Syntheses of 2-Azatricyclo[4,3,1,$0^{4,9}$]decane and 2-Azatricyclo[4,4,0,$0^{4,9}$]decane

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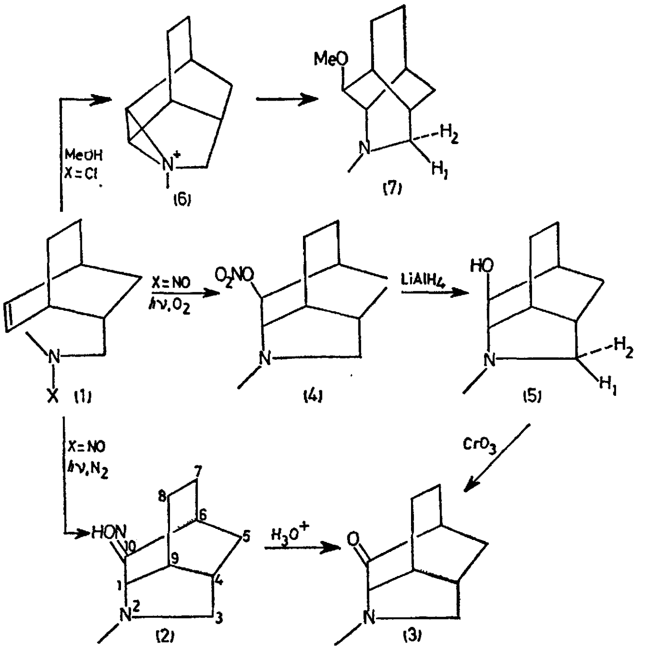
Summary Derivatives of 2-azatricyclo[4,3,1,$0^{4,9}$]decane and azatricyclo[4,4,0,$0^{4,9}$]decane were synthesised and the structure of the former was confirmed crystallographically.

BRIDGED azapolycyclics are a little investigated class of compounds[1] in comparison to their carbocyclic analogues. We now report the preparation of some derivatives of 2-azatricyclo[4,3,1,$0^{4,9}$]decane (2-azaisotwistane) and 2-azatricyclo[4,4,0,$0^{4,9}$]decane (2-azatwistane). We have carried out intramolecular aminium radical[2] or nitrenium ion[3] additions to a double bond incorporated in a suitable molecular framework such as (**1**). The synthesis of the bicyclic amine derivatives (**1**) was by known procedures with some alterations.

Photolysis of the nitrosamine (**1**; X = NO) in dilute hydrochloric acid gave the corresponding aminium and nitric oxide radicals as reactive intermediates, and then an aminium radical initiated cyclization takes place exclusively to form a 5-membered rather than a 6-membered ring.[4] Under nitrogen, photolysis of (**1**; X = NO) gave *syn* and *anti*-oximes (**2**) (67%), a mixture of which was hydrolysed to ketone (**3**). A similar photolysis under oxygen[2] gave a good yield of nitrate (**4**) as the primary product which on basification gradually underwent a cleavage reaction similar to that observed in analogous cases.[5] Rapid isolation of (**4**) followed by immediate $LiAlH_4$ reduction gave azatricyclic alcohol (**5**) (24%) which was oxidized to ketone (**3**). These compounds give satisfactory elemental analyses and i.r. and mass spectral data for the assigned structures. The n.m.r. spectrum of (**5**) shows the H_1 (τ 7·47, dd, J 10 and 4 Hz) and H_2 protons (τ 7·26, d, J 10 Hz) as the AB portion of an ABX system, in which the coupling pattern is consistent with those predicted from the Karplus relation.[6]

The solvolysis of (**1**; X = Cl) in refluxing methanol gave the methoxy amine (**7**) (analysed as the picrate, m.p. 171—171·5°) which exhibited a different coupling pattern for H_1 (τ 7·58, d, J 9 Hz) and H_2 (τ 7·32, dd, J 9 and 4·5 Hz) from that of (**5**). This change of pattern is predicted from the Karplus relation as applied to the twistane structure of (**7**). The nitrenium ion generated from the solvolysis[3] is expected to form the aziridinium intermediate (**6**) which should be cleaved preferentially by the nucleophile to 2-azatwistane (**7**) on the basis of considerable C–H bond eclipsing in 2-azaisotwistane systems (**2**)—(**5**).



To confirm the structural assignment, the structure of the HCl salt of the *syn*-oxime (**2**) was determined crystallographically. *Crystal data:* $(C_{10}H_{17}N_2O)^+Cl^-$, colourless crystals, orthorhombic, space group *Pbca*, $a = 11{\cdot}655(5)$, $b = 12{\cdot}514(5)$, $c = 14{\cdot}947(6)$ Å, $U = 2180{\cdot}0$ Å^3, $D_m = 1{\cdot}31$ g cm^{-3}, $Z = 8$, $D_c = 1{\cdot}32$. The structure has been refined to $R = 6{\cdot}6\%$ for 653 observed reflections measured with a computer controlled diffractometer using Mo-K_α radiation.

Consistent with the amphoteric nature of amino oximes the cation of (**2**) is linked to the chloride atom by a hydrogen bond involving the amine nitrogen (3·11 Å) and the oxime oxygen atom (3·11 Å) of an adjacent cation.

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[1] A. Belanger, J. Poupart, and P. Deslongchamps, *Tetrahedron Letters*, 1968, 2127; S. Dube and P. Deslongchamps, *ibid.*, 1970, 101; D. Perelman, S. Sicsic, and Z. Welvart, *ibid.*, 1970, 103; S. Sicsic and N. T. Luong-Thi, *ibid.*, 1973, 171; K. Heusler, *ibid.*, 1970, 97.

[2] Y. L. Chow, *Accounts Chem. Res.*, 1973, 6, 354.

[3] P. G. Gassman, *Accounts Chem. Res.*, 1970, 3, 26.

[4] Y. L. Chow, R. A. Perry, B. C. Menon, and S. C. Chen, *Tetrahedron Letters*, 1971, 1545; Y. L. Chow, R. A. Perry, and B. C. Menon, *ibid.*, 1971, 1549.

[5] K. S. Pillay, R. W. Lockhart, T. Tezuka, and Y. L. Chow, *J.C.S. Chem. Comm.*, 1974, 80.

[6] L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Spectroscopy in Organic Chemistry,' 2nd edn., Pergamon Press, Oxford, 1969, 280.