

## Reductive Cleavage of Propellane-type Hydrazinium Dications as a Route to Medium-sized Ring Bicyclic Diamines with Bridgehead Nitrogen Atoms

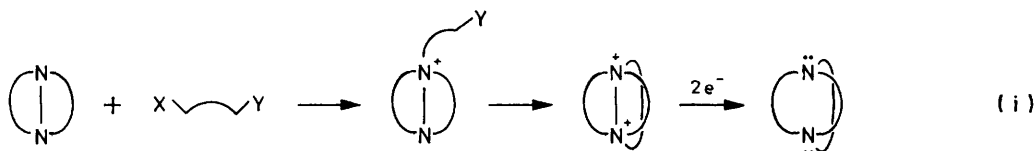
By Roger W. Alder,\* Richard B. Sessions, Andrew J. Bennet, and Richard E. Moss, School of Chemistry, University of Bristol, Bristol BS8 1TS

Procedures are described for the preparation of 1,5-diazoniatricyclo[3.3.2.0]decane (9), 1,5-diazoniatricyclo[3.3.3.0]undecane (10), 1,6-diazoniatricyclo[4.3.3.0]dodecane (11), 1,6-diazoniatricyclo[4.4.3.0]tridecane (12), and 1,6-diazoniatricyclo[4.4.4.0]tetradecane (13) salts by the alkylation of 1,5-diazabicyclo[3.3.0]octane and 1,6-diazabicyclo[4.4.0]decane with suitable difunctional molecules  $X[CH_2]_mY$ . The central N-N bond of these propellane-type hydrazinium dications may be cleaved by a variety of reducing agents to yield the bicyclic diamines 1,5-diazabicyclo[3.3.2]decane (21), 1,5-diazabicyclo[3.3.3]undecane (22), 1,6-diazabicyclo[4.3.3]dodecane (23), 1,6-diazabicyclo[4.4.3]tridecane (24), and 1,6-diazabicyclo[4.4.4]tetradecane (25). The scope and limitations of this synthetic route to medium-sized ring bicyclic diamines are discussed.

We have recently reported, in preliminary form, the syntheses of a series of bicyclic diamines built from medium-sized rings and containing bridgehead nitrogen atoms.<sup>1-3</sup> These compounds show unusual and interesting physical and chemical properties due to the enforced interaction of the nitrogen lone pairs imposed by the triple constraint of the ring systems. The synthetic strategy which gives access to most of these molecules is shown in diagrammatic form in equation (i). In this

important macrobicyclic structures<sup>8</sup> (e.g. the cryptands) on the other. The smallest known macrobicyclic system is 1,7-diaza-4,10,15-trioxabicyclo[5.5.5]heptadecane (2) ([1.1.1]cryptand).<sup>9</sup> It is plain that concern about synthetic problems has been a major impediment to the development of this area of chemistry, since there was little doubt that medium-sized ring bicyclic molecules would show interesting properties.

Syntheses of these ring systems might be attempted by



paper, we describe the synthesis of five diamines by this approach and discuss the scope and limitations of the method. The physical and chemical properties of these diamines will be described in detail elsewhere.<sup>4</sup>

### DISCUSSION

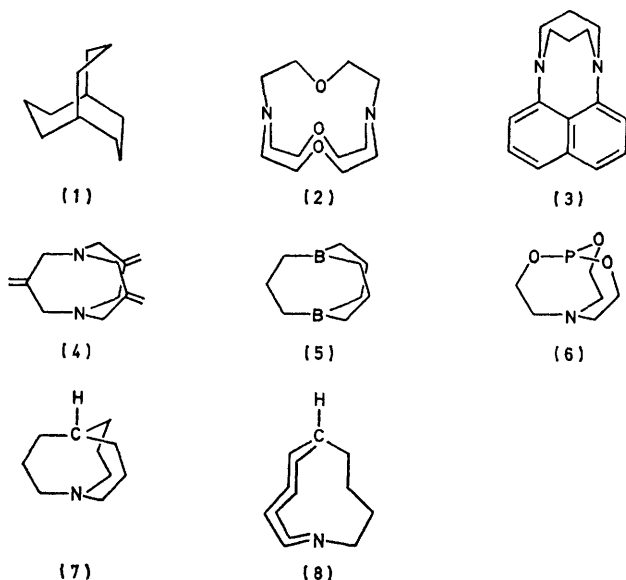
There are just ten bicyclic systems constructed entirely from rings conventionally regarded as medium-sized (8- to 11-membered). These are:

bicyclo[3.3.3]undecane	bicyclo[4.4.3]tridecane
bicyclo[4.4.2]dodecane	bicyclo[6.3.3]tetradecane
bicyclo[4.3.3]dodecane	bicyclo[5.4.3]tetradecane
bicyclo[5.4.2]tridecane	bicyclo[4.4.4]tetradecane
bicyclo[5.3.3]tridecane	bicyclo[5.4.4]pentadecane

Inclusion of systems containing 7- and 12-membered rings gives rise to a further 17 basic hydrocarbons. Bicyclo[3.3.3]undecane (manxane) (1),<sup>5</sup> some derivatives,<sup>6a,b</sup> and some heterocyclic analogues<sup>6c</sup> are known, as are some derivatives of bicyclo[4.4.2]dodecane and bicyclo[5.4.2]tridecane,<sup>7</sup> but most of these ring systems were unexplored in any shape or form when we began work in this area. This represents a remarkable gap in our chemical knowledge between the well known bicyclic systems built from small and common rings (3- to 7-membered) on the one hand and the increasingly

cyclisation, by ring expansion, and by ring cleavage. In a cyclisation route, two medium-sized rings must be created simultaneously in the final cyclisation step and this is expected to be difficult. We obtained a naphtho-derivative (3) of 1,5-diazabicyclo[3.3.3]undecane in 5% yield by this route,<sup>1</sup> but an attempt to make the parent diamine this way failed.<sup>10</sup> Compounds (4),<sup>6a</sup> (5),<sup>6e</sup> and (6)<sup>6f</sup> were made by cyclisation routes; the presence of several trigonal atoms may well be helpful to this approach but it should become increasingly difficult for the larger ring systems unless perhaps modified by the presence of a central (template) atom. Double ring expansion from a bicyclo[3.3.1]nonane was used to make manxane; in general this method is bound to be tedious. By far the most fruitful general strategy appears to be one based on ring cleavage of a tricyclic precursor, especially a propellane derivative or a related system which is constructed from common-sized rings. This approach was first used by Leonard in his synthesis of manxine (7).<sup>6c</sup> We have extended his method for monoamines to the preparation of *out*-6H-1-azabicyclo[4.4.4]tetradecane, (8).<sup>11</sup> For the synthesis of bridgehead diamines, hydrazinium dications were required, and while their reductive cleavage was expected to occur easily, it was by no means clear when we began work that they were sufficiently stable to be handled successfully as

synthetic intermediates. Diprotonated hydrazines are well known as reaction intermediates in benzidine rearrangements, but the second  $pK_a$  values of hydrazines are quite low.<sup>12</sup> The first fully substituted hydrazinium

