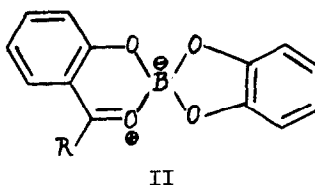
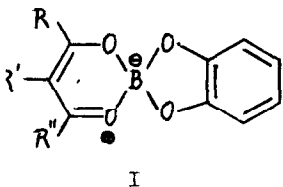


1,3,2-Dioxaborinium and 4,5-benzo-1,3,2-dioxaborinium
cations, novel aromatic systems

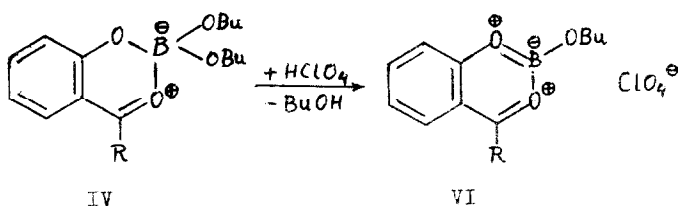
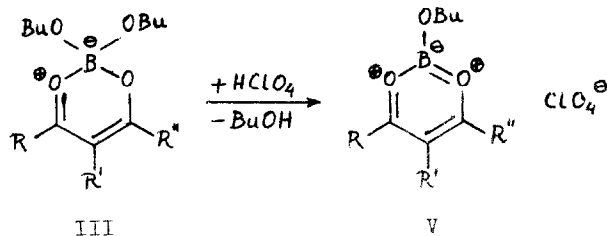
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In a previous study of the reaction between 2-alkoxy-1,3,2-dioxaboroles and bidentate ligands (1), it was shown that with enolizable 1,3-diketones or benzoderivatives such as *o*-hydroxyacetophenone, crystalline amphionic spiroborates I and II are formed.



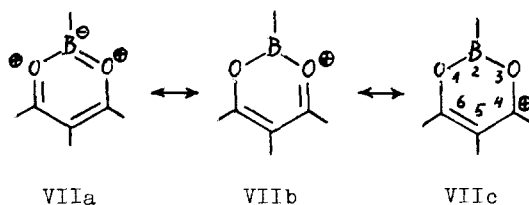
No crystalline products III and IV could be obtained from bidentate ligands and tri-*n*-butyl borate. However, on treating an equimolar mixture of tri-*n*-butyl borate and 1,3-diketone with a solution of anhydrous perchloric acid in methylene dichloride (2), crystalline perchlorates are formed (with aliphatic diketones, petroleum ether must be added).

Elemental analyses and the mode of formation indicate for these compounds formulas V and VI, respectively; in their infrared spectra, bands due to the perchlorate anion (625 and 1100 cm^{-1}) are always present.



Thus acetylacetone affords V ($R = R'' = \text{Me}$, $R' = \text{H}$), m.p. 176° dec. (from dioxane - petroleum ether); UV bands in methylene dichloride 252 sh and 293 μ ; in acetonitrile 225, 249 sh and 292 μ ; IR bands in nujol: 840, 900, 928, 970, 1007, 1025, 1570 broad, 3085 and 3145 cm^{-1} . 3-Methyl-2,4-pentanedione affords V ($R = R' = R'' = \text{Me}$), m.p. 175° dec. (from acetonitrile); UV bands in methylene dichloride 264 sh and 313 μ ; in acetonitrile 232, 264 sh and 311 μ ; IR bands in nujol: 888, 935, 1002, 1211, 1335, 1525 broad and 1575 cm^{-1} . Dibenzoylmethane in benzene affords V ($R = R'' = \text{Ph}$, $R' = \text{H}$), yellow, which may be recrystallized from acetonitrile and explodes without melting; an excess of perchloric acid leads to a by-product with m.p. 260° which was not further investigated; UV bands in methylene dichlo-

ride 250 sh, 277, 310, 382 and 400 mp ; in acetonitrile 239, 250 sh, 275, 307, 379 and 397 mp ; IR bands in nujol and in potassium bromide pellet : 610, 675, 719, 728, 789, 910, 1002, 1041, 1171, 1193, 1268, 1313, 1360, 1385, 1439, 1494, 1520, 1560 broad, 1606, 3080 and 3150 cm^{-1} . *o*-Hydroxyacetophenone affords VI (R = Me), yellow, m.p. 223° (from acetonitrile) ; UV maxima in methylene dichloride 254, 295, 330 and 387 mp ; in acetonitrile 252, 290, 327 and 380 mp ; the compound is very hygroscopic and the bands at 252-4 and 327-30 mp due to *o*-hydroxyacetophenone formed by hydrolysis gradually increase ; prominent IR bands in nujol : 730, 771, 812, 1005, 1023, 1150, 1178, 1208, 1258, 1290, 1408, 1495, 1520 broad, 1588 and 1629 cm^{-1} . The IR spectral data evidence that in these systems there is strong chelation of the carbonyl groups and there is no free enol group, in agreement with formulas V and VI.



These compounds are derivatives of the 1,3,2-dioxaborinium cation VII for which several limiting structures may be written. Structure VIIa and the two structures VIIb evidence that this system can be regarded as a boroxaropyrylium cation (3), while the two structures VIIc denote that positions 4 and 6 must be strongly electrophilic. At the same time, this new aromatic system may be regarded as a Z-homologue (4) of 1,3,2-dioxaboroles.

Reactions and further derivatives of these systems are under investigation and will be reported in Revue Roumaine de Chimie.

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