Aromatic boronic acids with neighboring amine groups capable of coordinating internally to boron form an interesting group of compounds. The facile change of the coordination state of the boron atom shows up in the catalytic properties of these compounds. This facility should also have consequences in the complexation abilities of boronic acids. It is well-known that borate anions form cyclic esters with vicinal dihydroxy compounds. However, in aqueous solution borate is not a predominant species until at rather high pH values. It can be anticipated that the boronic acids which maintain the tetracoordination at low pH values are better esterifying agents for vicinal dihydroxy compounds than boric acid.

Compound 1, \((N_3^3-B)\)-2-[1-(o-dihydroxyboryl-phenyl)-2-phenylethyl]-2-imidazoline, has been synthesized previously and showed complexing properties with pyrocatechol derivatives but not with \(\alpha\)-hydroxy acids. It was anticipated that the insertion of large substituents into the molecule might favorably modify the solubilities of the complexes. The benzyl derivative of 1, \((N_3^3-B)\)-2-[1-(o-dihydroxyborylphenyl)-2-phenylethyl]-2-imidazoline (2) was synthesized starting from benzyl cyanide, which was benzylated, the resulting 2,3-diphenyl-propionitrile (3) was allowed to react with 2-aminoethyl-ammonium tosylate according to the general procedure of Oxley and Short to give 2-(1,2-diphenylethyl)-2-imidazoline (4). Compound 2 or actually its hydrochloride was obtained from 4 by a reaction with boron trichloride and aluminium chloride in boiling xylene and hydrolyzing the product.

The hydrochloride of compound 2 is a white crystalline solid with moderate solubility in water. Its aqueous solution is quite acidic, the \(pK_a\) determined from the half-neutralization point being ca. 3.0. The \(pK_a\) values of imidazolines are generally within the range from 10 to 11. The only reasonable explanation for this large deviation is the ringchain equilibrium where the cyclic form (2) is essentially neutral.

When mixing equal volumes of ca. 0.01 M aqueous solution of the hydrochloride of compound 2 and ca. 5% solutions of dihydroxy compounds, a precipitate was formed with glycolic, lactic, 2-hydroxyisobutyric, malic, tartaric, citric, gluconic, quinic, mucic, saccharic, salicylic, and oxalic acids, and with pyrocatechol. No precipitate was formed with 3-hydroxypropionic, 3-hydroxybutyric, \(\beta\)-hydroxybenzoic, and malonic acids, nor with 1,2-ethanediol, 1,2-propanediol, glycerol, mandelic, 2,3-dimethyl-2,3-butanediol. The results show that \(\alpha\)-hydroxy acids are generally precipitated whereas \(\beta\)-hydroxy acids and glycols are not. The exceptions are salicylic acid and pyrocatechol. The potentiality of the reactions as an analytical test is obvious. In the case of tartaric acid opalescence was observed even on mixing ca. 10⁻⁴ M solution of the acid with the organoboron reagent. This observation is leading to a microanalytical assay of tartaric acid which will be published separately.

Experimental. 2,3-Diphenylpropionitrile (3).
To a suspension of 27 g of sodium hydride in 450 ml of ether was added dropwise with stirring 127 g (1.08 mol) of freshly distilled benzyl cyanide. After 4 h of stirring under reflux the mixture was cooled to room temperature and 63 g (0.5 mol) of benzyl chloride.

was added dropwise as fast as possible without excessively vigorous reaction. After 12 h of stirring ether was evaporated and 450 ml of benzene added. The benzene solution was washed successively with 1 M hydrochloric acid, saturated solution of sodium carbonate and water. The solution was dried with \( \text{Na}_2\text{SO}_4 \) benzene evaporated and the residue distilled under reduced pressure. The fraction boiling at \( 120 - 140 ^\circ \text{C}/2 \) mmHg solidified and was recrystallized from ethanol to give 67 g (68 %) of 2,3-diphenylpropionitrile, m.p. 55.5 - 56.5 \(^\circ\)C (lit. 46 - 47 \(^\circ\)C, 55 - 56 \(^\circ\)C).

