

ORGANOBORON COMPOUNDS

CDVIII *. REACTION OF 1-BORAADAMANTANE WITH AROMATIC NITRILES

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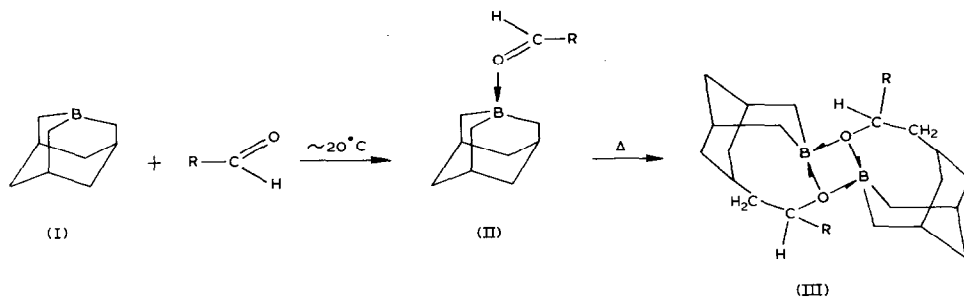
Summary

1-Boraadamantane has been shown to react with benzonitrile, and with *o*- and *p*-methylbenzonitriles with the formation of 1/1 complexes, which are converted at 200°C into 5-substituted 3-bora-4-aza-1,1-bihomoadamant-4-enes which exist in the dimer form. Starting from 5-phenyl-3-bora-4-aza-1,1-bihomoadamant-4-ene and 8-hydroxyquinoline, 7-benzimidoylmethyl-3-borabicyclo[3.3.1]nonyl-8-hydroxyquinolate has been prepared. This compound has been converted into 7-benzoylmethyl-3-borabicyclo[3.3.1]nonyl-8-hydroxyquinolate by acid hydrolysis.

Introduction

1-Boraadamantane, which is a polyhedral boron compound (I), differs significantly in its chemical properties from trialkylboranes. The specificity of chemical

SCHEME 1



* For part CDVII see ref. 7.

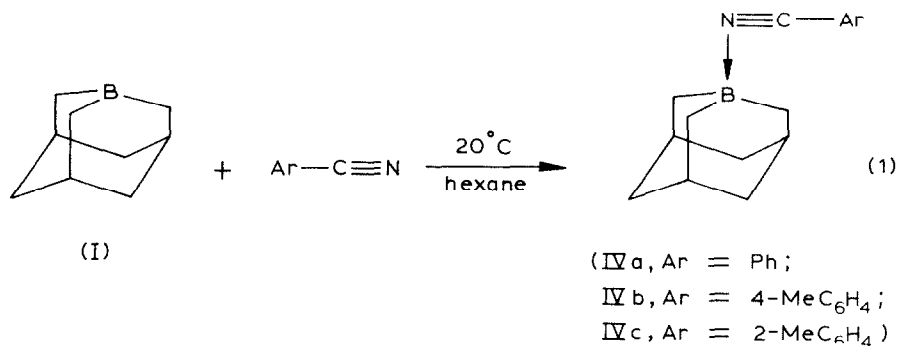
behaviour of 1-boraadamantane with respect to various reagents is revealed, particularly, in its reaction with carbonyl compounds. Unlike trialkylboranes, 1-boraadamantane is capable of forming, at room temperature, coordinate compounds II with aldehydes and ketones which undergo a rearrangement at 60–80°C, being converted with ring expansion, to 5-substituted 4-oxa-3-bora-1,1-bihomoadamantanes, which exist in the dimeric form III [1] — Scheme 1.

It is noteworthy that trialkylboranes react with aldehydes only at high temperatures (80–150°C), reducing the latter to alcohols and eliminating an olefin [2].

The present work deals with the results obtained in an investigation of interaction of 1-boraadamantane with aromatic nitriles.

Results and discussion

Benzonitrile and the nitriles derived from *o*- and *p*-toluic acids have been used as the aromatic nitriles. The reaction of these nitriles with 1-boraadamantane in hexane at room temperature produces the corresponding complexes (IVa–c) in 82–92% yield (eq. 1).

