cubation of the sample with carboxypeptidase A[15] caused the liberation of Leu, His, and Phe, while with leucine aminopeptidase,[16] the sample was degradated completely to nine amino acid residues, leaving no decapeptide. These data confirm the stereochemical purity of the product.

The preparation was chromatographed on Toyo Roshi No. 51 paper (solvent: 1-butanol–acetic acid–water, 7:1:2) and on Serva tlc thin layer (solvent: *sec*-butyl alcohol–3% ammonium hydroxide, 100:44); the R_f values, 0.51 and 0.71, respectively, were identical with those of natural human angiotensin I.[4] The chemical identity was confirmed further by the cochromatography of a mixture of the preparations from the synthesis and the human origin with the Bio-Gel column (solvent: 0.1 *N* acetic acid). The rat pressor activity[4] of the synthetic decapeptide was identical with that of natural human angiotensin I and 48% of that of synthetic octapeptide (Ile^5-angiotensin II).[17] Both synthetic and natural human angiotensin I thus showed quite identical chromatographical and biological properties.

The results obtained here further confirm the correctness of the structure of human angiotensin I as the decapeptide of the amino acid sequence mentioned above.

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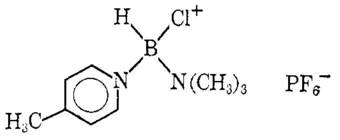
An Optically Active Boron Cation

Sir:

We wish to report the synthesis of a salt containing an asymmetric boron atom and the first resolution of a boron cation into optically active isomers.

Trimethylamine monoiodoborane was prepared by a modification of the method of Noeth[1] by adding solid iodine (0.050 mole) in portions to a cooled and stirred benzene solution of trimethylamine borane (0.110 mole). Reaction of the resulting solution with dry 4-picoline (94 ml) in an ice bath gave within 5 min a precipitate of the iodide salt of the picolinetrimethylaminedihydroboron cation (0.096 mole, mp ∼150° dec). The water-soluble iodide was readily converted to the less soluble hexafluorophosphate by addition of excess NH_4PF_6.[2] Recrystallization from hot water gave pure $CH_3C_5H_4N(CH_3)_3NBH_2PF_6$ (93% yield, mp 146.5–147.0°). *Anal.* Calcd for $C_9H_{18}BF_6N_2P$: C, 34.87; H, 5.85; B, 3.49; F, 36.77; N, 9.04; P, 9.99. Found: C, 34.92; H, 5.96; B, 3.39; F, 36.56; N, 8.92; P. 9.80. The dihydro compound reacted with chlorine[3] in methylene chloride solution at room temperature producing the asymmetric boron compound (I) in nearly quantitative yield.


I

Recrystallization from methylene chloride–tetrahydrofuran–diethyl ether gave 97% recovery of pure product, mp 119.8–120.3°. *Anal.* Calcd for $C_9H_{17}BClF_6N_2P$: C, 31.38; H, 4.97; B, 3.14; Cl, 10.29; F, 33.09; N, 8.13. Found: C, 31.52; H, 5.02; B, 3.06; Cl, 10.44; F, 33.30; N, 8.15.

The ^{11}B resonance spectra are in agreement with the expected structures, showing a triplet for the dihydro compound (δ 17.8 ± 0.5 ppm,[4] J_{B-H} = 90 ± 5 cps) and a doublet for the monochloro compound (δ 9.3 ± 0.8 ppm, J_{B-H} = 140 ± 15 cps). The proton nmr spectra of the PF_6^- salts, obtained in CH_2Cl_2 and referred to external tetramethylsilane, gave resonances at δ (ppm) 2.67 (9 H), 2.63 (3 H), 7.78 (2 H, doublet, J = 7 cps), and 8.55 (2 H, doublet, J = 7 cps) and for the monochloro compound at δ (ppm) 2.78 (9 H), 2.70 (3 H), 7.87 (2 H, doublet, J = 6 cps), and 8.75 (2 H, doublet, J = 7 cps). Boron-attached hydrogens could not be detected because of excessive line broadening.

