tolyl, α-naphthyl, β-naphthyl, biphenyl-4-yl) was prepared by a transdiazepination reaction [5] of *NN'*-dimethylethylenediamine on the corresponding *NN'*-unsubstituted dihydrodiazepinium salts. Previous experience [5] had indicated that this reaction was not of general application and, in particular, steric factors seem to interfere. In the present work the 1,4-dimethyldihydrodiazepinium salts did not react with ethylenediamine, and no reactions took place between the 6-phenyl salt (8) and 1,2-diamino-2-methylpropane or between the 5-methyl-6-phenyldihydrodiazepinium salt and *NN'*-dimethylethylenediamine.

Electrophilic Substitution; Bromination.—Dihydrodiazepinium salts unsubstituted at the 6-position readily undergo bromination at that site [6,7] and, indeed, some 6-substituted derivatives are also attacked by bromine at the 6-position.[8] Wheland-type intermediates can be formed by electrophilic attack at the 6-, but not at the 5- and 7-positions; [9] this 6-site is also shown by n.m.r. spectra to be intrinsically electron-rich.[10-12] It seemed



(8) (9) (10)

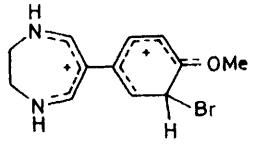
possible that such reactivity might be transmitted to the *p*-position of a 6-phenyl group; [11] other workers had also considered this possibility on the basis of n.m.r. spectra.[12]

The 6-phenyl derivative (8) reacts readily with bromine in methanol at room temperature to give a good yield of the 6-*p*-bromophenyl compound (10), reaction presumably proceeding *via* a dication intermediate (9). Various substituted derivatives of (8) (1-methyl, 1,4-dimethyl, 1,4-diethyl, 2-methyl, 2,2-dimethyl, 2,3-tetramethylene) reacted similarly. This result naively suggests the unusual feature of activated substitution at the *p*-position of a benzene ring by an 'onium group, but the present 'onium group is in fact an electron-rich species. The reactivity of 6-phenyl substituents may be con-

trasted with the unreactivity towards electrophiles of 5- and 7-phenyl substituents.[7]

The assumed mechanism demands coplanarity of the dihydrodiazepinium and benzene rings. This could be sterically hindered by *o*-substituents and, in accord with supposition, the 6-*o*-tolyl- and 5-methyl-6-phenyl-dihydrodiazepinium cations are not attacked by bromine. This steric effect is also evident from ^{13}C n.m.r. spectra (see below).

Substituents at the *p*-position of the 6-phenyl group also inhibit reaction; thus the 6-*p*-methoxyphenyl and 6-*p*-tolyl analogues of (8) are unattacked by bromine. The *o*-positions of the phenyl groups are sterically hindered whilst attack at the *m*-positions, which could be activated by the *p*-methyl or methoxy groups, would produce intermediates such as (11) which could be destabilised by interaction between the neighbouring positively charged systems.



(11)

6-α- and 6-β-Naphthyl derivatives were also brominated readily, in the case of the α-naphthyl derivative presumably at the 4'-position, this being the usual favoured site for further substitution of naphthalenes already substituted at the 1-position by electron-donating substituents.[13] ^{13}C N.m.r. spectra are in accord. The signal which is most shifted on bromination is the naphthalene signal which occurs at highest field (δ 125.43) in the unbrominated molecule, and which is likely to represent the 4'-carbon atom.[13] This signal shifts to δ 121.58 in the brominated compound and its relative intensity is also lowered. The site of bromination of the β-naphthyl derivative remains unassigned.

The 6-(biphenyl-4-yl)dihydrodiazepinium cation was not substituted by bromine. Presumably in this case formation of a Wheland-type intermediate is inhibited in that it involves the loss of delocalisation energy of two benzene rings and the dihydrodiazepinium system.

1,4-Diphenyldihydrodiazepinium salts have been brominated both at the 6-position of the diazepine ring[7,14] and in the phenyl groups.[7] Surprisingly the 1,4,6-triphenyldihydrodiazepinium salt (7a) was unreactive towards bromine. Possibly with three substituent phenyl groups, the nucleophilic electrons that are present in excess are now too thinly spread, or their conjugation into the phenyl groups is sterically hindered because of buttressing interactions involving the phenyl groups and the intervening 5,7-hydrogen atoms. Correspondingly, the ^{13}C n.m.r. spectra (see below) indicate a lowered electron density in the 6-phenyl ring in these cases. The 1,6-diphenyl and 1,4-dibenzyl-6-phenyl derivatives also did not react with bromine; the latter case is surprising since its 1,4-dimethyl- and 1,4-diethyl-6-phenyl analogues reacted readily; the reason for this is not clear. That there may be electronic interaction between the benzyl groups and the dihydrodiazepinium ring is indicated by the enhanced molar absorptivity when benzyl groups replace hydrogen atoms or methyl groups at the 1- and 4-positions.

1,4-Bis-*p*-methoxyphenyldihydrodiazepinium perchlorate undergoes only monobromination, at the 6-position, even with 3 equivalents of bromine. Unlike its triphenyl analogue, 1,4-bis-*p*-methoxyphenyl-6-phenyldihydrodiazepinium perchlorate is also brominated, at the *p*-position of the 6-phenyl group. Presumably the methoxyphenyl groups increase the nucleophilicity of this cation *vis-a-vis* its triphenyl analogue. However the 6-*p*-methoxyphenyl-1,4-diphenyl analogue is again unattacked by bromine.

It was also found that the open-chain 3-phenylvinamidinium salt (2) is unattacked by bromine. This difference from the cyclic compound (8) may reflect the much greater rigidity of (8), which could assist the process of electrophilic substitution.

Reactions with N-*Halogenosuccinimides*.—6-Unsubstituted dihydrodiazepinium salts are halogenated at the 6-position by *N*-chloro-, *N*-bromo-, or *N*-iodo-succinimide.[5,7] The 6-phenyl compound (8), and its 2-methyl derivative, were brominated and iodinated at the *p*-position of the phenyl ring by the appropriate *N*-halogenosuccinimide, but did not react with *N*-chlorosuccinimide. The 1,4-dimethyl-6-phenyl derivative (1; Ar = Ph, $R^1 = R^4 = Me$) reacted with *N*-bromosuccinimide but not with *N*-iodosuccinimide; the 2,2-dimethyl-6-phenyl-substituted salt reacted with *N*-iodosuccinimide but was recovered unchanged after being heated with *N*-bromosuccinimide.

Nitration.—6-Unsubstituted dihydrodiazepinium salts have been nitrated at the 6-position, using either nitric acid–sulphuric acid mixtures[15,16] or nitric acid (83%) alone.[16] The 6-phenyldihydrodiazepinium salt (8) was readily nitrated at the *p*-position of the phenyl ring in cold diluted nitric acid. This ease of nitration again emphasises the electron-donating and activating character of a 6-dihydrodiazepinium substituent on a benzene ring. Under identical conditions the 1-methyl, 2-methyl, and 1,4-dimethyl derivatives of (8) provided *p*-nitrobenzoic acid. In these cases nitration has presumably been followed by acid hydrolysis of the seven-membered ring and oxidation of the resultant *p*-nitrophenylmalonaldehyde. Nitration must have preceded hydrolysis and oxidation both because the product was *p*- rather than *m*-substituted and since benzoic acid would not itself have been nitrated in these dilute-acid conditions. An attempted nitration of the 3-phenylvinamidinium salt (2) also provided *p*-nitrobenzoic acid, again suggesting initial nitration of this salt, prior to hydrolysis.

Attempted Reduction of a 6-p-*Nitrophenyldihydrodiazepinium Salt*.—6-Nitro-substituents on dihydrodiazepinium rings may be reduced without affecting the dihydrodiazepinium system.[16,17] In one experiment the 6-*p*-

nitrophenyldihydrodiazepinium cation was reduced to its 6-*p*-aminophenyl analogue by hydrazine hydrate and palladium–charcoal, but repeated further attempts failed to bring about reduction. Addition of acid to the *p*-aminophenyl compound caused a hypsochromic shift in its u.v. spectrum (from 270 and 325 nm to 240 and 300 nm), as is shown by 6-aminodihydrodiazepinium salts,[17] and which was reversed on addition of alkali. The amino-group was also acetylated.

Reaction with Sulphuric Acid.—The 6-phenyl-substituted salt (8) dissolved in concentrated sulphuric acid to give an intensely blue solution. E.s.r. spectroscopy indicated that radicals or radical ions were formed. It seems likely that radical formation is associated with interaction between the phenyl and dihydrodiazepinium rings because 6-unsubstituted dihydrodiazepinium salts do not behave in this way. The radicals or radical ions which are formed must be fairly stable, for e.s.r. spectra showed that they were still present after 24 h, and the u.v. spectrum stayed almost unchanged in this time. The salt (8) could be recovered from these acid solutions. The blue colour persisted for nearly 4 days. Further confirmation that a radical species is generated comes from the ^{1}H n.m.r. spectrum of (8) recorded in deuteriosulphuric acid. After *ca.* 45 min all the signals were broadened and the aryl and 5,7-signals totally disappeared after about 75 min. The 6-*p*-tolyl analogue of (8) gave a similar blue solution in sulphuric acid. Radical ions have been postulated as products of electro-oxidation of some pyrrolodiazepines.[18]

Reaction with Nucleophiles.—5,7-Unsubstituted dihydrodiazepinium salts react with nucleophiles to displace atoms 1—4 of the ring.[5] As discussed earlier in this paper, this type of reactivity has been utilised to convert 6-aryldihydrodiazepinium salts into their *NN'*-dimethyl derivatives. The 6-phenyl compound (8) was also attacked by piperidine in methanol to give a complex mixture of products containing no diazepine.

