We have found the complexes of the sugar with the gel matrix to correspond to the sugar-borate complexes in solution; their formation is pH-dependent. Optimal separation is obtained at pH > 9. The configuration of the sugar hemiacetal ring is of special importance for complex formation as it is well known that sugars form borate complexes preferentially in their furanose form[2]; Fig. 1 confirms this finding. Furanose formation of the terminal glucose also provides an explanation for the separation of maltose from isomaltose (Fig. 2a). An increase in the number of *cis*-hydroxyl groups leads to more extensive complex formation; thus lactose and raffinose can be separated quantitatively (Fig. 2b). The disaccharide pairs maltose and cellobiose, and maltose and lactose, however, show only very slight differences in their elution maxima since none of them yields a furanose form and they all contain the same number of *cis*-hydroxyl groups.

Compared with the procedures used hitherto[3-5], chromatography on "boric acid gels" offers the following advantages:

1. The use of volatile buffers permits rapid working up of the fractions since the separated sugar components can be isolated quantitatively in high purity without desalting. Also the absence of borate residues is of particular importance in structural chemical work with oligosaccharides[6].

2. By suitable choice of gel and gel volumes both mono- and oligo-saccharides can be optimally separated, even if they differ only very slightly in complex formation constants.

Experimental:

A chromatographic column (1/20 cm) is filled with swollen "boric acid gel"[1], then washed with 0.5 N HCl, and finally washed neutral. The sugar mixture (each 1 mg per mono- or oligo-saccharide) is dissolved in the eluant (0.2 ml), placed on the column and eluted with 0.1% aqueous ammonia (pH = 10.5), fractions of 4 ml per hour being collected. Aliquot parts (0.2 ml) of the fractions are monitored by the phenol/sulfuric acid reagent for presence of sugars[7] (test batch: 0.2 ml of fraction solution + 0.1 ml of 90% phenol + 1 ml of H_2O, shake, then add 3 ml of concentrated H_2SO_4). The sugars that are separated are identified by borate electrophoresis.

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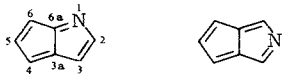
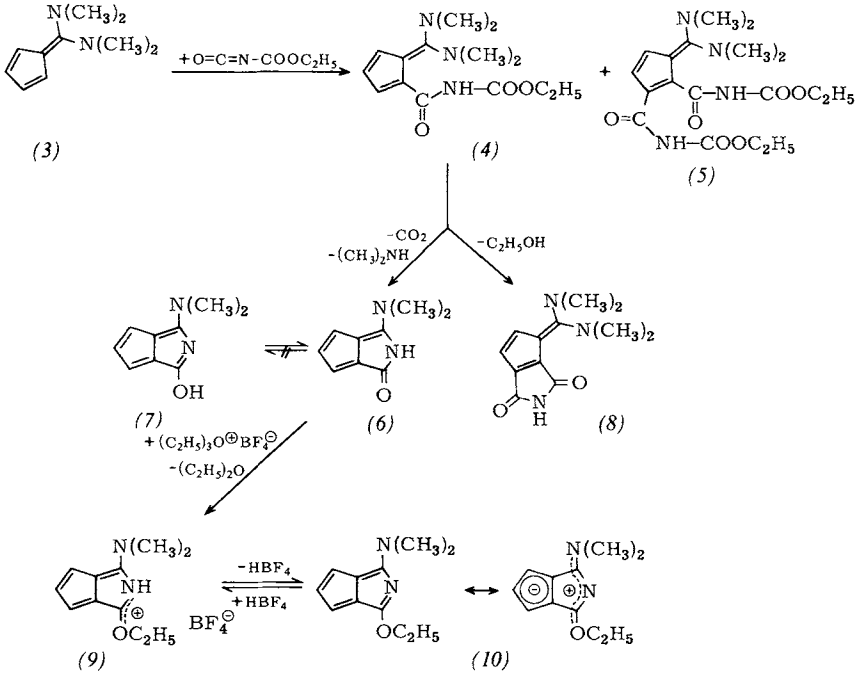
A Stable 2-Azapentalene[**]

By *Klaus Hafner* and *Frank Schmidt*[*]

After the synthesis of simple carbocyclic pentalenes[1] the aza analogs attract particular interest because their properties are likely to depend markedly on the position of the nitrogen atoms. As 8π-electron systems 1- *(1)* and 2-azapentalene *(2)*, as well as polyazapentalenes with C-fusion of the two five-membered rings, should not be "aromatic". In spite of many attempts no such bicyclic azapentalene has hitherto been prepared. The thermal instability of benzo[*b*]- and benzo[*f*][1]azapentalene precludes their



(1) *(2)*



(3) *(4)* *(5)* *(6)* *(7)* *(8)* *(9)* *(10)*

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isolation[2]. Neither the various known azapentalene anions[3] nor the "aromatic" 1,3a,4,6a-tetraazapentalenes[4] and 3a,6a-diazapentalenes[5] allow valid conclusions about the properties of *(1)* and *(2)*. Both the structures *(1)* and *(2)* formally combine a pentafulvene and an azapentafulvene system, and this consideration led us, starting from 6,6-bis(dimethylamino)fulvene *(3)*[6], to synthesize the first stable 2-azapentalene.