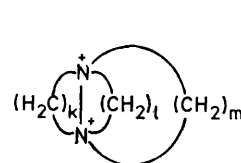


dication was obtained by two-electron oxidation of (3) with  $SbF_5$  in  $SO_2ClF$ ; this species was extremely sensitive to nucleophilic attack, being destroyed instantly by traces of water.<sup>1</sup>

Early attempts<sup>13</sup> to prepare salts of the 1,5-diazonia-tricyclo[3.3.3.0]undecane dication (10) by reaction of 1,3-dibromopropane with 1,5-diazabicyclo[3.3.0]octane<sup>14</sup> \* in organic solvents led to intractable red-brown oils [we now recognize that (10) was formed but was unstable under these conditions]. We have since learnt that Grob and Gmünder<sup>10</sup> had even earlier obtained evidence for (10) as a reaction intermediate but had been unable to isolate salts. Our initial preparation of (10)  $2BF_4^-$  was entirely fortuitous, but nicely illustrates the conditions appropriate for the isolation of salts of (10). We had made the monoalkylated salt (15; X = Br, Y = OH) by reaction of 1,5-diazabicyclo[3.3.0]octane with 3-bromopropan-1-ol, intending to use this in a more devious synthesis of bicyclic diamines. As this salt was hygroscopic, conversion into the corresponding  $BF_4^-$  salt was attempted. When (15; X = Br, Y = OH) was dissolved in aqueous 40%  $HF_4$  and left overnight, crystalline (10)  $2BF_4^-$  was obtained

\* In the preparation of 1,5-diazabicyclo[3.3.0]octane-2,6-dione, we have found that the use of a bomb can be dispensed with and that after the initial period of heating at 150 °C as described by Stetter and Findeisen there is very little of the final bicyclic product present (<sup>1</sup>H n.m.r.); the final cyclisation clearly occurs during the distillation. The following simple procedure is convenient. Hydrazine hydrate (25 ml) is added slowly with cooling to methyl acrylate (135 ml; 50% excess) in the base of a large sublimation vessel. The cold finger condenser is fitted and the apparatus heated to 280 °C under 18 mmHg pressure. After about 20 min the crystalline product mixed with some oil begins to collect on the cold finger. Heating is continued for 1 hour. The product is crystallised from ethanol; yield 19.6 g (28%).

in 80% yield. The use of a highly ionising solvent, and the avoidance of nucleophilic or basic anions and of high temperatures, are all favourable for the isolation of a dication which is sensitive to nucleophilic attack. It is also clear that the alkylation steps in equation (i) ought to be performed separately, since reaction conditions appropriate for the first and second alkylations are so different. In practice, it emerges that the second (cyclo-)alkylation to give (10) is the most rapid of any



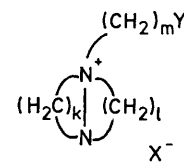
$$(9) \quad k = l = 3, m = 2$$

$$(10) \quad k = l = m = 3$$

$$(11) \quad k = 4, l = m = 3$$

$$(12) \quad k = l = 4, m = 3$$

$$(13) \quad k = l = m = 4$$



$$(14) \quad k = l = 3, m = 2$$

$$(15) \quad k = l = m = 3$$

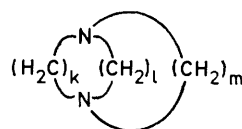
$$(16) \quad k = l = 3, m = 4$$

$$(17) \quad k = l = 3, m = 5$$

$$(18) \quad k = l = 4, m = 3$$

$$(19) \quad k = l = m = 4$$

$$(20) \quad k = l = 4, m = 5$$



$$(21) \quad k = l = 3, m = 2$$

$$(22) \quad k = l = m = 3$$

$$(23) \quad k = 4, l = m = 3$$

$$(24) \quad k = l = 4, m = 3$$

$$(25) \quad k = l = m = 4$$

we have studied. The nitrogen atoms of 1,5-diazabicyclo[3.3.0]octane are relatively unhindered and formation of the 5-membered ring is particularly rapid. In many other cases it is possible to isolate a monocation salt from reaction of a bicyclic hydrazine and an  $\alpha,\omega$ -dihalogenoalkane without the second alkylation occurring under reaction conditions which are unsuitable for the isolation of the dication. Thus, (14), (16), and (17), all with X = Y = Br, could be made in good yield by mixing 1,5-diazabicyclo[3.3.0]octane and the appropriate dibromide in dichloromethane, reflecting the lower rates of cyclisation to 4-, 6-, and 7-membered rings. 1,6-Diazabicyclo[4.4.0]decane<sup>15</sup> is considerably less reactive than 1,5-diazabicyclo[3.3.0]octane in both first and second alkylations. The salt (18; X = Y = Br), is a borderline case. It may be prepared by heating 1,6-diazabicyclo[4.4.0]decane in an excess of  $Br[CH_2]_3Br$  at 70 °C for 4 h (higher temperatures cause decomposition); however the product contains about 30% of cyclised product [(12)  $2Br^-$ ]. It appears that the dication salt only survives under these conditions because of its insolubility. When 1,6-diazabicyclo[4.4.0]decane and  $Br[CH_2]_3Br$  were refluxed in acetonitrile, a brown tar was obtained and no trace of (12)  $2Br^-$  was found.

Compounds (19) and (20) ( $X = Y = \text{Br}$ ) were obtained by heating the hydrazine in the neat dibromide at 100 °C for several hours. This is indeed fortunate, because an attempt to prepare (19;  $X = \text{Cl}$ ,  $Y = \text{OH}$ ) from 1,6-diazabicyclo[4.4.0]decane and 4-chlorobutan-1-ol led only to the hydrazine hydrochloride and, presumably, tetrahydrofuran. Reaction of 1,6-diazabicyclo[4.4.0]decane with *O*-methyltetrahydrofuranium fluorosulphate resulted only in methylation; this is surprising since this salt normally reacts with nucleophiles by ring opening.<sup>16</sup> We suggest that the  $S_N2$  reactions of 1,6-diazabicyclo[4.4.0]decane are severely sterically hindered. 4-Chlorobutan-1-ol and 1,5-diazabicyclo[3.3.0]octane gave (16;  $X = \text{Cl}$ ,  $Y = \text{OH}$ ) in good yield in refluxing acetonitrile. Similarly (14;  $X = \text{Br}$ ,  $Y = \text{OH}$ ), was prepared from 2-bromoethanol and 1,5-diazabicyclo[3.3.0]octane.