6-Bromodihydrodiazepinium salts react readily with nucleophiles with displacement of the bromine atom either by the nucleophile or by a hydrogen atom.[2] In contrast the 6-*p*-bromophenyl analogue did not react with sodium methoxide. This difference is entirely reasonable for in this case the bromine atom is *para* to an electron-donating substituent, while formation of the alternative tautomer (12), corresponding to the postulated intermediate [2] in reactions of 6-bromo-derivatives, is unlikely to contribute since it involves loss of the delocalisation energy of both rings.

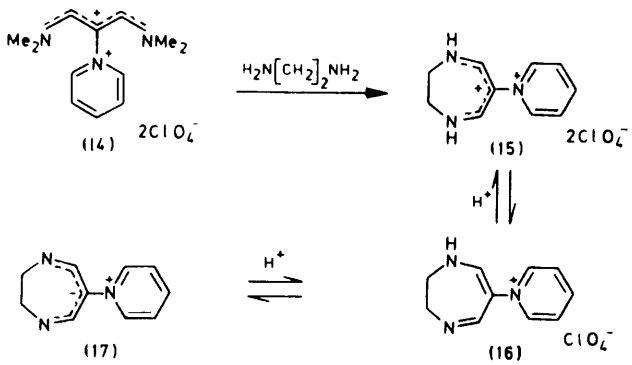
(12)

Hydrolysis.—The 6-phenyl derivative (8) is resistant to concentrated hydrochloric acid, but alkaline hydrolysis of this compound provided the sodium salt of phenylmalonaldehyde, reaction presumably proceeding by nucleophilic attack on the 5- and 7-positions. The 6-α-naphthyl analogue of (8) was hydrolysed similarly in alkaline conditions. It is possible that in these cases the species involved in the hydrolysis is the alternative tautomeric form (13). The products were identified by conversion into 6-aryl-1,4-diphenyldihydrodiazepinium salts by reaction with 1,2-dianilinoethane. This reagent does not convert the initial 6-aryldihydrodiazepinium

(13)

salts into their 1,4-diphenyl analogues in a transdiazepination reaction as described earlier in this paper, but does react with 3-arylmalonaldehydes.

6-N-*Pyridyldihydrodiazepinium Diperchlorate* (15) *in Base.*—When the 3-*N*-pyridylvinamidinium salt (14) reacted with ethylenediamine the isolated product was the dihydrodiazepinium diperchlorate (15). Treatment



of this compound with 1 molar equivalent of potassium hydroxide in methanol caused a change in the position of the u.v. maxima from 268, 328, 340sh nm [for (15)] to 265, 322, 355sh nm. This change was reversed by addition of perchloric acid. It is assumed that the change is due to the formation of the monocation (16). Addition of water precipitated a pale yellow compound, whose elemental analysis supported this structure but indicated that it still contained some dication (15). Addition of further methanolic potassium hydroxide provided a purple-red solution which may contain the pyridinium ylide (17). The new species was very unstable however, and all attempts to isolate it provided only polymeric material. Its mode of formation, colour, and instability are all consistent with the suggested ylide structure. When it was generated in the presence of 2,4-dinitrobenzaldehyde no tractable products could be isolated.

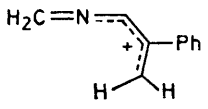
^{13}C *N.m.r. Spectra.*—As for other dihydrodiazepinium salts,[11] the most striking feature of the ^{13}C n.m.r. spectra of the 6-phenyl derivatives is the large difference in chemical shift between the signals for the 6-C (δ *ca.* 105

p.p.m.) and 5,7-C (δ *ca.* 160 p.p.m.), showing the alternating polarity in the vinamidinium chain. The effect of the 6-phenyl substituent on the shift for the 6-C is very similar to that caused in bis-phenyl derivatives [*e.g.* (1; Ar = R^1 = R^4 = H) 88.01 p.p.m., (1; Ar = Ph, R^1 = R^4 = H) 102.68 p.p.m.]. A similar alternation is seen in the open-chain vinamidinium salts, *e.g.* (2), 2-C, 162.91 p.p.m., 3-C, 105.15 p.p.m.

Conjugative interaction between the dihydrodiazepinium system and its 6-phenyl substituent is necessarily into the benzene ring, and the *p*-position of the phenyl group becomes rather electron-rich.[10] This is shown by ^{13}C n.m.r. spectra,[11] and is reflected in the electrophilic reactivity at this site. In the latter connexion it was shown (see above) that this reactivity is prevented either by steric factors forcing the two rings out of coplanarity, or by further phenyl substitution at the 1,4-positions, which spreads out the electron distribution. Both of these factors are also reflected in the ^{13}C n.m.r. spectra. Introduction of a vicinal methyl group at C-5 lowers the value for [δ(*m*) − δ(*p*)] in the benzene ring from 2.49 to 1.28. In the case of the 6-*o*-tolyl compound (1; Ar = *o*-tolyl, R^1 = R^4 = H) it was not possible to assign all the phenyl resonances with certainty, but whereas its aryl *C*H signals occur in the range 127.09—131.97, the aryl *C*H signals for its 6-phenyl analogue occur in the range 126.17—128.66. The effect of introducing extra phenyl groups at the 1,4-positions is shown in the decrease of [δ(*m*) − δ(*p*)], *viz.* 6-phenyl, 2.49, 1,6-diphenyl, 2.04, 1,4,6-triphenyl, 1.28.

Mass Spectra.—The mass spectra of dihydrodiazepinium salts are most conveniently investigated by conversion of the salts into iodides.[19] As for their 6-unsubstituted analogues,[19] the most intense peak of the molecular ion cluster for the 6-aryl derivatives is usually that of the related base. Also like their 6-unsubstituted analogues, 6-aryldihydrodiazepinium salts showed, in general, peaks of low intensity at *m/e* corresponding to the molecular ion of the cation, but this is most likely to represent the ^{13}C-isotope peak of the related base.[19] Thus thermal dissociation of the salt, where possible, would appear to precede electron bombardment. Exceptional cases where large molecular-ion peaks corresponding to the cations were observed were those of the 5-methyl-6-phenyl and 2,2,3,3-tetramethyl derivatives (73% and 85% intensity peaks respectively). These are the first recorded examples of dihydrodiazepinium salts providing true molecular ion peaks.

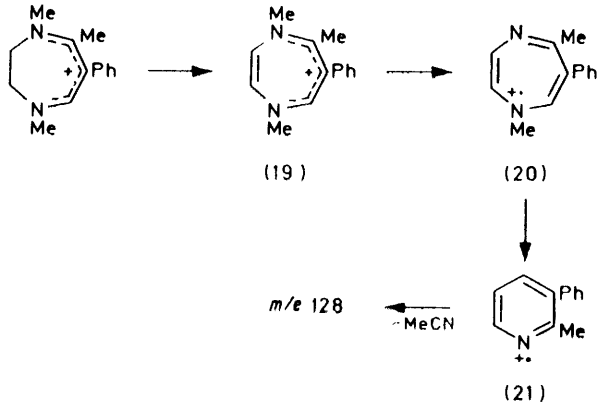
As found previously, both for 6-unsubstituted dihydrodiazepinium salts[19] and for dihydrodiazepines,[20] the major fragmentation process, which is confirmed by the observation of metastable peaks, was the elimination of the N(1)–C(2) fragment, leaving an ion such as (18)



(18)

[from (8)]. This species usually provides the base peak. Ion (18) breaks down further, typically to give peaks corresponding to the phenylcyclopropenium cation (45%), $[C_7H_7]^+$ (22%) and phenyl (67%). A large peak corresponding to $[PhC{=}CH]^{+\cdot}$ (60%) was also observed in this spectrum. For the 6-aryl compounds, as for their 6-unsubstituted analogues,[19] $Me_2C{=}N^+$ is lost preferentially to $H_2C{=}N^+$ from 2,2-dimethyl derivatives.

Two cases worthy of comment are those of the 1,4,5-trimethyl-6-phenyl and 2,3-tetramethylene-6-phenyl derivatives. Peaks at *m/e* 213 (30%) and 198 (100%) from the former are attributed to ions (19) and (20).

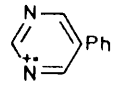


(19) (20)

(21)

Loss of a methyl group from the 4- rather than from the 1-position seems more likely because the 4-substituent is the more crowded of the two. Some support for this comes from a peak at *m/e* 169 (32%) which is attributed to the pyridinium ion (21), and which in turn loses methyl cyanide. This is formed from an *N*-demethylated dihydrodiazepine (*cf.* ref. 19), demethylation having occurred at the 4-position. Had the initial loss of a methyl group been from N(1), 4-methyl-3-phenylpyridine would have resulted rather than (21), and this would lose HCN rather than MeCN. There is a report of the thermal conversion of a dihydrodiazepine into a pyridine, with concomitant loss of ammonia.[21]

A 2,3-tetramethylenedihydrodiazepinium ion cannot readily lose the preferred N(1)–C(2) fragment. A peak



(22)

at *m/e* 156 (45%) is attributed to the pyrimidinium cation (22). A similar fragmentation has been recorded for 5,7-dimethyl- and 5,7-diphenyl-2,3-tetramethylenedihydrodiazepinium cations.[19]