(3) reacts with ethyl isocyanatoformate in acetonitrile at 20 °C, yielding 6,6-bis(dimethylamino)-1-[*N*-(ethoxycarbonyl)carbamoyl]fulvene *(4)*[7] [yield 22%; yellowish crystals, m. p. 150—151 °C; UV (dioxane): λ_{max} (log ε) = 258 (4.25), 335 (3.93), 369 nm (4.13); 60-MHz-NMR ($CDCl_3$): τ = 2.14 (broad, NH); double doublet centered at 3.37 (J = 3.5 Hz and J = 2.0 Hz) and 3.77 (J = 3.5 Hz and J = 2.0 Hz, 2-H, 4-H), 3.96 (t, J = 3.5 Hz, 3-H), 5.79 (q, CH_2), 6.96 (s, $2N(CH_3)_2$), 8.71 (t, CH_3)], and 7% of 6,6-bis(dimethylamino)-1,2-bis-(*N*-ethoxycarbonyl)carbamoyl]fulvene *(5)* (pale yellow crystals of m. p. 172—174 °C).

In boiling pyridine/H_2O (80 h), *(4)* undergoes intramolecular cyclization with loss of CO_2 and $(CH_3)_2NH$, yielding 3-(dimethylamino)-2*H*-2-azapentalen-1-one *(6)* [yield 47%; orange needles, dec. > 250 °C; UV (CH_3OH): λ_{max} (log ε) = 217.5 (4.39), 252 (4.14), 360 (4.02), 444 nm (3.44); IR (Nujol): 3180 (NH), 1685 cm^{-1} (CO); 60-MHz-NMR ([D_6]DMSO): τ = 0.42 (broad, NH); A_2B system: τ_A = 3.75 (4-H, 6-H), τ_B = 3.96 (5-H) (J_{AB} = 3.4 Hz), 6.71 (s, N—CH_3), 6.78 (s, N—CH_3)]. In addition, 0.5% of 6,6-bis(dimethylamino)fulvene-1,2-dicarboximide *(8)* was isolated (yellow crystals, m. p. 174—175 °C). The IR and UV spectra of the lactam *(6)* give no evidence for an equilibrium with the pentalenoid lactim *(7)*.

As expected, *(6)* can be converted by triethyloxonium tetrafluoroborate in CH_2Cl_2 at 0 °C by *O*-alkylation into the tetrafluoroborate *(9)*. The deprotonation of *(9)* by 50% aqueous K_2CO_3 solution leads to the lactim ether, 3-(dimethylamino)-1-ethoxy-2-azapentalene *(10)*, isolated as bluish-violet needles of m. p. 78—79 °C (yield 37%). The 100-MHz-NMR spectrum (in $CDCl_3$) of *(10)*, which proves its structure, resembles that of 1,3-bis(dimethylamino)pentalene[8] regarding the chemical shifts of the five-membered ring protons and provides no evidence for an induced ring current. [ABX system at $\tau_{A,B} \approx 3.85$ (4-H, 6-H) and τ_X = 4.15 (5-H), 6.66 (s, N—CH_3), 6.76 (s, N—CH_3), 5.57 (q, OC_2H_5), 8.57 (t, OC_2H_5).] The UV spectrum of *(10)* (in *n*-hexane) agrees reasonably with the values obtained by an SCF—CI calculation[9] and shows absorption maxima at 221 (log ε = 4.36), 274 (4.03), 281 (sh), 393 (4.16), and 598 nm (2.75). The spectrum resembles that of 1,3-bis(dimethylamino)pentalene. However, as with azulenes[10], replacing a methine group of a pentalene by nitrogen at a position of high charge density causes a hypsochromic shift of the longest-wavelength maximum.

In atmospheric oxygen *(10)* is stable for some days at room temperature, and shows a marked basicity (dissolves in 0.1 N acetic acid). It is converted by proton acids, in a quantitatively reversible reaction, into the conjugate acid *(9)* [perchlorate, carmine-red needles, dec. > 195 °C; UV (CH_2Cl_2): λ_{max} (log ε) = 260 (4.00), 267 (4.01), 272 (3.87), 372 (4.08), 381 (4.11), 522 nm (3.24); 100-MHz-NMR (CD_3CN): τ = 0.91 (broad NH), ABX system with $\tau_{A,B} \approx 3.15$ (4-H, 6-H) and τ_X = 3.60 (5-H), 6.63 (s, N—CH_3), 6.70 (s, N—CH_3), 5.40 (q, OC_2H_5), 8.48 (t, OC_2H_5)].

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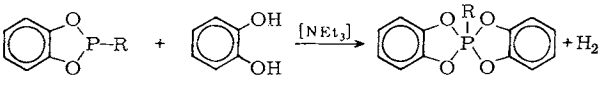
Alkyl- and Aryl-hydridobis(*o*-phenylenedioxo)-phosphate(1−), a Stable Spiroanion Containing Hexacoordinated Phosphorus[**]

By *Markus Wieber* and *Keywan Foroughi*[*]

Reactions of derivatives of quinquevalent phosphorus often occur by way of an intermediate containing a hexacoordinated phosphorus atom[1]. When converting trivalent into quinquevalent phosphorus by the reaction[2]

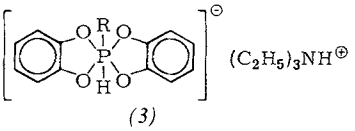


(1) *(2)*

R = CH_3, C_6H_5

we have isolated the first stable intermediate containing hexacoordinated phosphorus.

Hydridomethyl (or phenyl)bis(*o*-phenylenedioxo)phosphate(1−) can be obtained as its triethylammonium salt *(3)* by treating 1,3,2-benzodioxaphospholes *(1)* with pyrocatechol and triethylamine in the molar ratio 1 : 1 : 1.



(3)

R = CH_3, C_6H_5

As shown by the NMR spectra (Table 1), the products exist, even in polar solvents, in the spiro form with coor-

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