A survey of the rates of the second (cyclo-)alkylations was made by <sup>1</sup>H n.m.r.; the results are shown in the Table. For a given hydrazine, 5-membered rings close

Rates of cyclisation of hydrazine salts

Reactant	Leaving group Y	$t_1$ /min, in aq. 40% HBF <sub>4</sub>	$t_1$ /min, in aq. 40% HBF <sub>4</sub> with 1.8M-AgBF <sub>4</sub>
(14; $X = \text{Br}$ )	Br	NR <sup>a</sup>	<1
(14; $X = \text{Br}$ )	OH	NR	
(15; $X = \text{Br}$ )	OH	7	
(15; $X = \text{Br}$ )	Cl <sup>b</sup>	1 ± 0.5	
(16; $X = \text{Br}$ )	Br	720	<1
(17; $X = \text{Br}$ )	Br	NR	Slow <sup>c</sup>
(18; $X = \text{Br}$ )	OH	22 00	
(19; $X = \text{Br}$ )	Br	NR	<1
(20; $X = \text{Br}$ )	Br	NR	NR

<sup>a</sup> NR = no reaction. <sup>b</sup> Made, in poor yield, from 1,5-diazabicyclo[3.3.0]octane and Br[CH<sub>2</sub>]<sub>3</sub>Cl, and obtained as a white solid which became rapidly discoloured even under N<sub>2</sub>. <sup>c</sup> Only ca. 20% of the reaction results in cyclisation, the remainder being solvolysis (see main text).

most rapidly, as expected,<sup>17</sup> followed by 6-, 4-, and 7-membered rings. Closure of a 7-membered ring is barely competitive with solvolysis in HBF<sub>4</sub>-AgBF<sub>4</sub> even for the most favourable case (17). Reaction of (17;  $X = Y = \text{Br}$ ) with Ag(CH<sub>3</sub>CN)<sub>4</sub>BF<sub>4</sub> in (CF<sub>3</sub>CO)<sub>2</sub>O-CF<sub>3</sub>CO<sub>2</sub>H was better, giving ca. 50% cyclisation, but satisfactory conditions for the isolation of the 1,7-diazoniatriacyclo[5.3.3.0]tridecane salt have not been found so far. This points to one of the limits of our method, though in fact this dication may well be available from the known<sup>18</sup> 1,7-diazabicyclo[5.3.0]decane and 1,3-dibromopropane.

The Table shows that derivatives of 1,5-diazabicyclo[3.3.0]octane hydrazine always cyclise much faster than corresponding derivatives of 1,6-diazabicyclo[4.4.0]decane. The latter probably exist, in part, in unproductive *trans*-decalin conformations, and even when in a *cis*-decalin form are more hindered and may well have a poorer orbital alignment for  $S_N2$  displacement.

It is clear that the addition of AgBF<sub>4</sub> greatly increases cyclisation rates for halides; its use is essential in many cases. Cyclisation of the alcohols is obviously subject to acid catalysis. An <sup>1</sup>H n.m.r. investigation of the

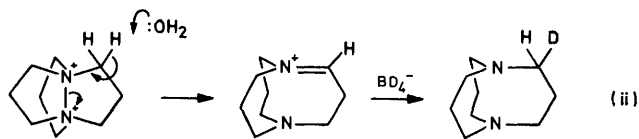
cyclisation of (15;  $X = \text{Br}$ ,  $Y = \text{OH}$ ) in sulphuric acid solutions showed that the rate continued to increase with increasing acid concentration right up to the fully concentrated acid.

The best conditions found for the preparation of the salts (9)–(13) 2BF<sub>4</sub><sup>-</sup> are given in the Experimental section. With the exception of (9) 2BF<sub>4</sub><sup>-</sup>, all these salts are reasonably stable in acidic aqueous solution. An approximate order of stability was derived by following the disappearance of dication (starting concentration 0.3M) by <sup>1</sup>H n.m.r. in D<sub>2</sub>O solution: (9)  $t_1$  < 5 min; (10)  $t_1$  ca. 2 days < (11) < (12) < (13) (almost indefinitely stable). Hydrolysis produces acid, which probably slows further reaction. A thorough study of hydrolysis will be undertaken but it is worth noting here whereas that (9) is hydrolysed to form (14;  $Y = \text{OH}$ ) ( $S_N2$  attack on the 4-membered ring), all the other salts appear to be hydrolysed by loss of protons from  $\alpha$ -CH<sub>2</sub> groups with concomitant N–N cleavage (*E2* reaction).<sup>3</sup> Hydrolysis in alkaline solution is rapid for all the dications. We do not yet have a good explanation for the extreme instability of the dication derived from (3).<sup>1</sup>

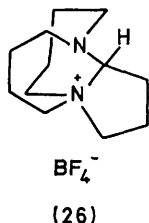
A variety of reducing agents were tried for the conversion of (10) 2BF<sub>4</sub><sup>-</sup> into 1,5-diazabicyclo[3.3.3]undecane (22). Reductions with metals in dilute aqueous acid were clean; the most convenient reagent was iron powder in dilute tetrafluoroboric acid, giving a 92% yield. The [3.3.3]diamine (22) is easily oxidised, exposure to air for a few minutes causing decomposition to, eventually, a sticky yellow oil which has not been identified. It is conveniently stored as a diprotonated salt. Oxidative decomposition is more troublesome for the [4.3.3]-, [4.4.3]-, and [4.4.4]-diamines (23)–(25), and for the latter two it proved advantageous to carry out the reduction with sodium in liquid ammonia. This is undoubtedly an unnecessarily powerful reductant but it does permit a convenient work-up procedure in which, after addition of methanol to destroy the excess of sodium, the solvents were removed in a stream of nitrogen and then the diamine was sublimed directly from the solid residues.

Preparation of the [3.3.2]diamine (21) posed different problems, since the corresponding hydrazinium dication is rapidly attacked by nucleophiles. Reduction with sodium in liquid ammonia did work, but was irreproducible, probably owing to the presence of varying amounts of sodium amide. Eventually it was found that zinc in fairly strong HBF<sub>4</sub> solution provided the most reliable procedure. The [3.3.2]diamine (21) is much more stable in air than (22)–(25), reflecting its higher ionisation potential.<sup>4</sup>

The [3.3.3]diamine (22) was also formed by reduction of the hydrazinium dication salt (10) 2BF<sub>4</sub><sup>-</sup> with NaBH<sub>4</sub> in H<sub>2</sub>O. Reduction with NaBD<sub>4</sub> in either H<sub>2</sub>O or D<sub>2</sub>O gives (22) with one deuterium incorporated at a carbon  $\alpha$  to nitrogen. This reaction therefore proceeds by a different mechanism [equation (ii)] from the dissolving metal reductions.