EXPERIMENTAL

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

3-Aryl-1,1,5,5-tetramethyl-1H-1,5-diazapentadienium Perchlorates (2).—Phosphoryl chloride (0.3 mol) was added to stirred, cooled dimethylformamide (0.5 mol), followed by the appropriate arylacetic acid (0.1 mol). When any exothermic reaction had ceased, the mixture was heated and stirred at 80—90 °C until carbon dioxide was no longer evolved (3—6 h). The cooled reaction mixture was mixed with ice (100 g), and the aqueous mixture was shaken with a small amount of charcoal and then filtered. Sodium perchlorate (14 g) was added to the filtrate. The diazapentadienium perchlorate crystallised out and was filtered off and washed with a small amount of aqueous sodium perchlorate. By this means the following salts were prepared: 3-phenyl [22] (66%), 3-*p*-nitrophenyl [23] (72%), 3-p-*bromophenyl* (60%), m.p. 130—132 °C (from ethanol), $\lambda_{max.}$ 316 nm (ε 35 100), τ[$(CD_3)_2SO$] 2.24 (2 H, s), 2.32—2.40 and 2.66—2.75 (4 H, AA'BB' pattern), 6.74 (6 H, s), and 7.53 (6 H, s) (Found: C, 40.0; H, 4.85; N, 7.25. $C_{13}H_{18}BrClN_2O_4$ requires C, 40.9; H, 4.75; N, 7.35%), 3-p-*chlorophenyl* (69%), m.p. 244—245 °C (from ethanol), $\lambda_{max.}$ 316 nm (ε 27 000), τ[$(CD_3)_2SO$] 2.22 (2 H, s), 2.45—2.54 and 2.61—2.70 (4 H, AA'BB' pattern), 6.74 (6 H, s), 7.53 (6 H, s) (Found: C, 46.1; H, 5.45; N, 8.15. $C_{13}H_{18}Cl_2N_2O_4$ requires C, 46.3; H, 5.4; N, 8.3%), 3-p-*tolyl* (50%), m.p. 150—152 °C (from ethanol), $\lambda_{max.}$ 316 nm (ε 49 400), τ[$(CD_3)_2CO$] 2.20 (2 H, s), 2.72 (4 H, s), 6.65 (6 H, s), 7.42 (6 H, s), and 7.62 (3 H, s) (Found: C, 53.0; H, 6.7; N, 9.0. $C_{14}H_{21}ClN_2O_4$ requires C, 53.1; H, 6.7; N, 8.85%), 3-o-*tolyl* (48%) m.p. 182—183 °C (from ethanol), $\lambda_{max.}$ 315 nm (ε 48 150), τ (CF_3COOH) 2.37 (2 H, s), 2.62—2.78 (4 H, m), 6.66 (6 H, s), 7.46 (6 H, s), and 7.73 (3 H, s) (Found: C, 52.85; H, 6.7; N, 9.05. $C_{14}H_{21}ClN_2O_4$ requires C, 53.1; H, 6.7; N, 8.85%), 3-p-*methoxyphenyl* (51%), m.p. 126—127 °C (from ethanol), $\lambda_{max.}$ 316 nm (ε 40 600), τ[$(CD_3)_2CO$] 2.20 (2 H, s), 2.64—2.73 and 2.93—3.02 (4 H, AA'BB' pattern), 6.16 (3 H, s), 6.65 (6 H, s), 7.40 (6 H, s) (Found: C, 50.5; H, 6.3; N, 8.3. $C_{14}H_{21}ClN_2O_5$ requires C, 50.5; H, 6.35; N, 8.4%), 3-α-naphthyl [22] (89%), 3-β-*naphthyl* (85%), m.p. 203—204 °C (from ethanol), $\lambda_{max.}$ 317 nm (ε 50 800), τ[$(CD_3)_2SO$] 1.93 (2 H, m), 2.0—2.58 (7 H, m), 6.69 (6 H, d), 7.53 (6 H, d) (Found: C, 57.25; H, 6.1; N, 7.8. $C_{17}H_{21}ClN_2O_4$ requires C, 57.85; H, 6.1; N, 7.9%).

3-Biphenyl-4-yl-1,1,5,5-tetramethyl-1H-1,5-diazapentadienium Perchlorate.—Phosphoryl chloride (7 ml) was added to cooled, stirred dimethylformamide (9.1 g). Biphenyl-4-ylacetic acid (5.3 g) was then added and the mixture was heated at 80—90 °C for 20 h. Ice (30 g) was added and the mixture was extracted with chloroform (3 × 30 ml). The extract was dried (Na_2SO_4) and concentrated *in vacuo* to provide a syrup to which methanol (5 ml) and perchloric acid (60%; 5 ml) were added. The brown rubbery material which separated out was triturated with water and the resultant solid was filtered off and washed with ether. This *salt* had m.p. 142—145 °C, $\lambda_{max.}$ 315 nm (ε 25 800), τ[$(CD_3)_2SO$] 2.21 (2 H, s), 2.23—2.66 (9 H, m), 6.75 (6 H, s), and 7.50 (6 H, s) (Found: C, 59.8; H, 5.9; N, 7.1. $C_{19}H_{23}ClN_2O_4$ requires C, 60.25; H, 5.9; N, 7.4%).

1,1,5,5-Tetramethyl-3-pyridinio-1H-1,5-diazapentadienium Diperchlorate (14).—Phosphoryl chloride (43 ml) was added slowly to cooled stirred dimethylformamide (58.4 g). *N*-(Carboxymethyl)pyridinium chloride (27.2 g; prepared from pyridine and chloroacetic acid in acetonitrile) was added slowly and the mixture was stirred and heated at 60—70 °C for 12 h and then kept overnight at room temperature. It was cooled in an ice–salt mixture and stirred while methanol (200 ml) was added very slowly, followed by perchloric acid (70%; 20 ml) and then ether (100 ml). The diperchlorate (20 g, 32%) was filtered off and had m.p. 180—182 °C, $\lambda_{max.}$ 236sh and 305 nm (ε 10 400), τ[$(CD_3)_2CO$] 0.77 (2 H, d), 1.04 (1 H, t), 1.59 (2 H, d), 1.82 (2 H, s), 6.62 (6 H, s), and 7.45 (6 H, s) (Found: C, 34.6; H, 4.75; N, 10.0. $C_{12}H_{19}Cl_2N_3O_8$ requires C, 35.65; H, 4.75; N, 10.4%). Repeated analyses did not improve this result, but the sample provided a dihydrodiazepinium salt satisfactorily.

Direct Preparation of 2,3-Dihydro-1,4-diazepinium Salts from 3-Aryldiazapentadienium Salts.—The 1,2-diamine (4.5 mmol) in methanol (10 ml) was added in one portion to the diazapentadienium perchlorate (4.5 mmol) in methanol (150 ml) and the mixture was heated under reflux for the times indicated. Evaporation *in vacuo* of the solvent provided the dihydrodiazepinium perchlorates, as follows: 6-phenyl [4] (20 min) (89%), 1-*methyl*-6-*phenyl* (1.5 h) (88%), m.p. 150—151° (from ethanol), $\lambda_{max.}$ 251 and 363 nm (ε 12 700 and 10 200), τ[$(CD_3)_2CO$] 1.95—1.99 (2 H, m), 2.62 (5 H, s), 6.02 (4 H, s), and 6.32 (3 H, s) (Found: C, 50.2; H, 5.25; N, 9.75. $C_{12}H_{15}ClN_2O_4$ requires C, 50.1; H, 5.35; N, 9.8%), 1,4-*dimethyl*-6-*phenyl* (2.5 h) (82%), m.p. 154—156 °C (from ethanol), $\lambda_{max.}$ 253 and 367 nm (ε 12 800 and 12 200), τ[$(CD_3)_2CO$] 2.02 (2 H, s), 2.65 (5 H, s), 6.2 (4 H, s), and 6.51 (6 H, s) (Found: C, 51.85; H, 5.85; N, 9.45. $C_{13}H_{17}ClN_2O_4$ requires C, 51.85; H, 5.65; N, 9.3%), 1,4-*dibenzyl*-6-*phenyl* (3 h) (82%), m.p. 218—222 °C (from acetonitrile), $\lambda_{max.}$ 253 and 372 nm (ε 17 900 and 13 000), τ(CF_3COOH) 1.97 (2 H, s), 2.54—2.65 (15 H, complex), 5.13 (4 H, s), 6.26—6.52 (4 H, br) (Found: C, 66.1; H, 5.9; N, 6.1. $C_{25}H_{25}ClN_2O_4$ requires C, 66.2; H, 5.5; N, 6.2%), 2-*methyl*-6-*phenyl* (3 h) (86%), m.p. 105 °C (from ethanol), $\lambda_{max.}$ 245 and 353 nm (ε 12 200 and 8 000), τ[$(CD_3)_2CO$] 1.86 (1 H, d), 1.97 (1 H, d), 2.63 (5 H, s), 5.60—5.86 (1 H, br), 6.16 (2 H, d), and 8.56—8.63 (3 H, d) (Found: C, 50.05; H, 5.35; N, 9.8. $C_{12}H_{15}ClN_2O_4$ requires C, 50.2; H, 5.25; N, 9.75%), 2,2-*dimethyl*-6-*phenyl* (3 h) (60%), m.p. 156—158 °C (from ethanol), $\lambda_{max.}$ 246 and 352 nm (ε 10 500 and 6 800), τ[$(CD_3)_2CO$] 0.05—0.5 (2 H, br), 1.76—1.90 (1 H, br), 1.98—2.12 (1 H, br, d), 2.62 (5 H, s), 6.2—6.46 (2 H, br), and 8.54 (6 H, s) (Found: C, 51.8; H, 5.7; N, 9.55. $C_{13}H_{17}ClN_2O_4$ requires C, 51.85; H, 5.65; N, 9.3%), 2,3-*tetramethylene*-6-*phenyl* (8 h) (74%), m.p. 226—227 °C (from ethanol), $\lambda_{max.}$ 247 and 355 nm (ε 14 500 and 8 600), τ[$(CD_3)_2SO$] −0.6 to 0.0 (2 H, br), 2.22 (2 H, s), 2.62 (5 H, s), 6.6—6.88 (2 H, m), and 8.06—8.82 (8 H, m) (Found: C, 54.9; H, 6.0; N, 8.4. $C_{15}H_{19}ClN_2O_4$ requires C, 55.1; H, 5.8; N, 8.55%), 6-p-*tolyl* (1 h) (84%), m.p. 206—210 °C (from ethanol), $\lambda_{max.}$ 248 and 358 nm (ε 14 300 and 6 800), τ[$(CD_3)_2CO$] 2.05 (2 H, d), 2.80 (4 H, s), 6.20—6.34 (4 H, m), 7.96 (3 H, s) (Found: C, 50.85; H, 5.3; N, 9.5. $C_{12}H_{15}ClN_2O_4$ requires C, 50.25; H, 5.25; N, 9.8%), 1-*methyl*-6-p-*tolyl* (3 h) (80%), m.p. 118—120° (from ethanol), $\lambda_{max.}$ 252 and 366 nm (ε 14 550 and 9 600), τ[$(CD_3)_2CO$–CF_3CO_2H] 1.86 (2 H, s), 2.76 (4 H, s), 6.0 (4 H, m), 6.33 (3 H, s), and 7.67 (3 H, s) (Found: C, 51.25; H, 5.8; N, 9.15. $C_{13}C_{17}ClN_2O_4$ requires C, 51.9; H, 5.7; N, 9.3%), 1,4-*dimethyl*-6-p-*tolyl* (2 h) (80%), m.p. 180—182 °C (from ethanol), $\lambda_{max.}$ 254 and 370 nm (ε 12 950 and 9 800), τ[$(CD_3)_2SO$] 2.05 (2 H, s), 2.79 (4 H, s), 6.23 (4 H, s), 6.54 (6 H, s), and 7.72 (3 H, s) (Found: C, 53.65; H, 6.65; N, 8.25. $C_{14}H_{19}ClN_2O_4$ requires C, 53.5; H, 6.05; N, 8.9%), 1,4-*dibenzyl*-6-p-*tolyl* (6 h) (76%), m.p. 178 °C (from acetonitrile), $\lambda_{max.}$ 248 and 360 nm (ε 31 500 and 13 600), τ[$(CD_3)_2SO$] 1.66 (2 H, s), 2.59 (10 H, s), 2.69 (2 H, d), 5.05 (4 H, s), 6.42 (4 H, s), and 7.66 (3 H, s) (Found: C,