2-(1,2-Diphenylethyl)-2-imidazoline (4). A mixture of 2,3-diphenylpropionitrile (31.1 g, 0.15 mol) and 2-aminoethylammonium tosylate \( \times \) (34.9 g, 0.15 mol) was heated at 203 - 205 \(^\circ\)C until no more ammonia was evolved (ca. 2 h). The resulting solid was dissolved in 700 ml of boiling water and 6 g of sodium hydroxide dissolved in 25 ml of water was added. The oily precipitate solidified at 5 \(^\circ\)C. It was dried and recrystallized from a mixture of toluene and light petroleum yielding 26.3 g (70 %) of white needles, m.p. 115 - 115 \(^\circ\)C. The mass spectrum showed the parent peak at \( m/e \) 250.

2-[1-(Dihydroxyborylphenyl)]-2-phenylethyl]-2-imidazoline (2). To a solution of 12 g (0.1 mol) of boron trichloride in 120 ml of ice-cold xylene 20 g (0.1 mol) of finely ground compound 4 was added. The mixture was stirred at 85 \(^\circ\)C for 1 h and at room temperature for 2 h. Finely ground anhydrous aluminium chloride (12.8 g, 0.1 mol) was added and the mixture was refluxed with stirring under a slow nitrogen flow for 20 h. To the cooled solution 65 ml of 2 M hydrochloric acid was cautiously added. Stirring was continued until the sticky mass dissolved. Xylene was decanted off and ca. 300 ml of acetone was added to the water layer. The lower layer was separated and allowed to stay overnight in a refrigerator. The precipitate was washed with acetone, dried under reduced pressure and recrystallized from a mixture of 80 ml acetonitrile and 6 ml of water. The yield was 10 g (38 %) of white crystals with no definite melting or decomposition point. Anal. \( \text{C}_{10}\text{H}_{19}\text{BN}_{2}\text{O}_{4}\cdot\text{HCl} \cdot \text{B} \). Neutralization equivalent, obs. 333.5, calc. 330.5.

No parent peak could be found in the mass spectrum of the compound 2. A pyrocatechol derivative could be easily prepared as in the case of analogous boron compounds. \(^2\) A thick white precipitate which formed when mixing aqueous solutions of the hydrochloride and pyrocatechol was filtered, washed with water and dried in a vacuum desiccator. The mass spectrum showed the parent peak at \( m/e \) 368.


A Stereoselectively Formed Dimer of 6-Benzyloxy-6-phenylfulvene

OLOF WENNERSTRÖM

Department of Organic Chemistry, Chalmers University of Technology and University of Göteborg, S-402 20 Göteborg, Sweden

Fulvenes are known to take part in Diels-Alder reactions and other cycloadditions, both as dienes and dienophiles.\(^1\)\(^2\) As dienophiles they can react both as \( 2\pi \) and \( 6\pi \) systems.\(^3\) There are, however, few examples of Diels-Alder dimerizations of fulvenes.\(^4\) The loss of the resonance energy in the fulvenes\(^5\) makes these reactions energetically less favourable than the well-known dimerization of cyclopentadiene. If substituted with different groups at the exocyclic carbon atom, a fulvene could either give a mixture of dimers or stereoselectively give only one dimer in a Diels-Alder reaction. In this paper the formation of such a dimer of 6-benzyloxy-6-phenylfulvene is reported.

Results and discussion. A cool ethyl ether solution of 6-benzyloxy-6-phenylfulvene \(^4\) slowly deposits a white precipitate. Analysis and MS show that this precipitate has the same composition as the fulvene. The compound was found to contain one single isomer, whose structure was elucidated by its \( ^1\text{H} \) NMR spectrum (Scheme 1). The spectrum showed the 1/1 ratio of olefinic to tertiary protons as expected for a normal Diels-Alder dimer. Decoupling experiments gave the chemical shifts and coupling constants for the eight protons in the tricyclo[5.2.1.0\(^5\),8\]decadiene ring system. The coupling constants \( J_{1,3} \) and \( J_{4,7} \) (4.2 Hz) show that the dimer has an endo configuration.\(^5\) The remaining structural problem, the configuration at the exocyclic double bonds, was solved by means of a shift reagent. The chemical shifts for the eight protons increased on addition of a shift reagent (Eu fod\(_3\)) to the fulvene dimer. A rigorous treatment of the problem is very complex and was not carried out. However, the following qualitative argument should be satisfactory. One can hardly explain the induced shifts without assuming that both ester groups coordinate with the europium salt. Rotation around the single bond between