Syntheses of Medium-ring 1,*k* + 2-Diazabicyclo[*k.l.m.*]alkanes by Reductive Cleavage of Hydrazinum Dications†

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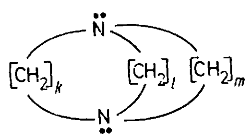
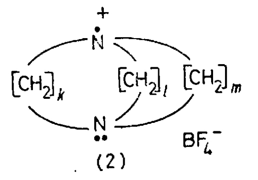
Summary 1,5-Diazabicyclo[3.3.3]undecane (**1a**) and 1,6-diazabicyclo[4.3.3]dodecane (**1b**) have been synthesized by reductive cleavage of the hydrazinium dications (**3a**) and (**3b**); a preliminary account of the properties of these species and the intermediate radical cations (**2a**) and (**2b**) is given.

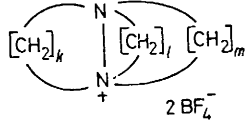


(1)



(2)

a; $k = l = m = 3$
b; $k = 4, l = m = 3$



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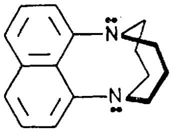
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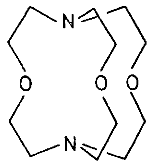

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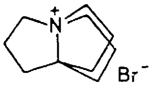

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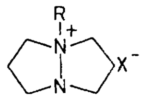
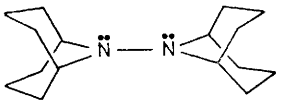


(7) R =$[CH_2]_3OH$, X = Br
(8) R = Me, X = I
(9) R = $CH_2CH{=}CH_2$, X = BF_4


(10)

Syntheses of bicyclo[*k.l.m.*]alkanes with *k*, *l*, and *m* in the range 3—5 pose the problems of medium-ring synthesis in particularly severe forms. For 1,*k*+2-diazabicyclo[*k.l.m*]-alkanes (**1**) the largest system prepared by a direct alkylative route was 1,5-diazabicyclo[3.2.2]nonane[1] until we recently obtained (**4**) in low yield from 1,8-diaminonaphthalene.[2a] The macrobicyclic amines[3] and cryptates[4] are prepared by lactam formation, (**5**) being the smallest system prepared in this way.[5] Neither of these routes is likely to be generally useful in the medium-ring range. A more promising approach is suggested by the preparation[6] of 1-azabicyclo[3.3.3]undecane by reductive cleavage of (**6**). We find that, despite several discouraging precedents, the reductive cleavage of hydrazinium dications is a good route to (**1a**) and (**1b**).

The second pK_a of hydrazine is *ca.* −1,[7] while the second protonation of phenylhydrazine is half-complete in 66% H_2SO_4 (H_0 −5·2).[8] We find that protonation of the pentamethylhydrazinium cation requires 70% H_2SO_4 (H_0 −5·8) for half-completion and have so far failed to alkylate this cation with $MeOSO_2F$.[9] The only known fully substituted hydrazinium dication, that formed by oxidising (**4**), is instantly destroyed by water.[2b] We were therefore surprised when the quaternary salt (**7**)‡ from 1,5-diazabicyclo-[3.3.0]octane[10] and 3-bromopropanol gave crystalline (**3a**), m.p. 242—246 °C (decomp.),‡ in 80% yield on standing overnight in a slight excess of 40% aqueous HBF_4. Compound (**3b**), m.p. 195—198 °C (decomp.),‡ was prepared in similar fashion starting from 4-chlorobutanol. Compounds (**3a**) and (**3b**) persist for hours in D_2O solution. On the other hand the dimethyl dication, formed by alkylating (**8**) with $MeOSO_2F$, is hydrolysed in a few minutes. The products of the slow hydrolysis of (**3a**) are complex but do not include (**7**) or (**9**). We suspect elimination to form an immonium ion is the initial step in hydrolysis.