Reduction of the [4.4.4.0]propellane dication salt (13)  $2\text{BF}_4^-$  with  $\text{NaBH}_4$  is slow and much less clean. In this case, the iminium ion intermediate cyclises to a tricyclic  $\alpha$ -amino-ammonium ion (26) which may be isolated as a  $\text{BF}_4^-$  salt.<sup>3</sup> Reduction of this with  $\text{NaBH}_4\text{-H}_2\text{O}$  is slow and is accompanied by hydrolysis, but it can be reduced with  $\text{LiAlH}_4$  to the [4.4.4]diamine. We are currently



developing alternative syntheses of related tricyclic  $\alpha$ -aminoammonium ions as another route to medium-sized ring bicyclic diamines.

#### EXPERIMENTAL

**1-(2-Bromoethyl)-1,5-diazabicyclo[3.3.0]octanium Bromide** (14; X = Y = Br).—1,5-Diazabicyclo[3.3.0]octane (2.0 g) in methylene chloride (15 ml) was mixed with a large excess of 1,2-dibromoethane (24 g) in methylene chloride (10 ml) and the mixture left overnight. The salt (14; X = Y = Br) crystallised from the solution as fine white *needles*. These were filtered off, washed with a little methylene chloride and dried (yield 4.55 g, 85%); decomp. above 165° (Found: C, 32.05; H, 5.3; N, 9.5.  $\text{C}_8\text{H}_{16}\text{Br}_2\text{N}_2$  requires C, 32.0; H, 5.4; N, 9.35%);  $\delta(\text{D}_2\text{O})$  2.40 (4 H, q) and 3.0—4.2 (12 H, m).

**1-(2-Hydroxyethyl)-1,5-diazabicyclo[3.3.0]octanium Bromide** (14; X = Br, Y = OH).—1,5-Diazabicyclo[3.3.0]octane (0.5 g) and 2-bromoethanol (0.56 g) were mixed in acetonitrile (2.5 ml) and left for 0.5 h. The acetonitrile was evaporated off leaving (14; X = Br, Y = OH) as a pale brown oil; attempts to crystallise this were unsuccessful;  $^1\text{H}$  n.m.r. ( $\text{D}_2\text{O}$ ) similar to that of (14; X = Br, Y = OH) [ $\delta$  2.40 (4 H, q) and 3.0—4.2 (12 H, m)].

**1-(3-Hydroxypropyl)-1,5-diazabicyclo[3.3.0]octanium Bromide** (15; X = Br, Y = OH).—1,5-Diazabicyclo[3.3.0]octane (5.0 g) was mixed with dry acetonitrile (5 ml) in a conical flask (50 ml) and cooled in ice. A solution of 3-bromopropan-1-ol (6.22 g) in acetonitrile (3 ml) was added dropwise over 10 min, while the mixture was stirred with a glass rod. Crystals began forming towards the end of addition. The flask was left at 0 °C for 4 h and the white deliquescent *crystals* of (15; X = Br, Y = OH) were filtered off (yield 9.03 g, 80%); m.p. 98° (Found: C, 42.0; H, 8.0; N, 10.8.  $\text{C}_9\text{H}_{18}\text{BrN}_2\text{O}$  requires C, 43.05; H, 7.65; N, 11.15%);  $\delta_{\text{H}}(\text{D}_2\text{O})$  2.1 (2 H, m), 2.39 (4 H, q), and 2.9—4.0 (12 H, m);  $\delta_{\text{C}}(\text{D}_2\text{O})$  24.6 (2C,  $\beta$ -ring carbon), 26.6 (1C,  $\beta$ -side-chain carbon), 54.6 (2C,  $\alpha$  to N), 58.2 (1C,  $\alpha$  to OH), 63.5 (1C, side chain  $\alpha$  to  $\text{N}^+$ ), and 63.8 (2C,  $\alpha$  to  $\text{N}^+$  in ring).

**1-(4-Bromobutyl)-1,5-diazabicyclo[3.3.0]octanium Bromide** (16; X = Y = Br).—1,5-Diazabicyclo[3.3.0]octane (0.5 g) in methylene chloride (10 ml) was mixed with a large excess of 1,4-dibromobutane (10 ml) and left for 0.5 h. Addition of ether (25 ml) caused (16; X = Y = Br) to precipitate as an oil. The solvents were decanted, and the product was redissolved in methylene chloride and reprecipitated with ether to remove any dibromobutane. The  $^1\text{H}$  n.m.r. spectrum of the product is consistent with the proposed structure and the crude product (1.41 g, 96%) was used directly for the cyclisation reaction;  $\delta(\text{D}_2\text{O})$  1.93 (4 H, m), 2.39 (4 H, q), and 3.1—4.0 (12 H, m).

**1-(4-Hydroxybutyl)-1,5-diazabicyclo[3.3.0]octanium Chloride** (16; X = Cl, Y = OH).—1,5-Diazabicyclo[3.3.0]octane (4.0 g) was mixed with 4-chlorobutan-1-ol (3.88 g) in acetonitrile (10 ml) and refluxed under nitrogen for 1 h. Evaporation left a quantitative yield of a colourless, viscous oil with a  $^1\text{H}$  n.m.r. spectrum similar to that of (16; X = Y = Br). All attempts to crystallise the oil were unsuccessful;  $\delta(\text{D}_2\text{O})$  1.93 (4 H, m), 2.40 (4 H, q), and 3.1—4.0 (12 H, m).

**1-(5-Bromopentyl)-1,5-diazabicyclo[3.3.0]octanium Bromide** (17; X = Y = Br).—Reaction of 1,5-diazabicyclo[3.3.0]octane (0.25 g) with 1,5-dibromopentane (2 ml) using the procedure described for the preparation of (16; X = Y = Br) gave (17; X = Y = Br) as a viscous oil. Attempts to crystallise (17; X = Y = Br) were unsuccessful, so the oil was used directly in the cyclisation experiments;  $\delta(\text{D}_2\text{O})$  1.4—2.2 (6 H, m), 2.38 (4 H, q), and 3.0—4.0 (12 H, m).

**1-(3-Hydroxypropyl)-1,6-diazabicyclo[4.4.0]decanium Bromide** (18; X = Br, Y = OH).—1,6-Diazabicyclo[4.4.0]decane (0.50 g), 1-bromopropan-1-ol (0.50 g), and dimethylformamide (2 ml) were heated to 100 °C for 5 h. Some crystals formed on cooling, and slow addition of ether completed the crystallisation of (18; X = Br, Y = OH) (0.78 g, 78%). Two recrystallisations from ethanol-ether (with the use of charcoal) afforded analytically pure *product*, m.p. 194—195° (Found: C, 47.05; H, 8.25; N, 9.95.  $\text{C}_{11}\text{H}_{23}\text{BrN}_2\text{O}$  requires C, 47.3; H, 8.3; N, 10.05%);  $\delta(\text{D}_2\text{O})$  1.9 (10 H, m) and 2.9—4.0 (12 H, m).