66.45; H, 5.45; N, 5.95. $C_{26}H_{27}ClN_2O_4$ requires C, 66.8; H, 5.8; N, 6.0%), 2-*methyl*-6-p-*tolyl* (4 h) (93%), m.p. 180—181 °C (from ethanol), $\lambda_{max.}$ 248 and 358 nm (ε 15 500 and 8 100), τ[$(CD_3)_2SO$] 2.05 (1 H, d), 2.18 (1 H, d), 2.80 (4 H, s), 5.85—6.2 (1 H, br), 6.44 (2 H, m), 7.69 (3 H, s), and 8.77 (3 H, d) (Found: C, 51.85; H, 5.85; N, 9.15. $C_{13}H_{17}ClN_2O_4$ requires C, 51.9; H, 5.7; N, 9.3%), 2,3-*tetramethylene*-6-p-*tolyl* (6 h) (41%), m.p. 208—210 °C (from ethanol), $\lambda_{max.}$ 248 and 360 nm (ε 17 000 and 8 200), τ[$(CD_3)_2SO$] 0.06—0.4 (2 H, br), 2.21 (2 H, d), 2.80 (4 H, s), 6.6—6.8 (2 H, br), 7.68 (3 H, s), and 8.02—8.60 (8 H, m) (Found: C, 56.05; H, 6.35; N, 8.0. $C_{16}H_{21}ClN_2O_4$ requires C, 56.4; H, 6.2; N, 7.55%), 6-p-*methoxyphenyl* (1 h) (95%), m.p. 204—208 °C (from ethanol), $\lambda_{max.}$ 248 and 362 nm (ε 12 900 and 5 900) τ[$(CD_3)_2CO$] 2.04 (2 H, s), 2.70 (2 H, d), 3.03 (2 H, d), 6.14 (4 H, s), and 6.20 (3 H, s) (Found: C, 47.8; H, 5.05; N, 9.65. $C_{12}H_{15}ClN_2O_5$ requires C, 47.55; H, 4.95; N, 9.25%), 1,4-*dibenzyl*-6-p-*methoxyphenyl* (4 h) (52%), m.p. 174—176 °C (from ethanol), $\lambda_{max.}$ 253 and 380 nm (ε 18 800 and 12 100), τ[$(CD_3)_2CO$] 1.76 (2 H, s), 2.57 (10 H, d), 2.64 (2 H, d), 2.94 (2 H, d), 4.96 (4 H, s), 6.20 (4 H, s), and 6.25 (3 H, s) (Found: C, 64.45; H, 5.55; N, 5.75. $C_{26}H_{27}ClN_2O_5$ requires C, 64.6; H, 5.6; N, 5.8%), 6-p-*methoxyphenyl*-2-*methyl* (5 h) (86%), m.p. 174—176 °C (from ethanol), $\lambda_{max.}$ 253 and 376 nm (ε 9 500 and 7 500), τ[$(CD_3)_2SO$] 2.15 (2 H, d), 2.76 (2 H, d), 3.05 (2 H, d), 5.8—6.1 (1 H, m), 6.24 (3 H, s), 6.46 (2 H, m), and 8.78 (3 H, d) (Found: C, 49.25; H, 5.4; N, 8.75. $C_{13}H_{17}ClN_2O_5$ requires C, 49.25; H, 5.35; N, 8.85%), 6-p-*methoxyphenyl*-2,2-*dimethyl* (5 h) (91%), m.p. 137—138 °C (from ethanol), $\lambda_{max.}$ 247 and 360 nm (ε 16 700 and 6 800), τ[$(CD_3)_2SO$] 2.00 (1 H, d), 2.30 (1 H, d), 2.71 (2 H, d), 3.07 (2 H, d), 6.2 (3 H, s), 6.6 (2 H, s), and 8.65 (6 H, s) (Found: C, 50.7; H, 5.75; N, 8.6. $C_{14}H_{19}ClN_2O_5$ requires C, 50.8; H, 5.75; N, 8.45%), 6-p-*nitrophenyl* (15 min) (72%), m.p. 192 °C (from ethanol–perchloric acid), $\lambda_{max.}$ 345 nm (ε 18 300), τ[$(CD_3)_2SO$] 1.72 (2 H, d), 1.82 (2 H, s), 2.36 (2 H, d), and 6.15 (4 H, m) (Found: C, 41.7; H, 3.85; N, 13.3. $C_{11}H_{12}ClN_3O_6$ requires C, 41.6; H, 3.8; N, 13.2%), 1,4-*dimethyl*-6-p-*nitrophenyl* (2 h) (68%), m.p. 161—162 °C (from ethanol), $\lambda_{max.}$ 356 nm (ε 20 250), τ[$(CD_3)_2SO$] 1.77 (2 H, d), 1.84 (2 H, s), 2.35 (2 H, d), 6.13 (4 H, s), and 6.45 (6 H, s) (Found: C, 45.3; H, 4.7; N, 12.15. $C_{13}H_{16}ClN_3O_6$ requires C, 45.15; H, 4.65; N, 12.15%), 1,4-*dibenzyl*-6-p-*nitrophenyl* (4 h) (82%), m.p. 162 °C (from acetonitrile), $\lambda_{max.}$ 364 nm (ε 22 800), τ[$(CD_3)_2SO$] 1.46 (2 H, s), 1.68 and 2.23 (4 H, AA'BB' pattern), 2.57 (10 H, s), 5.03 (4 H, s), and 6.37 (4 H, s) (Found: C, 60.55; H, 4.4; N, 8.3. $C_{25}H_{24}ClN_3O_6$ requires C, 60.3; H, 4.85; N, 8.45%), 6-p-*chlorophenyl* (1 h) (76%), m.p. 140 °C (from ethanol), $\lambda_{max.}$ 255 and 354 nm (ε 20 400 and 9 800), τ[$(CD_3)_2SO$–CF_3COOH] 2.03 (2 H, d), 2.61 (4 H, s), and 6.25 (4 H, br) (Found: C, 42.95; H, 3.85; N, 9.0. $C_{11}H_{12}Cl_2N_2O_4$ requires C, 43.0; H, 3.95; N, 9.1%), 6-p-*bromophenyl* (10) (1 h) (91%), m.p. 285—287 °C (from ethanol–perchloric acid), $\lambda_{max.}$ 254 and 352 nm (ε 16 500 and 7 800), τ[$(CD_3)_2SO$] 2.04—2.12 (2 H, m), 2.47 (2 H, d), 2.71 (2 H, d), 6.23 (4 H, s) (Found: C, 37.5; H, 3.4; N, 7.9. $C_{11}H_{12}BrClN_2O_4$ requires C, 37.55; H, 3.45; N, 7.95%), 6-*biphenyl*-4-*yl* (20 min) (89%), m.p. 295 °C (decomp.) (from acetonitrile), $\lambda_{max.}$ 275 and 390 nm (ε 31 800 and 7 300), τ[$(CD_3)_2SO$] 1.96 (2 H, d), 2.27—2.64 (9 H, m), and 6.22 (4 H, m) (Found: C, 58.55; H, 4.7; N, 7.8. $C_{17}H_{17}ClN_2O_4$ requires C, 58.55; H, 4.9; N, 8.05%), 6-α-*naphthyl* (30 min) (99%), m.p. 100—102 °C (from acetonitrile), $\lambda_{max.}$ 293 and 350 nm (ε 9 500 and 8 200), τ(CF_3COOH) 2.06 (2 H, d), 2.41—2.60 (7 H, m), 6.00 (4 H, s) (Found: C, 56.0; H, 5.05; N, 9.0. $C_{15}H_{15}ClN_2O_4$ requires C, 55.8; H, 4.7; N, 8.7%), 1-*methyl*-6-α-*naphthyl* (6 h) (69%), m.p. 94—96 °C (from ethanol), $\lambda_{max.}$ 294 and 358 nm (ε 9 250 and 9 800), τ[$(CD_3)_2SO$] 1.80 (1 H, d), 1.95 (1 H, s), 2.02—2.54 (7 H, m), 6.20 (4 H, s), and 6.45 (3 H, s) (Found: C, 57.8; H, 5.05; N, 7.85. $C_{16}H_{17}ClN_2O_4$ requires C, 57.05; H, 5.1; N, 8.3%), 1,4-*dimethyl*-6-α-*naphthyl* (7 h) (82%), m.p. 139—140 °C (from ethanol), $\lambda_{max.}$ 295 and 364 nm (ε 9 800 and 11 800), τ[$(CD_3)_2SO$] 1.98 (2 H, s), 2.02—2.56 (7 H, m), 6.07 (4 H, s), and 6.57 (6 H, s) (Found: C, 57.9; H, 5.4; N, 7.9. $C_{17}H_{19}ClN_2O_4$ requires C, 58.2; H, 5.45; N, 7.9%), 6-β-*naphthyl* (30 min) (90%), m.p. 168—170 °C (from ethanol), $\lambda_{max.}$ 297sh and 355 nm (ε 7 500), τ[$(CD_3)_2SO$] 1.89 (2 H, s), 2.02—2.54 (7 H, m), 6.22 (4 H, s) (Found: C, 55.5; H, 4.85; N, 8.55. $C_{15}H_{15}ClN_2O_4$ requires C, 55.8; H, 4.7; N, 8.7%), 1-*methyl*-6-β-*naphthyl* (6 h) (49%), m.p. 165 °C (from ethanol) $\lambda_{max.}$ 364 nm (ε 7 900), τ[$(CD_3)_2SO$] 1.81 (1 H, d), 1.94 (1 H, d), 2.02—2.54 (7 H, m), 6.20 (4 H, s), and 6.45 (3 H, s) (Found: C, 56.85; H, 5.3; N, 8.05. $C_{16}H_{17}ClN_2O_4$ requires C, 57.05; H, 5.1; N, 8.3%), 1,4-*dimethyl*-6-β-*naphthyl* (6 h) (89%), m.p. 184 °C (from ethanol), $\lambda_{max.}$ 286 and 370 nm (ε 12 750 and 10 750), τ[$(CD_3)_2SO$] 1.86 (2 H, s), 2.0—2.5 (7 H, m), 6.16 (4 H, s), and 6.47 (6 H, s) (Found: C, 58.4; H, 5.4; N, 7.95. $C_{17}H_{19}ClN_2O_4$ requires C, 58.2; H, 5.45; N, 8.0%), 1,4-*dibenzyl*-6-β-*naphthyl* (7 h) (85%), m.p. 182—184 °C (from acetonitrile), $\lambda_{max.}$ 376 nm (ε 12 650) τ[$(CD_3)_2SO$] 1.45 (2 H, s), 2.02—2.52 (7 H, m), 2.56 (10 H, s), 5.0 (4 H, s), and 6.38 (4 H, br) (Found: C, 69.4; H, 5.5; N, 5.35. $C_{29}H_{27}ClN_2O_4$ requires C, 69.25; H, 5.4; N, 5.55%), 2,2-*dimethyl*-6-β-*naphthyl* (7 h) (83%), m.p. 191—192 °C (from ethanol), $\lambda_{max.}$ 358 nm (ε 7 300), τ[$(CD_3)_2SO$] 1.82 (1 H, d), 1.97 (1 H, d), 2.02—2.56 (7 H, m), 6.53 (2 H, br), and 8.64 (6 H, s) (Found: C, 57.9; H, 5.35; N, 7.85. $C_{17}H_{19}ClN_2O_4$ requires C, 58.2; H, 5.45; N, 8.0%), 2,3-*tetramethylene*-6-β-*naphthyl* (6 h) (64%), m.p. 198—200 °C, $\lambda_{max.}$ 360 nm (ε 6 600), τ[$(CD_3)_2SO$] 2.0—2.6 (9 H, m), 6.6—6.8 (2 H, m), and 8.2—8.8 (8 H, m) (Found: C, 60.45; H, 5.6; N, 7.4. $C_{19}H_{21}ClN_2O_4$ requires C, 60.55; H, 5.6; N, 7.45%), 6-*pyridinio diperchlorate* (30 min) (52%), m.p. 230—232 °C (from acetonitrile), $\lambda_{max.}$ 320 and 360sh nm (ε 8 450), τ[$(CD_3)_2SO$] 1.0—1.05 (2 H, m), 1.32—1.50 (1 H, m), 1.8—1.98 (2 H, m), 2.36 (2 H, s), and 6.37 (4 H, s) (Found: C, 32.2; H, 3.55; N, 11.15. $C_{10}H_{13}Cl_2N_3O_8$ requires C, 32.1; H, 3.5; N, 11.25%).