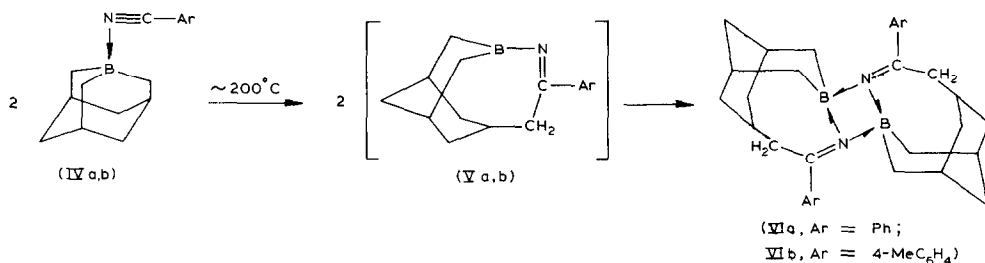


Compounds IVa–c are colourless, crystalline substances, which are stable in an inert gas atmosphere but are extremely unstable towards the moisture and oxygen in air. The structures of IVa–c have been proven by physico-chemical methods. The ¹¹B NMR spectra (upfield signals) and the IR spectra (a shift of the C≡N band of the complex to a region of lower frequencies by ~ 60 cm⁻¹ in comparison with the analogous band of the free nitrile) indicate the coordinative interaction between the B and the N atoms of the nitrile group. For example, a signal centered at -9.11 ppm in the ¹¹B NMR spectrum and an absorption band at 2230 cm⁻¹ (C≡N) in the IR spectrum are observed for IIa, whereas this band is, in the case of free benzonitrile, located in the region of 2296 cm⁻¹.

Like complexes II with aldehydes and ketones the complexes IV undergo, upon heating, an intramolecular rearrangement with ring expansion and formation of products of the insertion of the nitrile group at the B–C_α bond, namely 5-substituted 3-bora-4-aza-1,1-bihomoadamant-4-enes (Va,b). These last compounds have a tendency for intermolecular coordination, with the formation of dimers VIa,b (Scheme 2). It should be noted that heating the complex of 1-boraadamantane with *o*-tolunitrile does not result in the formation of a compound of the type VI, apparently due to steric hindrance.

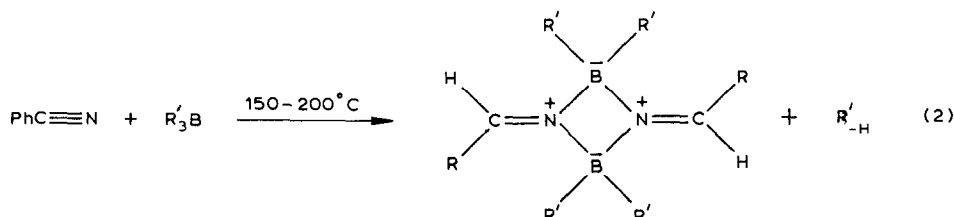
The compounds VIa,b are members of a new cage system, containing B and N

SCHEME 2

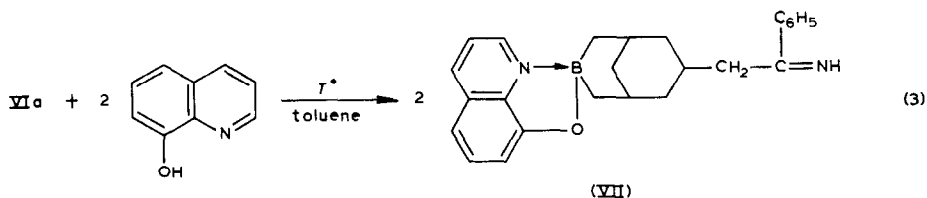


atoms. They are colourless, crystalline substances, which may be stored in air. The dimeric structure of these compounds was confirmed with the aid of their mass spectra, in which there are intense peaks of the parent ions M^+ .

Thus, 1-boraadamantane shows a different behaviour with respect to the nitriles than trialkylboranes. The latter compounds do not form complexes with nitriles but react with the elimination of an alkene [3,4] (eq. 2) (Only triallylborane interacts with nitriles with the formation of insertion products at the B-C bond [5].)