**1-(3-Bromopropyl)-1,6-diazabicyclo[4.4.0]decanium Bromide** (18; X = Y = Br).—1,6-Diazabicyclo[4.4.0]decane (4.0 g) and an excess of 1,3-dibromopropane (15 ml) were heated to 70 °C for 4 h. The mixture turned brown and crystals were precipitated. Crystallisation was completed by slow addition of dry ether (50 ml) to the cooled mixture. Filtration gave light brown crystals (6.8 g, 70%), shown by  $^1\text{H}$  n.m.r. to be a mixture of *ca.* 70% (18; X = Y = Br) and 30% (12)  $2\text{Br}^-$ . This mixture was used directly in the cyclisation reaction;  $^1\text{H}$  n.m.r. ( $\text{D}_2\text{O}$ ) signals ascribed to (18; X = Y = Br):  $\delta$  1.9 (10 H, m) and 2.9—4.0 (12 H, m).

**1-(4-Bromobutyl)-1,6-diazabicyclo[4.4.0]decanium Bromide** (19; X = Y = Br).—1,6-Diazabicyclo[4.4.0]decane (8.3 g) and a large excess of 1,4-dibromobutane (30 ml) were mixed in a round-bottomed flask (100 ml). The flask was flushed with nitrogen, stoppered, and heated at 100 °C for 3 h. The resulting crystalline mass was broken up under ether and the pale tan *crystals* of (19; X = Y = Br) were filtered off (18.1 g, 86%); slow decomp. above 220° (Found: C, 40.4; H, 6.8; N, 7.8.  $\text{C}_{12}\text{H}_{24}\text{Br}_2\text{N}_2$  requires C, 40.45; H, 6.8; N, 7.85%);  $\delta(\text{D}_2\text{O})$  1.9 (12 H, m) and 2.9—4.0 (12 H, m).

**1-(5-Bromopentyl)-1,6-diazabicyclo[4.4.0]decanium Bromide** (20; X = Y = Br).—This was prepared in 85% yield

from 1,6-diazabicyclo[4.4.0]decane and 1,5-dibromopentane using the procedure described for the preparation of (19; X = Y = Br). Recrystallisation from ethanol-ether gave an analytically pure *sample* of (20; X = Y = Br), m.p. 179° (Found: C, 42.1; H, 7.4; N, 7.6. C<sub>13</sub>H<sub>26</sub>Br<sub>2</sub>N<sub>2</sub> requires C, 42.2; H, 7.1; N, 7.55%);  $\delta$ (D<sub>2</sub>O) 1.85 (14 H, br, m), and 2.8—3.9 (12 H, m).

1,5-Diazoniatriacyclo[3.3.2.0]decane Bistetrafluoroborate (9) 2BF<sub>4</sub><sup>-</sup>.—A solution of (14; X = Y = Br) (6.10 g) in aqueous 40% tetrafluoroboric acid (15 ml) was added to a stirred solution of silver oxide (5.2 g) in aqueous 40% tetrafluoroboric acid (15 ml) over 5 min. After 20 min, the silver salts were filtered off and washed with aqueous 40% tetrafluoroboric acid (5 ml). Ethanol (60 ml) was added to the filtrate, causing (9) 2BF<sub>4</sub><sup>-</sup> to precipitate as white *microcrystals* (4.81 g, 75%); decomp. above 170° (Found: C, 30.5; H, 5.25; N, 8.8. C<sub>8</sub>H<sub>16</sub>B<sub>2</sub>F<sub>8</sub>N<sub>2</sub> requires C, 30.6; H, 5.15; N, 8.95%);  $\delta$ (CF<sub>3</sub>SO<sub>3</sub>H) 3.2—5.0 (12 H, m), and 5.01 (4 H, s);  $\nu_{\max}$ . (Nujol) 3 050m, 1 050sbr (B-F), and 955m cm<sup>-1</sup>.

1,5-Diazoniatriacyclo[3.3.3.0]undecane Bistetrafluoroborate (10) 2BF<sub>4</sub><sup>-</sup>.—A solution of (15; X = Br, Y = OH) (7.52 g) in aqueous 40% tetrafluoroboric acid (25 ml) slowly deposited colourless plate-like crystals of (10) 2BF<sub>4</sub><sup>-</sup>. These were filtered off after 24 h (6.77 g); addition of ethanol to the filtrate precipitated a further 1.8 g (total 87%). Recrystallisation from dilute aqueous tetrafluoroboric acid gave an analytically pure *sample*, m.p. 244—246° (decomp.) (Found: C, 32.85; H, 5.5; N, 8.45. C<sub>9</sub>H<sub>18</sub>B<sub>2</sub>F<sub>8</sub>N<sub>2</sub> requires C, 32.95; H, 5.55; N, 8.55%);  $\delta_{\text{H}}$ (D<sub>2</sub>O) 2.96 (6 H, q) and 4.47 (12 H, t) (*J* 6.3 Hz);  $\delta_{\text{C}}$ (D<sub>2</sub>O) 26.39 (3C) and 67.80 (6C);  $\nu_{\max}$ . (Nujol) 3 040m, 1 064sbr (B-F), 960m, 930m, and 890w;  $\nu_{\max}$ . (D<sub>2</sub>O) 3 040m, 3 000w, and 2 910w cm<sup>-1</sup>.

1,6-Diazoniatriacyclo[4.3.3.0]dodecane Bistetrafluoroborate (11) 2BF<sub>4</sub><sup>-</sup>.—The salt (16; X = Y = Br) was cyclised using the procedure described for the preparation of (9), giving (11) 2BF<sub>4</sub><sup>-</sup> in 61% yield. An analytically pure *sample* was obtained by recrystallisation from warm dilute aqueous tetrafluoroboric acid; m.p. 195—198° (decomp.) (Found: C, 35.05; H, 6.15; N, 8.2. C<sub>10</sub>H<sub>20</sub>B<sub>2</sub>F<sub>8</sub>N<sub>2</sub> requires C, 35.15; H, 5.9; N, 8.2%);  $\delta_{\text{H}}$ (D<sub>2</sub>O) 2.24 (4 H, m), 3.03 (4 H, m), 4.26 (4 H, m), and 4.54 (8 H, d of t);  $\delta_{\text{C}}$ (D<sub>2</sub>O) 15.61 (2C), 20.58 (2C), 60.26 (2C), and 63.05 (4C);  $\nu_{\max}$ . (Nujol) 3 050m, 1 340w, 1 290w, 1 050brs (B-F), and 925w;  $\nu_{\max}$ . (D<sub>2</sub>O) 3 050m, 3 010m, 2 980w, and 2 940w cm<sup>-1</sup>.