Reactions of Vinamidinium Salts (2) *with Piperidine.*—(a) 1,1-*Dimethyl*-5,5-*pentamethylene*-3-*phenyl*-1H-1,5-*diazapentadienium perchlorate*. Piperidine (0.51 g, 6 mmol) in methanol (20 ml) was added to the vinamidinium salt (2) (0.9 g, 3 mmol) in methanol (100 ml). The mixture was kept at room temperature for 2 h and solvent was then removed *in vacuo* to give the crystalline *perchlorate* (0.5 g, 86%), which was washed with ether and had m.p. 166—168 °C (from ethanol), $\lambda_{max.}$ 316 nm (ε 51 800), τ[$(CD_3)_2SO$] 2.22 (2 H, s), 2.55 (5 H, m), 6.38 (2 H, br), 6.67 (3 H, s), 7.1 (2 H, br), 7.48 (3 H, s), 8.23 (4 H, br), and 8.7 (2 H, br) (Found: C, 55.6; H, 6.8; N, 7.8. $C_{16}H_{23}ClN_2O_4$ requires C, 56.05; H, 6.75; N, 8.15%).

(b) 1,1:5,5-*Bispentamethylene*-3-*phenyl*-1H-1,5-*diazapentadienium perchlorate*. A solution of the preceding 5,5-pentamethylene salt (0.68 g, 2 mmol) and piperidine (1.1 g, 12 mmol) in methanol (50 ml) was heated under reflux for 2 h. Solvent was removed *in vacuo* and the resultant crystalline *bispentamethylene perchlorate* (0.6 g, 70%) was

filtered off and washed with ether, and had m.p. 228—230 °C (from acetonitrile), $\lambda_{max.}$ 316 nm (ε 53 600), τ(CF_3-COOH) 2.5br (2 H, m), 2.7br (5 H, m), 6.7br (8 H, m), and 8.4br (12 H, m) (Found: C, 58.7; H, 7.3; N, 7.3. $C_{19}H_{27}ClN_2O_4$ requires C, 59.6; H, 7.1; N, 7.3%). This salt was also prepared by heating a solution of the vinamidinium salt (2) (1 mmol) and piperidine (2 mmol) in acetonitrile under reflux for 10 h. The *p*-tolyl, α-naphthyl, and β-naphthyl analogues of (2) similarly provided bispentamethylene derivatives when heated with 2 mol equiv. of piperidine in acetonitrile, but the *o*-tolyl analogue of (2) only had one dimethylamine group substituted when heated with 10 mol equiv. of piperidine in methanol for 3 h.