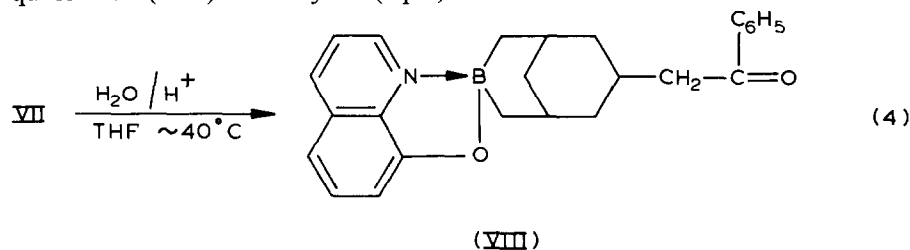


Unlike their oxygen analogues (III), 3-bora-4-aza-1,1-bihomoadamant-4-ene derivatives do not react with alcohols, even high-boiling ones. Cleavage of the B-N bond in VI was carried out successfully by the action of 8-hydroxyquinoline. Thus, compound VIa reacts with this reagent in boiling toluene over a period of 10 h, to form 7-benzimidoylmethyl-3-borabicyclo[3.3.1]nonyl-8-hydroxyquinolinatate (VII) in 93.5% yield (eq. 3).



The structure of VII was based on its mass and IR spectra.

Treatment of the chelate VII with a THF-H₂O mixture in the presence of a trace of HCl at $\sim 40^\circ\text{C}$ produced 7-benzoylmethyl-3-borabicyclo[3.3.1]nonyl-8-hydroxyquinolinatate (VIII) in 90% yield (eq. 4).



Experimental

All the organoboron compounds were used in an atmosphere of dry argon.

IR spectra were recorded on a UR-20 spectrometer and ^1H NMR spectra on a Tesla BS-497 (100 MHz) instrument relative to TMS. ^{11}B NMR spectra were obtained on a Bruker WP-80 spectrometer with an effective frequency of 25.67 MHz for ^{11}B ($\text{BF}_3 \cdot \text{Et}_2\text{O}$ as internal reference, chemical shifts are given in δ -scale). Mass spectra were recorded on a CH-6 Varian MAT apparatus.

1-Boraadamantane was prepared according to published details [5].

Complex of 1-boraadamantane with benzonitrile (IVa)

To 6.5 g (0.047 mol) of 1-boraadamantane (I) in 20 ml of hexane was added, dropwise, at $\sim 20^\circ\text{C}$, 4.85 g (0.047 mol) of benzonitrile in 5 ml of hexane. The colourless, crystalline precipitate which formed was washed with hexane (3×5 ml) to yield 10.4 g (92%) of IVa, m.p. $126\text{--}128^\circ\text{C}$ (sealed capillary under argon). IR spectrum (ν , CCl_4): 2230 cm^{-1} ($\text{C}\equiv\text{N}$). ^{11}B NMR spectrum (δ , CCl_4): -9.11 ppm.

Complex of 1-boraadamantane with p-tolunitrile (IVb)

To 2.34 g (0.017 mol) of 1-boraadamantane (I) in 8 ml of hexane was added dropwise, at $\sim 20^\circ\text{C}$, 2.04 g (0.017 mol) of *p*-tolunitrile. Treatment as described above gave 3.8 g (87%) of IVb, m.p. $142\text{--}145^\circ\text{C}$ (sealed capillary under argon). IR spectrum: (ν , CCl_4): 2232 cm^{-1} ($\text{C}\equiv\text{N}$) (for comparison: 2290 cm^{-1} in free nitrile ($\text{C}\equiv\text{N}$)). ^1H NMR spectrum (δ , ppm, CCl_4): 0.59 m (BCH_2), 1.47 m (CH_2), 2.00 m (CH), 2.37 s ($\text{CH}_3\text{--Ph}$).

Complex of 1-boraadamantane with o-tolunitrile (IVc)

To 2.25 g (0.017 mol) of 1-boraadamantane (I) in 6 ml of hexane was added dropwise, at $\sim 20^\circ\text{C}$, 1.95 g (0.017 mol) of *o*-tolunitrile. Workup as described above gave 3.88 g (92%) of IVc, m.p. $128\text{--}131^\circ\text{C}$ (sealed capillary under argon). IR spectrum (ν , CCl_4): 2230 cm^{-1} ($\text{C}\equiv\text{N}$) (for comparison: 2288 cm^{-1} ($\text{C}\equiv\text{N}$) in free nitrile). ^{11}B NMR spectrum (δ , CCl_4): -12.1 ppm. ^1H NMR spectrum (δ , ppm, CCl_4): 0.65 d (BCH_2), 1.48 m (CH_2), 2.03 m (CH), 2.52 s ($\text{CH}_3\text{--Ph}$), 7.25–7.88 m (H arom).