1,6-Diazoniatriacyclo[4.4.3.0]tridecane Bistetrafluoroborate (12) 2BF<sub>4</sub><sup>-</sup>.—Silver oxide (5.0 g) was dissolved in aqueous 40% tetrafluoroboric acid (30 ml). The partially cyclised (18; X = Y = Br) was added to this solution over 10 min while the mixture was stirred with a glass rod. After 0.5 h the mixture was filtered over Celite. Addition of ethanol (200 ml) to the filtrate caused (12) 2BF<sub>4</sub><sup>-</sup> (4.0 g, 57%) to precipitate as an off-white micro-crystalline *powder*. Several recrystallisations from methanol-aqueous tetrafluoroboric acid gave analytically pure (12) 2BF<sub>4</sub><sup>-</sup>, m.p. 211—213° (Found: C, 36.9; H, 6.35; N, 7.9. C<sub>11</sub>H<sub>22</sub>B<sub>2</sub>F<sub>8</sub>N<sub>2</sub> requires C, 37.1; H, 6.25; N, 7.85%);  $\delta_{\text{H}}$ (D<sub>2</sub>O) 2.30 (8 H, br, s), 3.04 (2 H, q), 4.27 (8 H, br, s), and 4.53 (4 H, t) (*J* 7.0 Hz);  $\delta_{\text{C}}$ (D<sub>2</sub>O) 16.01 (4C), 18.58 (1C), and 61.10 (6C, br);  $\nu_{\max}$ . (Nujol) 3 050m, 1 330m, 1 280w, 1 050br s (B-F), 910m, 880m, and 850w;  $\nu_{\max}$ . (D<sub>2</sub>O) 3 050m, 3 020m, and 2 990m cm<sup>-1</sup>.

1,6-Diazoniatriacyclo[4.4.4.0]tetradecane Bistetrafluoro-

borate (13) 2BF<sub>4</sub><sup>-</sup>.—Silver oxide (3.4 g) was dissolved in aqueous 40% tetrafluoroboric acid (25 ml). Solid (19; X = Y = Br) (5.0 g) was added to this solution in small portions during 15 min, while the mixture was stirred with a glass rod. The mixture was heated briefly on a steam-bath and then filtered through a fine sintered glass funnel under reduced pressure. The silver salts were washed with aqueous 40% tetrafluoroboric acid (10 ml). Slow addition of ethanol (200 ml) to the combined filtrates caused (13) 2BF<sub>4</sub><sup>-</sup> to crystallise (3.47 g). A further 0.53 g of *product* was obtained on addition of ether to the filtrate (total 77%). Recrystallisation from ethanol-aqueous 40% tetrafluoroboric acid gave analytically pure (13) 2BF<sub>4</sub><sup>-</sup>, m.p. 221—225° (decomp.) (Found: C, 38.5; H, 6.3; N, 7.45. C<sub>12</sub>H<sub>24</sub>B<sub>2</sub>F<sub>8</sub>N<sub>2</sub> requires C, 38.95; H, 6.55; N, 7.55%);  $\delta_{\text{H}}$ (D<sub>2</sub>O) 2.35 (12 H, m), 3.82 (6 H, br, d), and 5.02 (6 H, m);  $\delta_{\text{C}}$ (D<sub>2</sub>O) 15.81 (6C) and 60.66 (6C);  $\nu_{\max}$ . (Nujol-hexachlorobutadiene) 3 060w, 3 000m, 2 980w, 2 920w, 1 050br, s (B-F), 985m, 950m, and 880m;  $\nu_{\max}$ . (D<sub>2</sub>O) 3 050m, 3 000m, and 2 920w cm<sup>-1</sup>.

1,6-Diazabicyclo[3.3.2]decane (21).—A solution of (9) 2BF<sub>4</sub><sup>-</sup> (3.6 g) in aqueous 40% tetrafluoroboric acid (20 ml) was rapidly added to a stirred mixture of zinc dust (1.6 g) and aqueous 40% tetrafluoroboric acid (2 ml) in a round-bottomed flask (100 ml). The mixture was left for 20 min, then cooled in an ice-bath while powdered sodium hydroxide was added until the solution became strongly alkaline. The diamine (21) was extracted directly from the flask with ether (5 × 40 ml). The ethereal solution was dried (MgSO<sub>4</sub>) and evaporated leaving a semi-solid residue, which was triturated with light petroleum (b.p. 30—40 °C) (100 ml). The petroleum solution was dried (MgSO<sub>4</sub>) and evaporated leaving (21) as a white solid (1.14 g, 77%). Sublimation (100 °C; 10 Torr) gave waxy, hygroscopic, but air-stable *crystals*, m.p. 105—112° (sealed tube);  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 1.7 (4 H, m), 2.5—3.7 (8 H, m), and 3.04 (4 H, s);  $\delta_{\text{C}}$ [(CD<sub>3</sub>)<sub>2</sub>CO] 29.85 (2C), 53.03 (4C), and 55.51 (2C);  $\nu_{\max}$ . (CCl<sub>4</sub>, CS<sub>2</sub>) 2 930s, 2 990s, 2 850s, 1 460m, 1 445m, 1 360bm, 1 215m, 1 140m, 1 080m, 1 060m, and 1 030w cm<sup>-1</sup> (Found: *M*<sup>+</sup>, 140.1312; C<sub>8</sub>H<sub>16</sub>N<sub>2</sub> requires *M*, 140.1313);  $\lambda_{\max}$ . (iso-octane) 224 nm ( $\epsilon$  4 800).

1,5-Diazabicyclo[3.3.2]decane Bis(hydrogen trifluoroacetate) (21) 2CF<sub>3</sub>CO<sub>2</sub>H. —A solution of (21) (0.32 g) in dry ether (15 ml) was treated with an excess of trifluoroacetic acid (0.6 g, 2.5 equiv.) in dry ether (10 ml). The white precipitate which formed immediately was filtered off giving (21) 2CF<sub>3</sub>CO<sub>2</sub>H (0.79 g, 92%) as a white powder. Recrystallisation from a small amount of hot ethanol afforded colourless *prisms* (decomp. with efferv. above 195°) (Found: C, 39.35; H, 4.95; N, 7.45. C<sub>12</sub>H<sub>14</sub>F<sub>6</sub>N<sub>2</sub>O<sub>4</sub> requires C, 39.15; H, 4.95; N, 7.6%);  $\delta_{\text{H}}$ (CF<sub>3</sub>SO<sub>3</sub>H) 2.47 (4 H, m), 3.81 (8 H, m), 3.95 (4 H, s) and 8.35 (br s, <sup>+</sup>N-H)  $\delta_{\text{C}}$ (D<sub>2</sub>O) 21.97 (2C), 49.97 (2C), and 54.39 (4C);  $\nu_{\max}$ . (Nujol) 3 030br s (<sup>+</sup>N-H), 1 655s, 1 415m, 1 180s, 1 160s, 1 020m, 830s, 790s, and 615s cm<sup>-1</sup>.