Formation of Dihydrodiazepinium Salts from 3-Aryl-1,1,5,5-tetramethyl-1,5-diazapentadienium Salts by Addition of Ammonia followed by Addition of 1,2-Diamine.—Ammonia was bubbled through a solution of the diazapentadienium salt in methanol or ethanol, which was heated under reflux for 30 min. The diamine (1 mol equiv.) was then added and the mixture was heated under reflux for a further period ranging from 30 min to 4 h, as indicated. Removal of solvent *in vacuo* left the product which was either a solid, or an oil which solidified when kept overnight at 0 °C and/or triturated with ether. The following dihydrodiazepinium salts were prepared in this way: 6-phenyl [4] (30 min) (85%), *5-methyl-6-phenyl* [from the vinamidinium salt (3) (see below)] (1 h) 73%), m.p. 117—118 °C (from ethanol), $\lambda_{max.}$ 243 and 343 nm (ε 7 600 and 9 700), τ[$(CD_3)_2CO$], 2.36 (1 H, s), 2.62 (5 H, m), 6.07 (4 H, s), and 7.94 (3 H, s) (Found: C, 50.3; H, 5.3; N, 9.85. $C_{12}H_{15}ClN_2O_4$ requires C, 50.25; H, 5.25; N, 9.75%), *2,2,3,3-tetramethyl-6-phenyl* (4 h) (39%), m.p. 145—146 °C, (from ethanol), $\lambda_{max.}$ 245 and 350 nm (ε 9 300 and 5 100), τ[$(CD_3)_2SO$] 2.30 (2 H, d), 2.72 (5 H, s), 8.61 (6 H, s), and 9.10 (6 H, s) (Found: C, 54.2; H, 6.5; N, 8.3. $C_{15}H_{21}ClN_2O_4$ requires C, 54.8; H, 6.35; N, 8.5%), *1,4-diethyl-6-phenyl* (1 h) (76%), m.p. 68—70 °C (from ethanol), $\lambda_{max.}$ 253 and 369 nm (ε 14 300 and 11 700), τ[$(CD_3)_2SO$] 1.93 (2 H, s), 2.6 (5 H, s), 6.14 (4 H, s), 6.15 (4 H, q), and 8.65 (6 H, t) (Found: C, 54.95; H, 6.55; N, 8.45. $C_{15}H_{21}ClN_2O_4$ requires C, 54.80; H, 6.45; N, 8.5%), 1,4,5-trimethyl-6-phenyl (3 h) (59%), m.p. 178—180 °C (from ethanol), $\lambda_{max.}$ 250 and 359 nm (ε 7 700 and 14 000), τ[$(CD_3)_2SO$] 2.4 (1 H, s), 2.70 (5 H, m), 6.21br (4 H, m), 6.62 (6 H, s), and 7.97 (3 H, m) (Found: C, 50.6; H, 6.15; N, 9.85. $C_{14}H_{19}ClN_2O_4$ requires C, 53.4; H, 6.1; N, 8.9. Further recrystallisation did not improve this analysis, which is consistent with contamination with *ca.* 10% *NN'*-dimethylethylenediamine perchlorate; spectra concur), *6-o-tolyl* (1 h) (77%), m.p. 70 °C (from ethanolic perchloric acid), $\lambda_{max.}$ 238 and 347 nm (ε 7 200 and 9 900), τ[$(CD_3)_2SO$] 2.30 (2 H, d), 2.68 (4 H, m), 6.52br (4 H), and 7.75 (3 H, s) (Found: C, 49.3; H, 5.4; N, 9.55. $C_{12}H_{15}ClN_2O_4$ requires C, 50.3; H, 5.25; N, 9.75. Analysis not improved by further recrystallisation).

2-Methyl-1,3,5-triphenyl-1H-1,5-diazapentadienium Perchlorate (3) *and 2,3-Dihydro-1,5-dimethyl-6-phenyl-1,4-diazepinium Perchlorate.*—Aniline (25 g, 130 mmol) in ethanol (20 ml), was added to a stirred solution of 3-chloro-2-phenylbut-2-enal [24] (11.7 g, 65 mmol) in ethanol (50 ml). After 5 min, perchloric acid (60%, 5.5 g) was added slowly. Yellow crystals formed which after 30 min were filtered off and washed well with ether. The diazapentadienium perchlorate (13.5 g, 50%) had m.p. 145—146 °C, $\lambda_{max.}$ 280sh and 360 nm (ε 23 100) τ[$(CD_3)_2SO$] 1.67—1.93 (1 H, m), 2.30—2.83 (15 H, m), 6.15vbr (NH), and 7.53 (3 H, s). A solution of this salt (4.1 g, 10 mmol) in methanol (150 ml) was heated under reflux and ammonia was bubbled through it for 30 min. The solution was cooled, *N*-methylethylenediamine (0.74 g, 10 mmol) was added, and the mixture was heated under reflux for 6 h. Removal of solvent *in vacuo* left an oil, which, after being kept at 0 °C overnight followed by trituration with ether, gave, with difficulty, a solid *dihydrodiazepinium perchlorate* (2.2 g, 67%), m.p. 90 °C (from ethanol), $\lambda_{max.}$ 246 and 350 nm (ε 5 900 and 12 700), τ[$(CD_3)_2CO$] —0.6br (NH), 2.34 (1 H, s), 2.60 (5 H, s), 6.02 (4 H, s), 6.43 (3 H, s), and 7.9 (3 H, s) (Found: C, 51.8; H, 6.1; N, 9.65. $C_{13}H_{17}ClN_2O_4$ requires C, 51.9; H, 5.7; N, 9.3%).

2-Benzyl-3-methyl-1,5-diphenyl-1H-1,5-diazapentadienium Perchlorate (5).—*NN*-Dimethylformamide (5.5 ml) was added to cooled phosphoryl chloride (5 ml) and the mixture was stirred for 30 min in an ice-bath. 1-Phenylbutan-2-one (5 ml) was added dropwise during 30 min. The mixture was stirred for 2 days and then poured onto ice. The resultant mixture was extracted with methylene chloride, and the extract was washed with saturated aqueous sodium carbonate and water, and dried (Na_2SO_4). Removal of solvent *in vacuo* left 3-chloro-2-methyl-4-phenylbut-2-enal (5.2 g, 79%). Aniline (4.7 g, 50 mmol) in ethanol (15 ml) was added to a portion of this chloroacrylaldehyde (4.9 g, 25 mmol) in ethanol (10 ml), followed by perchloric acid (60%, 2.5 g). After 15 min the resultant *diazapentadienium perchlorate* (3 g, 29%) was filtered off and washed well with ether. It had m.p. 167—168 °C, $\lambda_{max.}$ 305sh and 340 nm (ε 34 150), τ[$(CD_3)_2SO$] 1.59br (1 H, m), 2.75br (15 H, m), 5.65 (2 H, s), 6.40br (NH), and 7.86 (3 H, s) (Found: C, 64.75; H, 5.3; N, 6.5. $C_{23}H_{23}ClN_2O_4$ requires C, 64.7; H, 5.45; N, 6.55%).

5-Benzyl-2,3-dihydro-6-methyl-1,4-diazepinium Perchlorate.—Ammonia was bubbled for 30 min through a solution of the diazapentadienium salt (5) (2.1 g, 10 mmol) in ethanol (175 ml) which was heated under reflux. The solution was cooled and ethylenediamine (0.3 g, 5 mmol) in ethanol (25 ml) was added. The mixture was heated under reflux for 4 h. Solvent was removed *in vacuo*; a small amount of ether was added to the residue and it was kept overnight at 0 °C. The *dihydrodiazepinium perchlorate* (1.1 g, 75%) was filtered off and washed thoroughly with ether, and had m.p. 93—94 °C, $\lambda_{max.}$ 246sh and 349 nm (ε 13 000), τ(CF_3CO_2H), 2.53 (1 H, d), 2.71 (5 H, m), 6.04 (2 H, s), 6.26 (4 H, m), 7.0 (3 H, s) (Found: C, 51.25; H, 5.85; N, 9.35. $C_{13}H_{17}ClN_2O_4$ requires C, 51.9; H, 5.7; N, 9.3%).

Sodium Salt of Phenylmalonaldehyde.—A solution of sodium hydroxide (1.0 g) in water (0.5 ml) and methanol (25 ml) was added to a solution of the vinamidinium salt (2) (3 g) in methanol (100 ml), and the mixture was heated under reflux for *ca.* 2.5 h. Solvent was then evaporated *in vacuo* to give the pure sodium salt in essentially quantitative yield.

Dihydrodiazepinium Perchlorates from Arylmalonaldehydes.—Dianilinoethane (1.06 g, 5 mmol) was added to phenylmalonaldehyde, liberated *in situ* by addition of perchloric acid (60%, 1 g, 10 mmol) to a solution of the sodium salt of the dialdehyde (0.85 g, 5 mmol), itself obtained by alkaline hydrolysis of the vinamidinium salt (2), in methanol (10 ml). After 30 min the yellow *2,3-dihydro-1,4,6-triphenyl-1,4-diazepinium perchlorate* (7a) (1.55 g, 59%) was filtered off, washed with ether, and had m.p. 199—200 °C (from ethanol), $\lambda_{max.}$ 254 and 405 nm (ε 21 500