Attempts to resolve the asymmetric boron cation with the ammonium salt of *d*-α-bromocamphor-π-sulfonic acid or with potassium *d*-antimonyl tartrate were unsuccessful because of unfavorable solubility relationships and because the boron compound slowly reduces the antimonyl complex in hot water. However, partial resolution was achieved without an optically active resolving agent in the following manner. Two grams of the hexafluorophosphate salt was dissolved in 50 ml of hot methylene chloride, and enough cyclohexane was added to cause a slight precipitate which was redissolved by the addition of 2–3 ml of acetone. On very slow cooling and evaporation there were produced relatively large crystals.

A few crystals were well defined having relatively sharp edges and rhombohedral faces. These crystals were weighed individually and then dissolved separately in methylene chloride. Optical rotations were measured on a digital readout polarimeter. Both negative and positive readings were observed. As an example, a crystal weighing 84 mg was dissolved in 1.2 ml of methylene chloride. The observed rotation was −0.315 ± 0.003°. In another case, a solution containing 257 mg of optically active boron compound per milliliter of methylene chloride gave a rotation of +1.120 ± 0.003°. Specific rotations of solutions of single crystals varied from $[\alpha]^{24}_{365\text{m}\mu}$ −5.1 to +4.1; the samples were therefore not optically pure. These rotations did not change significantly upon standing in stoppered tubes for periods as long as 5 days. For a given solution the amount of rotation was found to decrease with increasing wavelength. Nmr spectra taken before and after recrystallization showed no change other than a trace of acetone which apparently occluded during the crystallization process. We are now attempting large-scale and complete resolution

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(4) *Vs.* external $B(OCH_3)_3$.

by means of optically active transition metal complex anions.

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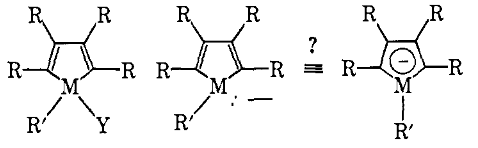
Functionally Substituted Sila- and Germacyclopentadienes. Anion Formation

Sir:

There has been much interest in whether anions (II) derived from sila- or germacyclopentadienes (I) would be stabilized by resonance since these anions have six π electrons and the resonance extremes would involve a silicon or germanium double bond to carbon. Rühlmann[1] recently prepared pentaphenylsilole (I, M = Si; R = R′ = C_6H_5; Y = H) and tetraphenylmethylsilole (I, M = Si; R = C_6H_5; R′ = CH_3; Y = H) by allowing 1,4-dilithiotetraphenylbutadiene[2] to react with phenyl- or methyldichlorosilane. Rühlmann also reported that treatment of these siloles with phenyllithium gave intense red-violet colors, but he could not decide if the color was due to an anion radical, a ring-addition product, or the silacyclopentadienide anion (II). Since the organodichlorisilanes, $RSiCl_2H$, used by Rühlmann are difficult to prepare and not readily available, a synthetic procedure employing the easily obtained $RMCl_3$ (M = Si, Ge) derivatives was sought. Such a procedure would also have the advantage that the silole or germole obtained would have Y = halogen in the structure (I), allowing for a wide variety of substitutions at the heteroatom (M).



