HETEROCYCLIC ORGANOBORON COMPOUNDS—XVI¹ CHELATED COMPOUNDS WITH α,β -UNSATURATED β -AMINOKETONES

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Abstract—The reaction of β -aminoenones 4 with diphenylborinic acid or 2-alkoxy-1,3,2benzodioxaborole affords chelated compounds whose UV, IR and NMR spectra are discussed.

Previous parts in this series described the formation of stable boron chelate compounds with boron-oxygen bonds (1) using bidentate ligands with equivalent conjugated oxygens. Thus 5membered chelate rings are formed with tropolones, 6-membered rings with 1,3-diketones and 7-membered chelate rings with dibenzoylcyclopentadiene (for leading references and summary of previous work, cf reviews^{2.3}). When the oxygens



of the chelate ring cannot be equivalent, the compounds are less stable; this is evidenced by comparing the chelating ability of tropolone with that of 3-hydroxypyrones,⁴ or of 1,3-diketones³ with 2hydroxyacetophenones;^{1.6} in this case the oxygens were made non-equivalent by the structure of the ligand. A different means of achieving nonequivalence in the ligand is to preserve the structure and to alter the nature of the atom(s) linked to the B atom, as depicted by formula 2. 5-Membered chelate rings with boron were explored starting from 2-aminotropolone.⁷ The present paper investigates 6-membered chelate rings using as bidentate ligands for the boron derivative (3), α,β unsaturated β -aminoketones (4). The resulting



compounds 5 have a 6-membered chelate ring with a sequence of O, B, N atoms, and three C atoms.

The following starting materials were used: diphenylborinic acid or its ester with 2aminoethanol (Flavognost), (3, R = Ph), boron trifluoride (3, R = F), or 2-n-butoxy-1,3,2benzodioxaborole (3, R and R' being a pyrocatechol group); as enaminoketones, β aminochalcone (4, R' = H, R'' = R''' = Ph),[§] 4-amino-3-penten-2-one (4, R' = H, R'' = R''' = Me),⁹ and 4amino-3-penten-2-one (4, R' = Ph, R'' = R''' = Me)¹⁰ were used.

There are three possible tautomeric forms of enaminoketones **4a-4c**.



Both last forms exist in equilibrium in solution, with 4c prevailing, whereas the non-conjugated 4acould not be evidenced.¹¹

Complexes of enaminaketones 6 or 7 with transition metal ions M are known,¹² but boron chelates do not seem to have been reported.¹³⁻¹⁵



The chelates 5 have structures similar to complexes 6. Confirmation of structure 5 comes from IR absorption spectra (absence of $\nu C=0$ bands), NMR data (cf Table 1) and electronic absorption spectra (cf Table 1).

In the electronic absorption spectra one can note two bands; since the band at 350–380 nm appears in all compounds with $\mathbf{R}'' = \mathbf{R}''' = \mathbf{Ph}$, one can admit that this electronic transition involves the β aminoketone portion of the chelate. It corresponds

| | | Formula 5 | | | | Absorption maxima: nm (ϵ) | | | PMR δ, CDCl ₃ | Spectra (ppm) |
|---|----|-----------|----|----|-----|--------------------------------------|--------------------|--------------------------------|-----------------------------|------------------|
| | R | R' | R″ | R‴ | °C | CH ₂ Cl ₂ | CH ₃ CN | C ₆ H ₁₂ | —СН, | |
| a | Ph | н | Me | Me | 228 | 262 329 | _ | | 1·40 2·05 | 5.14 |
| b | Ph | Ph | Ме | Ме | 110 | 260 (3300) 331 (7400) | _ | _ | 1·91 2·06 | 5-37 |
| с | Ph | H | Ph | Ph | 208 | 273 376 | 271 387 | 270 394 | - | 6∙20 |
| d | F | Н | Ph | Ph | 203 | 261 355 | 262 351 | 253 353 | _ | 6.35 |
| e | a | н | Ph | Ph | 226 | 278 360 | 280 253 | 255 350 | ь | 6 |

Table 1. Spectral data of boron chelates 5a-e

"o-Phenylenedioxa; "Not determined.

to the band at ca 330 nm of the compounds with R'' = R''' = Me.