and 22 500), τ[$(CD_3)_2SO$] 1.7 (2 H, s), 2.48br (15 H, m), and 5.5br (4 H) (Found: C, 64.85; H, 4.85; N, 6.45. $C_{23}H_{21}ClN_2O_4$ requires C, 64.95; H, 4.95; N, 6.6%). The same method was also used to prepare the following dihydrodiazepinium perchlorates: 1,4-*bis*-p-*methoxyphenyl*-6-*phenyl* (7b) (58%), m.p. 162—164 °C (from ethanol), $\lambda_{max.}$ 256 and 414 nm (ε 24 250 and 16 200), τ[$(CD_3)_2CO$] 1.84 (2 H, s), 2.42 and 2.94 (8 H, AA'BB' pattern), 2.66br (5 H, m), 5.40br (4 H), and 6.16 (6 H, s) (Found: C, 61.25; H, 5.25; N, 5.75. $C_{25}H_{25}ClN_2O_6$ requires C, 61.9; H, 5.2; N, 5.75%), 6-p-*methoxyphenyl*-1,4-*diphenyl* (7c) (33%), m.p. 78 °C, $\lambda_{max.}$ 253 and 414 nm (ε 23 300 and 16 800), τ[$(CD_3)_2CO$] 1.78 (2 H, s), 2.40 (10 H, m), 2.52 and 3.02 (4 H, AA'BB' pattern), 5.27 (4 H, m), and 6.16 (3 H, s) (Found: C, 63.7; H, 5.15; N, 6.8. $C_{24}H_{23}ClN_2O_5$ requires C, 63.3; H, 5.05; N, 6.15%), 1,4,6-*tris*-p-*methoxyphenyl* (7d) (48%), m.p. 70 °C (from ethanol), $\lambda_{max.}$ 229, 259, and 424 nm (ε 18 900, 19 050, and 20 950), τ[$(CD_3)_2CO$] 1.89 (2 H, s), 2.42 and 2.93 (8 H, AA'BB' pattern), 2.55 and 3.04 (4 H, AA'BB' pattern), 5.41 (4 H), and 6.17 (9 H, s) (Found: C, 60.65; H, 5.3; N, 5.2. $C_{26}H_{27}ClN_2O_7$ requires C, 60.65; H, 5.25; N, 5.4%), 6-p-*nitrophenyl*-1,4-*diphenyl* (7e) (73%), m.p. 260 °C (from acetonitrile), $\lambda_{max.}$ 235, 275sh, and 397 nm (ε 14 300 and 22 100), τ[$(CD_3)_2SO$] 1.60 (2 H, s), 1.76 and 2.12 (4 H, AA'BB' pattern), 2.40 (10 H, m), and 5.46br (4 H) (Found: C, 58.65; H, 4.25; N, 9.05. $C_{23}H_{20}ClN_3O_6$ requires C, 58.8; H, 4.3; N, 8.95%), 6-α-*naphthyl*-1,4-*diphenyl* (7f) (52%), m.p. 215—217 °C (from ethanol), $\lambda_{max.}$ 292sh and 403 nm (ε 23 200), τ[$(CD_3)_2SO$] 1.82 (2 H, s), 2.28br (7 H, m), 2.43 (10 H, m), 5.30br (4 H, m) (Found: C, 68.0; H, 4.8; N, 5.8. $C_{27}H_{23}ClN_2O_4$ requires C, 68.3; H, 4.9; N, 5.9%), 1,6-*diphenyl* (30%), m.p. 158—160 °C (from ethanol), $\lambda_{max.}$ 245 and 376 nm (ε 16 800 and 15 800), τ[$(CD_3)_2SO$–D_2O] 1.89 (2 H, m), 2.49 (10 H, m), 5.72br (4 H) (Found: C, 58.35; H, 5.1; N, 7.75. $C_{17}H_{17}ClN_2O_4$ requires C, 58.35; H, 4.85; N, 8.05%), 6-p-*nitrophenyl*-1-*phenyl* (44%), m.p. 196—197 °C (from acetonitrile), $\lambda_{max.}$ 230 and 374 nm (ε 14 800 and 19 550), τ[$(CD_3)_2CO$] 1.50 (1 H, d), 1.64 (1 H, d), 1.74 and 2.18 (4 H, AA'BB' pattern), 2.39 (5 H, m), 5.58 (2 H, m), and 5.68 (2 H, m) (Found: C, 51.7; H, 4.1; N, 10.85. $C_{17}H_{16}N_3ClO_6$ requires C, 51.85; H, 4.1; N, 10.65%).

6-Aryl-NN'-dimethyldihydrodiazepinium Perchlorates by Reaction of NN'-Unsubstituted Analogues with NN'-Dimethylethylenediamine.— 6-Biphenyl-4-yl-2,3-dihydro-1,4-diazepinium perchlorate (0.34 g, 1 mmol) and *NN'*-dimethylethylenediamine (0.88 g, 10 mmol) in acetonitrile (20 ml) were heated under reflux for 6 h. Removal of solvent *in vacuo* provided the 6-*biphenyl*-4-*yl*-1,4-*dimethyldihydrodiazepinium perchlorate* (0.3 g, 82%), m.p. 140 °C (from ethanolic perchloric acid), $\lambda_{max.}$ 370 nm (ε 10 900), τ[$(CD_3)_2SO$] 1.98 (2 H, s), 2.43 (9 H, m), 61.6 (4 H, s), and 6.48 (6 H, s) (Found: C, 60.5; H, 5.6; N, 7.4. $C_{19}H_{21}ClN_2O_4$ requires C, 60.6; H, 5.6; N, 7.45%). In similar fashion, 6-phenyl-, 6-*p*-tolyl-, 6-α-naphthyl-, and 6-β-naphthyl-dihydrodiazepinium salts were converted in high yield into their *NN'*-dimethyl analogues, identical (m.p., mixed m.p., spectra) with authentic samples.

Reactions of 6-Aryldihydrodiazepinium Salts with Bromine.—Bromine (0.64 g, 4 mmol) in methanol (10 ml) was added dropwise to a stirred solution of the 6-phenyldihydrodiazepinium salt (8) (1 g, 4 mmol) in methanol (40 ml) at room temperature. The mixture was stirred for a further 2 h. Addition of ether precipitated the 6-*p*-bromophenyl derivative (10) (65%), which was recrystallised from ethanolic perchloric acid and was identical (m.p., mixed m.p., spectra) with an authentic sample (see above). The following brominated derivatives were prepared similarly; solvent was evaporated *in vacuo* in some cases, rather than adding ether, to precipitate the product: 6-p-*bromophenyl*-1-*methyl* (53%), m.p. 184—186 °C, $\lambda_{max.}$ 258 and 360 nm (ε 15 200 and 9 700), τ[$(CD_3)_2SO$] 1.93 (1 H, s), 2.06 (1 H, d), 2.41 and 2.68 (4 H, AA'BB' pattern), 6.20 (4 H, s), and 6.47 (3 H, s) (Found: C, 39.6; H, 3.65; N, 7.6. $C_{12}H_{14}BrClN_2O_4$ requires C, 39.4; H, 3.85; N, 7.65%), 6-p-*bromophenyl*-1,4-*dimethyl* (40%), m.p. 180 °C, $\lambda_{max.}$ 262 and 366 nm (ε 19 400 and 13 400), τ[$(CD_3)_2SO$] 2.02 (2 H, s), 2.43 and 2.70 (4 H, AA'BB' pattern), 6.20 (4 H, s), and 6.67 (6 H, s) (Found: C, 40.85; H, 4.35; N, 7.3. $C_{13}H_{16}BrClN_2O_4$ requires C, 41.1; H, 4.2; N, 7.4%), 6-p-*bromophenyl*-1,4-*diethyl* (70%), m.p. 64 °C, $\lambda_{max.}$ 263 and 368 nm (ε 21 400 and 13 400), τ(CF_3CO_2H) 2.26 (2 H, s), 2.49 and 2.86 (4 H, AA'BB' pattern), 6.06 (4 H, s), 6.21 (4 H, q), and 8.57 (6 H, t) (Found: C, 44.65; H, 5.1; N, 7.0. $C_{15}H_{20}BrClN_2O_4$ requires C, 44.2; H, 4.95; N, 6.85%), 6-*p*-bromophenyl-1,4-bis-*p*-methoxyphenyl (62%), m.p. 128—130 °C, $\lambda_{max.}$ 223, 256, and 414 nm (ε 18 600, 16 900, and 24 800), τ[$(CD_3)_2CO$] 1.87 (2 H, s), 2.30 and 2.91 (8 H, AA'BB' pattern), 2.52br (4 H, m), 5.28 (4 H, m), and 6.15 (6 H, s) (Found: C, 53.8; H, 4.15; N, 4.2. $C_{25}H_{24}BrClN_2O_6$ requires C, 53.25; H, 4.3; N, 4.95%), 6-p-*bromophenyl*-2-*methyl* (40%), m.p. 228—231 °C, $\lambda_{max.}$ 255 and 354 nm (ε 16 700 and 8 400), τ[$(CD_3)_2SO$] —0.6br (2 H), 1.98 (1 H, d), 2.12 (1 H, d), 2.41 and 2.68 (4 H, AA'BB' pattern), 5.91br (1 H), 6.42 (2 H, m), and 8.76 (3 H, d) (Found: C, 39.5; H, 3.9; N, 7.75. $C_{12}H_{14}BrClN_2O_4$ requires C, 39.4; H, 3.85; N, 7.65%), 6-p-*bromophenyl*-2,2-*dimethyl* (33%), m.p. 214 °C (decomp.), $\lambda_{max.}$ 254 and 352 nm (ε 16 600 and 8 200), τ[$(CD_3)_2SO$] 1.86 (1 H, d), 2.26 (1 H, d), 2.42 and 2.67 (4 H, AA'BB' pattern), 6.65br (2 H), and 8.70 (6 H, s) (Found: C, 41.5; H, 3.5; N, 7.85. $C_{13}H_{16}BrClN_2O_4$ requires C, 41.3; H, 3.7; N, 7.4%), 6-p-*bromophenyl*-2,3-*tetramethylene* (32%), m.p. 278—280 °C, $\lambda_{max.}$ 256 and 356 nm (ε 17 850 and 7 700), τ[$(CD_3)_2SO$] 2.22 (2 H, s) 2.40 and 2.68 (4 H, AA'BB' pattern), 6.74br (2 H), and 8.4br (8 H, m) (Found: C, 44.9; H, 4.8; N, 7.1. $C_{15}H_{18}BrClN_2O_4$ requires C, 44.35; H, 4.75; N, 6.9%), 6-(4-*bromo*-1-*naphthyl*) (67%), m.p. 198—200 °C, $\lambda_{max.}$ 301, 323sh, and 348 nm (ε 9 800 and 8 000), τ[$(CD_3)_2SO$] 2.01 (2 H, s), 2.09—2.65 (6 H, m), and 6.12 (4 H, m) (Found: C, 44.95; H, 3.85; N, 6.75. $C_{15}H_{14}BrClN_2O_4$ requires C, 44.85; H, 3.5; N, 6.95%), 6-(?-bromo-β-naphthyl) (74%), m.p. 223—224 °C, $\lambda_{max.}$ 256, 285sh, 324sh, and 348 nm (ε 21 500 and 10 600), τ[$(CD_3)_2SO$] 1.68 (1 H, d), 1.77 (1 H, d), 1.84—2.50 (6 H, m), and 6.14 (4 H, m) (Found: C, 45.3; H, 3.7; N, 7.0. $C_{15}H_{14}BrClN_2O_4$ requires C, 44.85; H, 3.5; N, 6.95%).

