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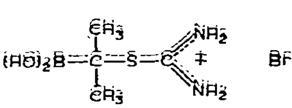
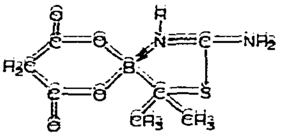
Chelates of a boronic acid with malonic and acetoacetic acid*

Mixed anhydrides of carboxylic and boronic acids hydrolyze very readily[1]. "Acetyl borate" (tetraacetyl diborate[2]) is commonly used for removing traces of water from acetic acid[3].

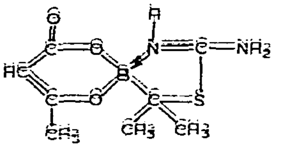
Contrary to expectation, mixing aqueous solutions of malonic acid and 2-S-thioureidopropane-2-boronic acid hydrobromide[4] (I) immediately yielded the crystalline mixed anhydride (II). Hydrobromic acid was released into the solution. The spiro chelate structure (II) is consistent with the unusual stability of the product. A similar chelate (III) was prepared from sodium acetoacetate and the boronic acid (I).



(I)



(II)



(III)

The structures of both chelates, (II) and (III), were proved by boiling with aqueous catechol, which rapidly liberated the carboxylic acids and yielded the catechol derivative of 2-S-thioureidopropane-2-boronic acid, identified by infrared comparison with an authentic sample[4].

Ultraviolet spectra indicate that these chelates are stable at high dilution in water or ethanol. However, mixing very dilute solutions of the boronic acid (I) and sodium malonate or acetoacetate did not yield any ultraviolet evidence for the chelates. The malonic acid chelate (II) showed only end absorption down to 200 mμ but lost a proton from the acidic methylene group in 10^{-3} *M* aqueous sodium hydroxide. The salt of (II) showed λ_{max} at 258 mμ, ε_{max} 9100, λ_{min} at 237 mμ. The acetoacetic acid chelate (III) in ethanol showed λ_{max} at 253 mμ, ε_{max} 9800, λ_{min} at 232 mμ.

Malonic acid did not react with benzeneboronic acid, and it appears likely that the thioureido group or, presumably, any basic group in a position to coordinate with the boron atom is essential to the stability of the mixed anhydride structure. The chelates (II) and (III) are somewhat related to dialkylboronium acetylacetonates[5] and ethyl acetoacetate chelates[1].

Experimental

Chelate of malonic acid with 2-S-thioureidopropane-2-boronic acid. A solution of 0.50 g of 2-S-thioureidopropane-2-boronic acid hydrobromide[4] in 2 ml of water was mixed with 0.23 g of malonic acid in 1 ml of water. Crystallization of the chelate was induced by scratching and cooling, yield 0.34 g (70%), m.p. after recrystallization from water 226–228°[6]. The NMR spectrum in perdeuteriodimethyl sulfoxide showed three singlets at τ 6.66 (NH and OH), τ 6.74 (CH_2), and τ 8.77 (CH_3) in the ratio 3 : 2 : 6. The infrared spectrum (KBr pellet) showed C=O and C=N bands at 5.78, 5.91, and 6.03 μ. (Found: C, 36.50; H, 4.96; B, 4.64; N, 12.37; S, 13.83. $C_7H_{11}BN_2O_4S$ calcd.: C, 36.54; H, 4.82; B, 4.70; N, 12.18; S, 13.93%.)

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Chelate of acetoacetic acid with 2-S-thioureidopropane-2-boronic acid. A solution of sodium acetoacetate prepared by boiling 0.28 g of ethyl acetoacetate briefly with 0.08 g of sodium hydroxide in 1 ml of water was mixed with 0.52 g of 2-S-thioureidopropane-2-boronic acid hydrobromide in 2 ml of water, immediately precipitating 0.28 g of the chelate, m.p. after recrystallization from acetonitrile 252–254° (dec.). (Found: C, 41.95; H, 5.93; B, 4.96; N, 12.48; S, 13.84. $C_8H_{13}BN_2O_3S$ calcd.: C, 42.13; H, 5.74; B, 4.74; N, 12.29; S, 14.06%.)

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