In comparing the solvatochromy of 5c with that of 5e, an opposite variation of the longest wavelength band is observed. This indicates that 5c is more polar than 5e, in agreement with the structure of these molecules: the formal negative charge of the boron atom can be delocalized by the phenyl groups of 5c, but not by the pyrocatechol group of 5e. The position of absorption bands is close to that of symmetrical boron chelates obtained from 1,3diketones¹⁶ instead of β -aminoketones.

The NMR spectra confirm the structures of the chelates, revealing at the same time interesting differences from boron chelates prepared from 1,3diketones.¹⁷ The presence of two peaks at ca 2(Table 1) reveals the existence of two nonequivalent Me groups in 5a and 5b. Both resonate at higher fields in the present chelates than in chelates prepared from 1,3-diketones.¹⁷ This fact can be assigned to a lower degree of delocalization in the 1-oxa-5-aza-pentadiene moiety of the present chelates, owing to the lack of symmetry in the ligand. An even more pronounced effect is observed for the methine hydrogen peak ($\Delta\delta$ of ca 0.6 ppm for $\mathbf{R}'' = \mathbf{R}''' = \mathbf{Me}$; and of *ca* 1 ppm for $\mathbf{R}'' = \mathbf{R}''' = \mathbf{Ph}$). The NH resonance cannot be seen in the NMR spectra. The multiplet due to aromatic protons was not included in Table 1.

The existence of the NH bond is confirmed by IR spectra. In KBr pellets a strong band appears at 3360 cm^{-1} in **5d** and 3400 cm^{-1} in **5c**. By deuterating the latter compounds, the ND stretching frequency appears at 2510 cm^{-1} .

Attempts to protodeboronate compounds 5a-c for obtaining a heteroaromatic ring (derived from 1,3,2-benzodioxaborinium salts¹⁸ by replacing an O^{\oplus} heteroatom by N) failed.

In conclusion, non-equivalence of the two atoms (N,O) linked to the B atom does not affect markedly

the stability and spectra of the chelates, because the electronic delocalization in the 1-oxa-5azapentadienic ligand is preserved. In contrast, previous data showed that non-equivalences due to absence of conjugation (as in 3-hydroxyketones) affect markedly these properties. Ligands like 2hydroxyacetophenone have an intermediate position in the stability series: 1,3-diketones > β aminoenones > 2-hydroxyphenones > 3hydroxyketones.

EXPERIMENTAL

Starting materials. Dibenzoylmethane and formamide afford β -amino-benzylideneacetophenone (β aminochalcone), m.p. 86° (from ethanol).[•] 4-Amino-3penten-2-one was prepared from acetylacetone and ammonia and had m.p. 43° (from anhyd ether).[•] 4-Anilino-3penten-2-one was prepared from acetylacetone and aniline and had m.p. 47° (from light petroleum).¹⁰

Spectra. IR absorption spectra were recorded with a Zeiss Jena UR-10 instrument, electronic absorption spectra with an Optica (Milan) CF-4 spectrophotometer, and NMR spectra with a Tesla B.S.-487 instrument operating at 80 MHz.

Reaction of β -amino-benzylideneacetophenone with diphenylborinic acid. Hot solns of β -aminobenzylideneacetophenone and the ester of diphenylborinic acid with ethanolamine (Flavognost), in equal amounts, in the minimal amounts of glacial AcOH were mixed. Yellow crystals of 5c appeared which after cooling and filtration were recrystallized from AcOH, m.p. 208°. (Found: C, 83:34; H, 5:72; N, 4:40. C₂₇H₂₂BNO requires: C, 83:74; H, 5:77; N, 3:61%).

Alternatively, 3g of sodium tetraphenylborate Kalignost) dissolved in 10 ml water were treated with 5 ml 15% HSO₄. The crystals of diphenylborinic acid were rapidly filtered off, washed with water until neutral, dissolved in MeOH and treated with β -aminobenzylideneacetophenone, yielding the same product identified by m.p. and IR spectrum.

Recrystallization from AcOD affords the N-deuterated product evidenced by IR spectroscopy.

Reaction of β -amino-benzylideneacetophenone with boron trifluoride. To the soln of the aminoketone in anhyd ether, BF₃-etherate was added dropwise in the cold. An exothermal reaction took place and the soln became turbid, with separation of an oil. This crystallized overnight, and **5d** was recrystallized from glacial AcOH, m.p. 203°. (Found: C, 67-03; H, 4-51; N, 5-56. C₁₃H₁₂BF₂NO requires: C, 66.46; H, 4-46, N, 5-17%).