6-Bromo-1,4-bis-p-methoxyphenyl-2,3-dihydro-1,4-diazepinium perchlorate. Bromine (0.16 g, 1 mmol) in methanol (4 ml) was added dropwise to a solution of the 1,4-bis-*p*-methoxyphenyldihydrodiazepinium perchlorate (0.4 g, 1 mmol). The mixture was stirred for 30 min. Removal of solvent *in vacuo* left the 6-*brominated salt* (87%), m.p. 204—206 °C (from ethanolic perchloric acid), $\lambda_{max.}$ 280sh, 288, and 419 nm (ε 17 200 and 27 600), τ(CF_3COOH) 2.20 (2 H, br s), 2.65 and 2.89 (8 H, AA'BB' pattern), 5.65br (4 H), and 6.06 (6 H, s) (Found: C, 46.6; H, 4.2; N, 6.0. $C_{19}H_{20}BrClN_2O_4$ requires C, 46.8; H, 4.15; N, 5.75%).

Brominations using N-Bromosuccinimide.—*N*-Bromosuccinimide (0.44 g, 2.5 mmol) and 6-phenyldihydrodiazepinium salt (8) (0.68 g, 2.5 mmol) in acetic acid (15 ml) were

heated under reflux for 15 min. When the mixture was cooled the product was filtered off, washed with a small amount of water, and recrystallised from ethanolic perchloric acid, providing the brominated salt (10) (37%), identical (m.p., mixed m.p., spectra) with an authentic sample. 1-Methyl- (31%), 1,4-dimethyl- (53%), and 2-methyl-6-*p*-bromophenyldihydrodiazepinium (31%) salts were prepared similarly except that the reaction mixtures were heated for 3 h.

Iodinations using N-*Iodosuccinimide*.—A mixture of *N*-iodosuccinimide (1.1 g, 5 mmol), the 6-phenyldihydrodiazepinium salt (8) 1.3 g, 5 mmol) and acetic acid (25 ml) was heated under reflux for 15 min. When the mixture was cooled, crystals separated which were filtered off, washed with ether, and recrystallised frim ethanolic perchloric acid. This **6**-*iodophenyl derivative* (1.5 g, 79%) had m.p. 298 °C, $\lambda_{max.}$ 259 and 356 nm (ε 19 100 and 8 300), τ[$(CD_3)_2SO$] −0.35br (NH), 2.04 (2 H, s), 2.26 and 2.84 (4 H, AA'BB' pattern), and 6.27 (4 H, s) (Found: C, 33.25; H, 2.95; N, 7.0. $C_{11}H_{12}ClIN_2O_4$ requires C, 33.2; H, 3.0; N, 7.05%). The following iodinated products were prepared similarly save that the reaction mixtures were heated (*a*) for 2.5 h, (*b*) for 6 h: (*a*) 6-p-*iodophenyl*-2-*methyl* (68%), m.p. 270—272 °C, $\lambda_{max.}$ 259 and 356 nm (ε 21 100 and 8 400,) τ[$(CD_3)_2SO$] −0.42br (NH), 2.01 (1 H, d), 2.14 (1 H, d), 2.27 and 2.85 (4 H, AA'BB' pattern), 5.06—6.14 (1 H, m), 6.44 (2 H, m), and 8.78 (3 H, d) (Found: C, 35.05; H, 3.5; N, 6.85. $C_{12}H_{14}ClIN_2O_4$ requires C, 34.9; H, 3.4; N, 6.8%); (*b*) 6-p-*iodophenyl*-2,2-*dimethyl* (39%), m.p. 234—237 °C, $\lambda_{max.}$ 259 and 352 nm (ε 23 300 and 8 500), τ[$(CD_3)_2SO$] 2.00 (1 H, d), 2.30 (1 H, d), 2.27 and 2.83 (4 H, AA'BB' pattern), 6.53br (2 H), and 8.7 (6 H, s) (Found: C, 36.75; H, 3.7; N, 6.55. $C_{13}H_{16}ClIN_2O_4$ requires C, 36.5; H, 3.75; N, 6.55%).

2,3-*Dihydro*-6-p-*nitrophenyl*-1,4-*diazepinium Nitrate*.—6-Phenyldihydrodiazepinium perchlorate (6 g) was added in small portions to an ice-cold, stirred mixture of nitric acid (60 ml) and water (12 ml). The mixture was stirred for a further 2.5 h and then poured into water (215 ml) which was stirred and cooled in an acetone–solid CO_2 mixture. The *nitro-compound* (2.8 g, 58%) was filtered off and had m.p. 240 °C (from methanol), $\lambda_{max.}$ 344 nm (ε 17 400), τ[$(CD_3)_2SO$] 1.78 (2 H, d), 1.83 (2 H, d), 2.38 (2 H, d), and 6.18 (4 H, m) (Found: C, 46.9; H, 4.2; N, 19.8. $C_{11}H_{12}N_4O_5$ requires C, 47.15; H, 4.3; N, 20.0%).

Reactions of 2,3-*Dihydro*-X-*methyl*-6-*phenyldihydrodiazepinium Perchlorates with Nitric Acid*.—When the 1-methyl-, 2-methyl-, or 1,4-dimethyl-derivative was treated with nitric acid as described in the preceding paragraph the isolated product was *p*-nitrobenzoic acid, identical (m.p., mixed m.p., n.m.r., and mass spectra) with an authentic sample.

Alkaline Hydrolysis of 6-*Aryl*-2,3-*dihydro*-1,4-*diazepinium Salts*.—A solution of 6-phenyldihydrodiazepinium perchlorate (0.27 g) and sodium hydroxide (0.8 g) in methanol was heated under reflux for 4 h. Removal of solvent *in vacuo* left a solid, which was filtered off and treated with a methanolic solution of dianilinoethane and perchloric acid. After *ca.* 1 h at room temperature yellow crystals of 1,4,6-triphenyldihydrodiazepinium perchlorate were filtered off, identical (m.p., mixed m.p., spectra) with an authentic sample. 2,3-Dihydro-6-α-naphthyldiazepinium perchlorate was similarly hydrolysed and converted into its *NN'*-diphenyl analogue.

We thank Mr. C. Millar and Mrs. M. Smith for recording, respectively, mass and n.m.r. spectra, Mr. J. Bews and Mrs. S. Smith for microanalyses, and the University of St. Andrews for a research studentship (to K. S. T.).

[0/894 *Received*, 11*th June*, 1980]

REFERENCES

[1] Part 24, G. Ferguson, W. C. Marsh, D. Lloyd, and D. R. Marshall, *J. Chem. Soc., Perkin Trans. 2*, 1980, 74.
[2] For surveys see D. Lloyd, H. P. Cleghorn, and D. R. Marshall, *Adv. Heterocycl. Chem.*, 1974, **17**, 1; D. Lloyd and H. McNab, *Heterocycles*, 1978, **11**, 549.
[3] D. Lloyd and H. McNab, *Angew. Chem.*, 1976, **88**, 496; *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 459.
[4] D. Lloyd, H. McNab, and D. R. Marshall, *J. Chem. Soc., Perkin Trans. 1*, 1978, 1453.
[5] D. Lloyd, H. McNab, and D. R. Marshall, *J. Chem. Soc., Perkin Trans. 1*, 1975, 1260.
[6] D. Lloyd and D. R. Marshall, *J. Chem. Soc.*, 1958, 118.
[7] A. M. Gorringe, D. Lloyd, F. I. Wasson, D. R. Marshall, and P. A. Duffield, *J. Chem. Soc. C*, 1969, 1449.
[8] C. Barnett, D. R. Marshall and D. Lloyd, *J. Chem. Soc., Perkin Trans. 2*, 1975, 325.
[9] C. Barnett, D. R. Marshall, L. A. Mulligan, and D. Lloyd, *J. Chem. Soc. B*, 1971, 1529.
[10] D. Lloyd, R. K. Mackie, H. McNab, and D. R. Marshall, *J. Chem. Soc., Perkin Trans. 2*, 1973, 1729.
[11] D. Lloyd, R. K. Mackie, H. McNab, K. S. Tucker, and D. R. Marshall, *Tetrahedron*, 1976, **32**, 2339.
[12] W. Grahn, *Z. Naturforsch*, 1976, **31b**, 1641.
[13] W. Kitching, M. Bullpitt, and D. Gartshore, *J. Org. Chem.*, 1977, **42**, 2411.
[14] C. Barnett, H. P. Cleghorn, G. E. Cross, D. Lloyd, and D. R. Marshall, *J. Chem. Soc. C*, 1966, 92.
[15] C. Barnett, *Chem. Commun.*, 1967, 637; *J. Chem. Soc. C*, 1967, 2436.
[16] A. M. Gorringe, D. Lloyd, D. R. Marshall, and L. A. Mulligan, *Chem. Ind. (London)*, 1968, 130; A. M. Gorringe, D. Lloyd, and D. R. Marshall, *J. Chem. Soc. C*, 1970, 617.
[17] A. M. Gorringe, D. Lloyd and D. R. Marshall, *Chem. Ind. (London)*, 1968, 1160.
[18] D. Lloyd, C. Nyns, C. A. Vincent, and D. J. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1441.
[19] D. Lloyd, H. McNab, and D. R. Marshall, *Austr. J. Chem.*, 1977, **30**, 365.
[20] H. A. Staab and C. Wünsche *Chem. Ber.*, 1965, **98**, 3479.
[21] H. Quast and J. Stawitz, *Tetrahedron Lett.*, 1977, 2709.
[22] C. Jutz, R. Kirchlechner, and H. J. Seidel, *Chem. Ber.*, 1969, **102**, 2301.
[23] Z. Arnold, *Collect. Czech. Chem. Commun.*, 1961, **26**, 3051.
[24] J. M. F. Gagan, A. G. Lane, and D. Lloyd, *J. Chem. Soc. C*, 1970, 2484.