I II

M = Si, Ge

Although attempts to prepare halogen-substituted siloles and germoles by the reaction of $(C_6H_5)_4C_4Li_2$ with chlorosilanes and -germanes have been reported to be unsuccessful,[3] it has been found that *reverse* addition of a diethyl ether suspension of 1,4-dilithiotetraphenylbutadiene[2] to a diethyl ether or tetrahydrofuran (THF) solution of $R'MCl_3$ or MCl_4 (M = Si, Ge) gives in 50–70% yield the corresponding heterocycle. Some of the new chloro-substituted siloles and germoles (I, R = C_6H_5) are: $(C_6H_5)_4C_4Si(Cl)C_6H_5$ (III), mp 181–183°; $(C_6H_5)_4C_4Si(Cl)CH_3$ (IV), mp 194–195°; $(C_6H_5)_4C_4GeCl_2$ (V), mp 197–199°; $(C_6H_5)_4C_4Ge(Cl)C_6H_5$ (VI), mp 210–211°. The chloride may be displaced by many reagents, *e.g.*, RO^-, R^-, and transition-metal carbonyl anions.[4] Of interest here are the hydrides which may be prepared in 70–90% yield by reduction with $LiAlH_4$: $(C_6H_5)_4C_4Si(H)C_6H_5$ (VII), mp 198–199°, ν_{SiH} 2120 cm^{-1}; $(C_6H_5)_4C_4Si(H)CH_3$ (VIII), mp 223–224°, ν_{SiH} 2122 cm^{-1}; $(C_6H_5)_4C_4GeH_2$ (IX), mp 192–193°, ν_{GeH} 2060 cm^{-1}; $(C_6H_5)_4C_4Ge(H)C_6H_5$ (X), mp 187–188°, ν_{GeH} 2056 cm^{-1}.

When *n*-butyllithium is added to X in THF at −78°, a bright red color is produced. The addition of water to this red solution regenerates the starting hydride X. If trimethylchlorosilane is added in place of water, the silyl derivative, $(C_6H_5)_4C_4Ge(C_6H_5)Si(CH_3)_3$, mp 178–180°, ν_{SiCH_3} 1250 and 850 cm^{-1}, τ_{SiCH_3} 9.77, is formed in 90% yield. Thus, the bright red color is ascribed to the germyllithium compound, $(C_6H_5)_4C_4Ge(Li)C_6H_5$ (XII).

On the other hand, when the silicon hydrides (VII and VIII) are treated with *n*-butyllithium in the same manner, a very intense, dark purple color is generated as was observed by Rühlmann.[1] The addition of water or D_2O to these solutions does not regenerate the starting hydrides (or deuterides) although the intense color is dispelled. Nmr spectra of the resins obtained after removal of the THF show broad unresolved absorptions in the region τ 10–7.7, and the area ratios indicate the presence of butyl groups in the resins. Furthermore, the splitting patterns of the H_2O- and D_2O-quenched reaction products are different, suggesting that H or D is incorporated in the resins. No Si–H or Si–D stretching frequencies are observed in the infrared spectra of the products, so the hydrogen or deuterium must be attached to the carbon skeleton. Unfortunately, the C–D stretching region is obscured by a weak overtone or combination band.

To determine if a hydrogen atom attached to the heteroatom was necessary to form these intensely colored solutions, *n*-butyllithium was added to the previously unreported $(C_6H_5)_4C_4Ge(C_6H_5)_2$, mp 198–199°. An intense purple color formed and this solution exhibited a very weak electron spin resonance (esr) signal at a *g* value near 2. The extreme weakness of the signal shows that radicals are not the predominant species in solution. Hence, in this case it is concluded that the butyllithium adds to the ring structure to give a conjugated C–Li derivative which is responsible for the intense colors observed.

The above results may be compared with the reactions of triphenylsilane and triphenylgermane with *n*-butyllithium. Triphenylgermane readily forms triphenylgermyllithium,[5] but triphenylsilane forms *n*-butyltriphenylsilane and lithium hydride.[6] Thus, there exists the possibility that $(C_6H_5)_4C_4Si(C_6H_5)(C_4H_9)$ (XIII) and LiH are formed when butyllithium is added to VII, and that the LiH then adds across a carbon–carbon double bond to form a highly colored C–Li derivative. This possibility was tested by adding crushed lithium hydride to a THF solution of XIII, which was prepared from III and butyllithium in benzene. No reaction was observed after stirring for 2 hr at room temperature. However, the addition of $LiAlH_4$ to a THF solution of XIII immediately causes an intense purple color. It is possible that LiH formed *in situ* is sufficiently more reactive than bulk LiH (which has a very low solubility in THF) that a direct comparison cannot be made.

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