Dimer of 5-phenyl-3-bora-4-aza-1,1-bihomoadamant-4-ene (VIa)

9.8 g (0.04 mol) of the complex IVa in 3 ml of decane was heated at $210\text{--}220^\circ\text{C}$ (in a bath of Wood's alloy) for 2 h. The crystalline product which formed was filtered off and washed with hexane, to give 5.0 g (51%) of VIa, m.p. $315\text{--}323^\circ\text{C}$. Found: C, 80.84; H, 8.69; B, 4.53. $\text{C}_{32}\text{H}_{40}\text{B}_2\text{N}_2$ calcd.: C, 81.03; H, 8.50; B, 4.55%. Mass spectrum: 454 (M^+). IR spectrum (ν , CCl_4): intense band at 1682 cm^{-1} ($\text{C}=\text{N}$). ^{11}B NMR spectrum (δ , PhCN): 3.5 ppm.

Dimer of 5-(4-methylphenyl)-3-bora-4-aza-1,1-bihomoadamant-4-ene (VIb)

3.8 g (0.015 mol) of the complex IVb was heated in 4 ml of decane at $\sim 190^\circ\text{C}$ during 4 h in a bath of Wood's alloy. After the heating had been completed, the formation of crystals was observed. The crystalline product was washed with hexane on the filter and then dissolved in 50 ml of benzene. Undissolved impurities were filtered off, and the filtrate evaporated to dryness to give 1.97 g (52%) of VIb, m.p.

292–296°C (after recrystallization from acetonitrile). Found: C, 80.96, H, 8.98; B, 4.22. $C_{34}H_{44}B_2N_2$ calcd.: C, 81.28; H, 8.83; B, 4.31%. Mass spectrum: 502 (M^+). IR spectrum (ν , CCl_4): intense band at 1680 cm^{-1} ($C=N$). 1H NMR spectrum (δ , ppm, CCl_4): 0.55–2.07 m (H aliphatic), 2.32 s (CH_3 -Ph), 2.52 broad signal ($CH_2-C\begin{smallmatrix} N \\ \diagup \\ Ar \end{smallmatrix}$), 7.02 s (H arom).

7-Benzimidoylmethyl-3-borabicyclo[3.3.1]nonyl-8-hydroxyquinolinate (VII)

To 0.56 g (0.0013 mol) of the dimer VIa in 15 ml of toluene was added at 20°C, over a period of 5 min, 0.34 g (0.002 mol) of 8-hydroxyquinoline in 10 ml of toluene, a yellow opalescent colouration being observed. After the reaction mixture had been refluxed for 10.5 h, 0.1 g of a solid product was obtained by filtration; which turned out to be starting material (IR). The filtrate was evaporated in vacuum, and the residual oil-like product was converted to yellow crystals by trituration. The crystals were washed with hexane, yielding 0.70 g (93.5% calcd. for VII reacted), m.p. 143–148°C. Found: C, 78.20; H, 7.32; B, 2.82; N, 6.98. $C_{25}H_{27}BN_2O$ calcd.: C, 78.53; H, 7.12; B, 2.83; N, 7.33%. M 382.30. Mass spectrum: 382 (M^+). IR spectrum (ν , cm^{-1} , CCl_4): 1508, 1581, 1619 (arom), 3030–3080 (CH arom), 1690 ($C=N$).

7-Benzoylmethyl-3-borabicyclo[3.3.1]nonyl-8-hydroxyquinolinate (VIII)

To 0.5 g (0.0013 mol) of compound VII was added a mixture of 0.2 ml of H_2O , 5 ml of THF, and a drop of 1 N HCl. The reaction mixture was kept at $\sim 40^\circ C$ for 30 min, low-boiling substances were distilled off, and the residue was extracted with ether. Evaporation of the ether from the extracts yielded a yellow crystalline substance, 0.45 g (VIII, 90%), m.p. 139–143°C (sealed capillary under argon). Found: C, 78.26, H, 7.01, B, 2.78, N, 3.85. $C_{25}H_{26}BNO_2$ calcd.: C, 78.34, H, 6.84, B, 2.82, N, 3.66%. IR spectrum (ν , cm^{-1} , CH_2Cl_2): 1510, 1585, 1620 (arom), 3030–3080 (CH arom), 1682 (intense band of $C=O$).

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