1,5-Diazabicyclo[3.3.3]undecane (22).—Compound (10) 2BF<sub>4</sub><sup>-</sup> (3.0 g) dissolved in dilute aqueous tetrafluoroboric acid (50 ml; 3% v/v) was added to iron filings (2.1 g) and 2*N*-hydrochloric acid (2 ml) in a round-bottomed flask (100 ml) during 5 min, while the mixture was stirred with a glass rod and the flask cooled in an ice-bath. The mixture was left for 0.5 h and then worked up using the procedure described for (21) to give white crystals of (22) (1.30 g, 92%). The diamine was purified by conversion into, and regeneration from, the bistetrafluoroborate salt and sublim-

ation (100 °C; 10 Torr). It may also be recrystallised from light petroleum (b.p. 30–40 °C) at –80 °C. The diamine (m.p. 134–136° in a sealed tube) is stable when stored under nitrogen at 0 °C;  $\delta_{\text{H}}[(\text{CD}_3)_2\text{CO}]$  1.48 (6 H, m) and 2.92 (12 H, t,  $J$  6.1 Hz);  $\delta_{\text{C}}[(\text{CD}_3)_2\text{CO}]$  25.91 (3C) and 48.48 (6C);  $\nu_{\text{max}}$  ( $\text{CCl}_4$ ,  $\text{CHBr}_3$ ) 2 990m, 2 950m, 2 900m, 2 850m, 1 455m, 1 380w, 1 360m, 1 210m, 1 125m, and 1 080m  $\text{cm}^{-1}$ .  $M^+$  154 (100%);  $\lambda_{\text{max}}$  (iso-octane) 217 ( $\epsilon$  5 700) and 278 nm (700).

1,5-Diazabicyclo[3.3.3]undecane Bis(hydrogen tetrafluoroborate) (22)  $2\text{HBF}_4$ .—A cooled solution of (22) (1.3 g) in acetonitrile (5 ml) was treated with a slight excess of aqueous 40% tetrafluoroboric acid (3.1 ml). Slow addition of dry tetrahydrofuran caused (22)  $2\text{HBF}_4$  to precipitate as a white powder (2.46 g, 88%). This was recrystallised from dilute aqueous tetrafluoroboric acid or dilute aqueous tetrafluoroboric acid–ethanol to give colourless prisms, m.p. 261–263° (decomp.) (Found: C, 32.7; H, 6.1; N, 8.5.  $\text{C}_9\text{H}_{20}\text{B}_2\text{F}_8\text{N}_2$  requires C, 32.75; H, 6.1; N, 8.5%);  $\delta_{\text{H}}(\text{D}_2\text{O})$  2.40 (6 H, q) and 3.51 (12 H, t,  $J$  6.0 Hz);  $\delta_{\text{C}}(\text{D}_2\text{O})$  17.03 (3C) and 47.36 (6C);  $\nu_{\text{max}}$  (Nujol) 3 160br s ( $^+\text{N}-\text{H}$ ), 1 330m, 1 300m, 1 050br s (B–F), and 880m  $\text{cm}^{-1}$ .

1,6-Diazabicyclo[4.3.3]dodecane (23).—Compound (11)  $2\text{BF}_4^-$  (0.30 g) was reduced using the procedure described for the preparation of the [3.3.3]diamine, except that after addition of the dication solution the mixture was set aside for a longer period (1 h) until all the radical cation colour (red) had disappeared. The reaction gave (23) (0.10 g, 80%), better than 98% pure by g.l.c. The diamine was sublimed (100 °C; 10 Torr) giving sticky white crystals. This amine was particularly air-sensitive, discolouring in a few minutes when exposed to traces of oxygen. The spectroscopic measurements were made on freshly prepared diamine:  $\delta_{\text{H}}[(\text{CD}_3)_2\text{CO}]$  1.1–1.9 (4 H, m, 3-carbon bridge), 1.7 (4 H, m, 4-carbon bridge), 2.9 (4 H, m), and 3.04 (8 H, m);  $\delta_{\text{C}}[(\text{CD}_3)_2\text{CO}]$  31.97 (2C), 32.16 (2C), 53.69 (4C), and 56.00 (2C);  $\nu_{\text{max}}$  ( $\text{CCl}_4$ ) 2 950m, 2 910m, 2 820m, 1 500w, 1 390m, 1 260w, 1 215w, and 1 150m  $\text{cm}^{-1}$ ;  $M^+$  168 (100%);  $\lambda_{\text{max}}$  (iso-octane) 222 ( $\epsilon$  6 800) and 280 nm (1 250).

1,6-Diazabicyclo[4.3.3]dodecane Bis(hydrogen tetrafluoroborate) (23)  $2\text{HBF}_4$ .—This salt was prepared in 70% yield by the method described for the preparation of (22)  $2\text{HBF}_4$  and recrystallised from ethanol–aqueous 40% tetrafluoroboric acid to give small off-white crystals which gradually discoloured on exposure to the air; m.p. 160–165° (decomp.) (Found: C, 34.65; H, 6.8; N, 8.05.  $\text{C}_{10}\text{H}_{22}\text{B}_2\text{F}_8\text{N}_2$  requires C, 34.95; H, 6.4; N, 8.15%);  $\delta_{\text{H}}(\text{D}_2\text{O})$  2.44 (8 H, m), 3.60 (12 H, t and br, s,  $J$  6.0 Hz);  $\delta_{\text{C}}(\text{D}_2\text{O})$  21.57 (2C), 22.02 (2C), 49.93 (4C), and 54.01 (2C);  $\nu_{\text{max}}$  (Nujol) 3 120br s ( $^+\text{N}-\text{H}$ ) and 1 050br s (B–F)  $\text{cm}^{-1}$ .

1,6-Diazabicyclo[4.4.3]tridecane (24).—Compound (12)  $2\text{BF}_4^-$  (0.50 g) was reduced with sodium in liquid ammonia using the method described below for the preparation of (25), giving the diamine (24) (0.19 g, 41%). The low yield is due, in part, to handling problems, as the diamine is in the form of very waxy and sticky white crystals. It may be stored in a fridge under nitrogen; however a good micro-analysis was not obtained owing to its sensitivity towards air. The analytical sample was sublimed four times (100 °C, 10 Torr) giving material of m.p. 87–89° (Found: C, 70.4; H, 11.8; N, 14.75.  $\text{C}_{11}\text{H}_{22}\text{N}_2$  requires C, 72.45; H, 12.15; N, 15.35%);  $\delta_{\text{H}}[(\text{CD}_3)_2\text{CO}]$  1.60 (10 H, m), 2.76 (8 H, m), and 2.98 (4 H, t,  $J$  5.0 Hz);  $\delta_{\text{C}}[(\text{CD}_3)_2\text{CO}]$  30.52 (1C), 32.76 (4C), 55.57 (2C), and 59.64 (4C);  $\nu_{\text{max}}$  ( $\text{CCl}_4$ ) 2 900m, 2 780m, 1 445w, 1 375m, 1 150w, 1 130m, and 1 080w  $\text{cm}^{-1}$ ;

$M^+$  182 (100%);  $\lambda_{\text{max}}$  (iso-octane) 218 ( $\epsilon$  8 400), 238 (6 700), and 270 nm (2 900).