Reaction β -amino-benzylideneacetophenone with 2-nbutoxy-1,3,2-benzodioxaborole. The aminoketone was treated with an excess of the borole in anhyd benzene affording a yellow soln. Addition of light petroleum separated an oily product which crystallied on standing, **5e**, m.p. 227-228°, from benzene. (Found: C, 73.56; H, 5.08; B, 3.17; N, 4.50. C₂₁H₁₆BNO₃ requires: C, 73.92; H, 4.73; B, 3.40; N, 4.10%).

Reaction of 4-anilino-3-penten-2-one and diphenylborinic ester. Equimolar amounts of aminoketone and Flavognost were refluxed for 30 min in MeOH. The solvent was evaporated and the residue (5b) was recrystallized from MeOH, m.p. 110°. (Found: N, 4.33. $C_{23}H_{22}BNO$ requires: N, 4.12%).

Reaction of 4-amino-3-penten-2-one with diphenylborinic ester. A methanolic soln of diphenylborinic acid prepared as for 5c was added to the aminoketone in equimolar amount. After refluxing for 10 min a ppt was formed (5a). It had m.p. 222° after recrystallization from benzene. By sublimation in vacuum (120-140°/2 Torr) m.p. 228°. (Found: N, 6.09; $C_{17}H_{18}BNO$ requires: N, 5.32%).

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REFERENCES

Part XV, E. Isfan and A. Barabas, *Rev. Roumaine Chim.*, 18, 1233 (1973)

- ²I. Bally and A, T. Balaban, Studii si Cercetări Chim. Acad. R.S. Romania, 17, 431 (1969)
- ³A. T. Balaban, in "La nature et les propriétés des liaisons de coordination", Colloq. 191, CNRS, Paris, p. 233 (1970)
- ⁴A. T. Balaban, I. Bally, R. J. Bishop, C. N. Rentea and L. E. Sutton, J. Chem. Soc. 1964, 2382
- ³A. T. Balaban, C. N. Renjea, M. Mocanu-Paraschiv and E. Romas, *Rev. Roumaine Chim.* 10, 849 (1965)
- ⁶A. T. Balaban, C. N. Rentea and M. Mocanu, *Tetrahedron Letters* 1964, 2049
- ⁷I. Bally, A. Arsene, A. T. Balaban and G. V. Boyd, *Rev. Roumaine Chim.* 13, 1391 (1968)
- ⁸H. Bredereck, R. Gompper and G. Morlock, *Chem. Ber.* 90, 942 (1957)
- ^oA. Combes and C. Combes, *Bull. Soc. Chim. Fr.* (3), 7, 778 (1892)
- ¹⁰E. Roberts and E. E. Turner, J. Chem. Soc. 1927, 1832
- "G. O. Dudek and R. H. Holm, J. Am. Chem. Soc. 83, 2099 (1961)
- ¹²J. P. Collman and E. T. Kittelman, *Inorg. Chem.* 1, 499 (1962); T. M. Hseu, D. F. Martin and T. Moeller, *Ibid.* 2, 587 (1963); G. W. Everett Jr. and R. H. Holm, *J. Am. Chem. Soc.* 87, 2117 (1965)
- ¹³A. Meller, Fortschr. Chem. Forsch. **15**, 146 (1970); W. Kliegl, Organometal. Chem. Revs. **8A**, 153 (1972)
- ¹⁴K. Niedenzu and J. W. Dawson, Boron-Nitrogen Compounds, Springer, Berlin (1965); K. Nicdenzu (chairman), Boron-Nitrogen Chemistry, Adv. Chem. Series Nr. 42, Am. Chem. Soc., Washington, D.C., (1964)
- ¹⁵H. Steinberg and R. J. Brotherton, Organoboron Chemistry, vol. 2, Interscience-Wiley, New York (1966)
- ¹⁶A. Arsene, A. T. Balaban, I. Bally, A. Barabas, M. Paraschiv and C. N. Rentea, Spectrochim. Acta. 23A, 1373 (1967)
- ¹⁷A. Trestianu, H. Niculescu-Majewska, I. Bally, A. Barabas and A. T. Balaban, *Tetrahedron* 24, 2499 (1968)
- ¹⁸A. T. Balaban, A. Arsene, I. Bally, A. Barabas, M. Paraschiv, M. Roman and E. Romaş, *Rev. Roumaine Chim.* 15, 635 (1970)