Compounds (**3a**) and (**3b**) are readily reduced to (**1a**) and (**1b**) by a variety of reagents. Iron and dilute hydrochloric acid give a 95% yield of (**1a**), conveniently purified and stored as its diprotonated bis(tetrafluoroborate), m.p. 260—263 °C.‡ Compounds (**1a**) and (**1b**) form volatile, waxy, crystals, m.p. 134—133 and 150—157 °C, respectively.‡ Room temperature n.m.r. spectra are consistent with apparent D_{3h} symmetry for (**1a**) and C_{2v} symmetry for (**1b**); in both cases spectra become temperature dependent below *ca.* −100 °C, and slow-exchange spectra have not yet been obtained. Both compounds are very readily oxidised, turning brown in the air, and decomposing quickly in solvents like CCl_4. Compound (**1a**) is quite basic, pK_{a1} 10·3, pK_{a2} 6·5.§ The u.v. spectrum of (**1a**) in 2,2,4-trimethylpentane shows a maximum at 217 nm (ϵ 5700) with a shoulder at 278 nm (ϵ 700). The vapour shows absorptions at 222, 239, and 293 nm (relative absorbance 1 : 0·76 : 0·12). This is similar to 1-azabicyclo[3.3.3]undecane,[11] but only the 222 nm band shows fine structure.

The photo-electron spectrum of (**1a**) shows a broad symmetrical peak at 6·86 eV and a second band at 7·80 eV

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† No reprints available.

‡ Satisfactory analytical and spectroscopic data have been obtained for all new compounds.

§ Approximate figures from the variation of the n.m.r. spectrum with pH; u.v. determination is complicated by the extreme ease of oxidation. 1-Azabicyclo[3.3.3]undecane has pK_a *ca.* 9·9 (ref. 6).

which resembles the first band for 1-azabicyclo[3.3.3]-undecane[12] in shape. As discussed for (**4**),[2a] ground state (**2a**) probably has its odd electron in an antisymmetric N–N orbital.

Solutions of (**2a**) and (**2b**) can be prepared by oxidation of (**1**) with Ag^+, reduction of (**3**) with limited amounts of $NaBH_4$, or simply by mixing (**1**) and (**3**) (in MeCN). These solutions are red with one broad band, λ_{max} 470 nm for (**2a**), 495 nm for (**2b**) in H_2O. Although (**2a**) is less stable than (**2b**) or the radical cation from (**4**), it still persists for many hours in H_2O or MeCN at room temperature. The e.s.r. spectrum of (**2a**) in Pr^nCN can be simulated with $2 \times a_N$ 1·47 mT, $6 \times a_H$ 2·20 mT, $6 \times a_{H'}$ 0·18 mT, line width 0·05 mT. The spectrum undergoes no gross changes over the temperature range −100 to +50 °C.

The spectrum of [3,3-$^2H_2$]-(**2a**) shows only $4 \times a_H$ splittings. The $a_{H'}$ splitting is therefore due to the γ-hydrogens, and (**2a**) may have a twisted D_3 structure; alternatives require an accidental coincidence (within the present linewidth limitations).

Study of the (**1**) $\rightleftharpoons$ (**2**) $\rightleftharpoons$ (**3**) equilibria by cyclic voltammetry has not proved easy, probably owing to adsorption phenomena. Best results have been obtained at a gold electrode[14] (MeCN solution, Et_4NBF_4 supporting electrolyte), where the (**1**) $\rightleftharpoons$ (**2**) equilibria behave ideally, $E°$ *vs.* SCE being −0·17 V for (**1a**) $\rightleftharpoons$ (**2a**) and −0·24 V for (**1b**) $\rightleftharpoons$ (**2b**). However the (**2**) $\rightleftharpoons$ (**3**) oxidation waves are distended (ΔE_p *ca.* 200 mV), E° being *ca.* +0·1 ± 0·1 V for both (**2a**) $\rightleftharpoons$ (**3a**) and (**2b** $\rightleftharpoons$ (**3b**). Oxidation is extraordinarily favourable, expecially for dication formation; dication formation requires +0·72 V for (**4**), +1·18 V for (**10**)[15] and +0·60 V for *NNN'N'*-tetramethyl-*p*-phenylenediamine.

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