1,6-Diazabicyclo[4.4.3]tridecane Hydrogen Tetrafluoroborate (24)  $\text{HBF}_4$ .—(12)  $2\text{BF}_4^-$  (1.10 g) was reduced as described above. After sublimation (24) was immediately dissolved in dry ether (40 ml). Addition of a solution of aqueous 40% tetrafluoroboric acid (0.5 ml) in dry ether (10 ml) caused (24)  $\text{HBF}_4$  to precipitate as an analytically pure, pale mauve powder (0.74 g, 88%); decomp. with partial melting above 215° (Found: C, 48.95; H, 8.6; N, 10.3.  $\text{C}_{11}\text{H}_{23}\text{BF}_4\text{N}_2$  requires C, 48.9; H, 8.6; N, 10.35%);  $\delta_{\text{H}}(\text{CDCl}_3)$  1.6–2.4 (10 H, br, m), 2.7 (6 H, m), 3.5 (6 H, m), and 7.9 (1 H, br, s);  $\delta_{\text{C}}(\text{CDCl}_3)$  23.14, 25.48, 27.96, 48.50, 51.01, 51.58, and 57.17;  $\nu_{\text{max}}$  (Nujol) 3 200s ( $^+\text{N}-\text{H}$ ), 1 320m, 1 290m, 1 270m, 1 250m, and 1 100br s (B–F)  $\text{cm}^{-1}$ .

1,6-Diazabicyclo[4.4.4]tetradecane (25).—Ammonia (40 ml) was distilled into a large sublimation vessel. Sodium (0.55 g) was added in small pieces while the solution was stirred vigorously with a magnetic follower and cooled to –75 °C. Fifteen min after the final addition of sodium the acetone–solid  $\text{CO}_2$  bath was removed and (13)  $2\text{BF}_4^-$  (1.50 g; as a fine powder) was added in small portions as fast as it was consumed. Fifteen min after the final addition of the dication salt, methanol was added dropwise until all the blue colour was discharged. The ammonia was allowed to boil off under a stream of nitrogen (while the liquid was swirled around the vessel to prevent bumping). Then a cold finger condenser was inserted and the [4.4.4]diamine sublimed out of the residues (100 °C, 10 Torr, 1 h; or 100 °C, 0.05 Torr, 0.25 h). The diamine was immediately re-sublimed to give crisp white crystals (0.666 g, 84%). It is stable when stored at 0 °C under nitrogen, but is very susceptible to traces of oxygen, which produces a white polymer. A good analysis was not obtained: the diamine, sublimed four times, had m.p. 170–175° (sealed tube) (Found: C, 72.4; H, 12.7; N, 13.95.  $\text{C}_{12}\text{H}_{24}\text{N}_2$  requires C, 73.4; H, 12.3; N, 14.25%);  $\delta_{\text{H}}[(\text{CD}_3)_2\text{CO}]$  1.50 (12 H, m) and 2.32 (12 H, m);  $\delta_{\text{C}}[(\text{CD}_3)_2\text{CO}]$  30.94 (6C) and 54.97 (CC);  $\nu_{\text{max}}$  ( $\text{CCl}_4$ ) 2 930m, 2 900m, 2 780m, 1 445m, 1 370m, and 1 120m  $\text{cm}^{-1}$ ;  $M^+$  196 (100%);  $\lambda_{\text{max}}$  (iso-octane) 233 ( $\epsilon$  8 200) and 261 nm (3 800).

out-1-Azonia-6-azabicyclo[4.4.4]tetradecane Hydrogen Tetrafluoroborate (25)  $\text{HBF}_4$ .—Compound (25) (0.97 g) dissolved in dry ether (60 ml) was rapidly filtered through a fine glass sinter funnel, under reduced pressure, into a solution of aqueous 40% tetrafluoroboric acid (1.15 g) in dry ether (80 ml). A white precipitate of (25)  $\text{HBF}_4$  formed immediately (1.35 g, 96%). The salt was stored under nitrogen as it gradually acquires a pink colour on exposure to air. A sample was recrystallised from a very small volume of dilute aqueous tetrafluoroboric acid, giving pale pink needles (slowly decomp. with partial melting between 230 and 260°) (Found: C, 50.6; H, 9.2; N, 9.7.  $\text{C}_{12}\text{H}_{25}\text{BF}_4\text{N}_2$  requires C, 50.7; H, 8.85; N, 9.85%);  $\delta_{\text{H}}(\text{D}_2\text{O})$  1.90 (12 H, m), 2.60 (6 H, t,  $J$  5.0 Hz), 3.47 (6 H, t,  $J$  5.0 Hz);  $\delta_{\text{H}}(\text{CDCl}_3)$  1.87 (12 H, m), 2.58 (6 H, t,  $J$  5.0 Hz), 3.50 (6 H, d of t,  $J$  5.0 and 4.0 Hz);  $\delta_{\text{C}}(\text{CDCl}_3)$  23.53 (3C), 27.27 (3C), 51.44 (3C), and 57.99 (3C);  $\nu_{\text{max}}$  ( $\text{CHCl}_3$ , Nujol) 3 170m ( $^+\text{N}-\text{H}$ ), 2 950m, 2 840m, 1 460m, and 1 080br s (B–F)  $\text{cm}^{-1}$ ;  $\lambda_{\text{max}}$  (0.1N-HCl) 205 nm ( $\epsilon$  3 300).

1-Azonia-6-azatricyclo[4.4.4.0<sup>1,5</sup>]tetradecane Tetrafluoroborate (26).—Aqueous potassium carbonate (0.5 g in 10 ml) was added to an aqueous solution of (13)  $2\text{BF}_4^-$  (0.5 g in 20 ml). The water was evaporated off at room temperature

and the solid residues were triturated with methylene chloride ( $2 \times 30$  ml). The methylene chloride solutions were combined, filtered, and evaporated to dryness, leaving crude (26) (0.38 g). Recrystallisation from hot ethanol (20 ml) gave pure (26) (0.31 g, 81%) as fine white *needles* (decomp. above  $250^\circ$ ) (Found: C, 51.2; H, 8.35; N, 9.55.  $C_{12}H_{23}BF_4N_2$  requires C, 51.1; H, 8.2; N, 9.9%);  $\delta_H(CD_3NO_2)$  1.7—3.8 (22 H, complex with strong resonances at  $\delta$  2.1 and 3.3), 5.41 (1 H, d of d,  $J$  4 and 12 Hz);  $\delta_C(CD_3NO_2)$  23.01 (2C), 24.85 (1C), 26.31 (1C), 29.37 (1C), 29.61 (1C), 46.89 (1C), 50.04 (1C), 60.72 (1C), 63.20 (1C), 63.63 (1C), and 100.52 (1C);  $\nu_{max}$  (Nujol) 1495m and 1050br s (B-F)  $cm^{-1}$  (700—1500  $cm^{-1}$  complex set of sharp bands).

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