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OBSERVATIONS ON THE REACTIVITY OF TRIS(TETRAMETHYLETHYLENEDIOXYBORYL)METHIDE ION

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Summary

Treatment of tetrakis(tetramethylethylenedioxyboryl)methane, $(Me_4C_2O_2B)_4C$, in THF with butyllithium at —78° generates the tris(tetramethylethylenedioxyboryl)methide ion, $(Me_4C_2O_2B)_3C^-$, which reacts with chlorotrimethylsilane at —78° to form trichlorosilyltris(tetramethylethylenedioxyboryl)methane, $(Me_4C_2O_2B)_3CSiMe_3$. The yield was low, but other attempts to form silyltriborylmethanes have failed altogether. The ion $(Me_4C_2O_2B)_3C^-$ reacts with tetraphenylcyclopentadienone at —78° to form the expected fulvene, 1,1-bis(tetramethylethylenedioxyboryl)-2,3,4,5-tetraphenylfulvene. The red color of the tetraphenylcyclopentadienone is converted immediately to the brown of the fulvene product, indicating that the β-elimination of boron and oxygen occurs rapidly under basic conditions at —78°.

Introduction

In previous work, it was shown that tetrakis(tetramethylethylenedioxyboryl)methane (the pinacol ester of methanetetraboronic acid) (I) reacts with methyllithium to serve as a source of the tris(tetramethylethylenedioxyboryl)methide ion (II) [1, 2]. At the time the present work was undertaken, it was thought necessary to warm the preparations to about 0° or above to complete formation of the $(Me_4C_2O_2B)_3C^-$, inasmuch as obvious changes in the appearance of the precipitate occurred on warming, including eventual coagulation to a gummy mass.

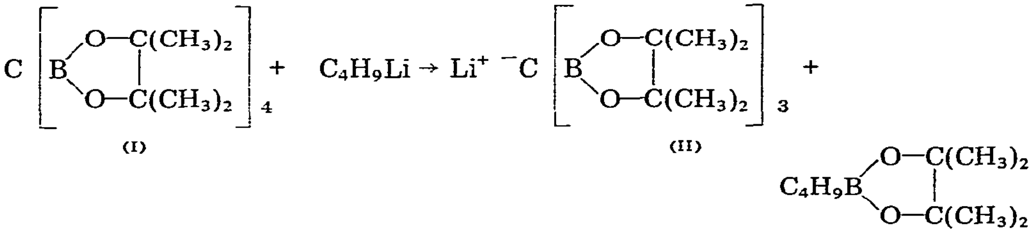
Previous papers on replacement of boron in tetraborylmethanes by Group IV metals did not include any silyltriborylmethanes [3, 4] because all attempts to cause triborylmethide anions to react with chlorosilicon compounds failed. Previous work also failed to provide any evidence about what stage of the reaction the β-elimination of boron and oxygen occurs in the condensation of triborylmethide anions with ketones because the substrates were not appropriately chosen [2]. The present work provides answers to these questions regarding mechanism and reactivities in reactions of triborylmethide anions. Evidence that free triborylmethide anions are in fact involved in these reactions has been presented and discussed elsewhere [1, 5].

Results and discussion

Formation of the triborylmethide anion(II)

Previously reported preparations of triborylmethide anions all vary in details [1—4], and it is only recently that the required reactant ratio and temperature have been well defined in the case of the tris(trimethylenedioxyboryl)-methide anion [5]. The difficulties in establishing necessary and sufficient conditions arise because of the sensitivity of the anions to air and moisture and, as indicated by more recent work [5], the protons in "aprotic" solvents.

The present work established that the reaction of tetrakis (tetramethylethylenedioxyboryl)methane (I) with one equivalent of butyllithium at —78° can serve as a source of the tris(tetramethylethylenedioxyboryl)methide ion (II). The other expected product, tetramethylethylenedioxyborylbutane (III), was isolated by gas chromatography and identified by its NMR spectrum (butyl group multiplet, pinacol group singlet) and partially satisfactory elemental analysis. The reaction time used was 24 h. Short reaction times appeared to be unsatisfactory in preliminary experiments, but the necessary minimum has not been established.



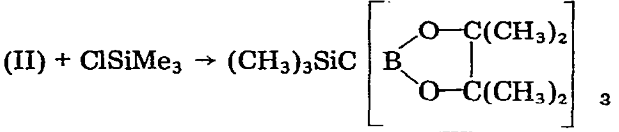
(I) (II) (III)

The yield of crude (III) was 90% from a reaction in which (II) was treated with chlorotrimethylsilane. This implies the stoichiometry illustrated for the formation of (II) and (III). However, we have found in other work that yields of products derived from (II) tend to be higher when two equivalents of alkyllithium are used [1], as if some of the (III) liberated consumes butyllithium to form $Bu_2{}^-BO_2C_2Me_4$. The present work shows that formation of (III) can be faster than its consumption under certain conditions, and we needed to avoid an excess of butyllithium in this work.

The trimethylsilyl derivative

No silyltriborylmethanes were reported in our papers on Group IV derivatives [3, 4] because all attempts to make chlorotriphenylsilane react with triborylmethide anions failed [6]. The reasons for the failures were unclear, though the fragmentary evidence suggested that the triborylmethide anions failed to attack the chlorotriphenylsilane and reacted either with the solvent or with proton sources introduced on work-up.

In the present work, we have found that chlorotrimethylsilane does react with the tris(tetramethylethylenedioxyboryl)methide ion (II) on standing at $-78°$ to form the expected trimethylsilyltris(tetramethylethylenedioxyboryl)-methane (IV).

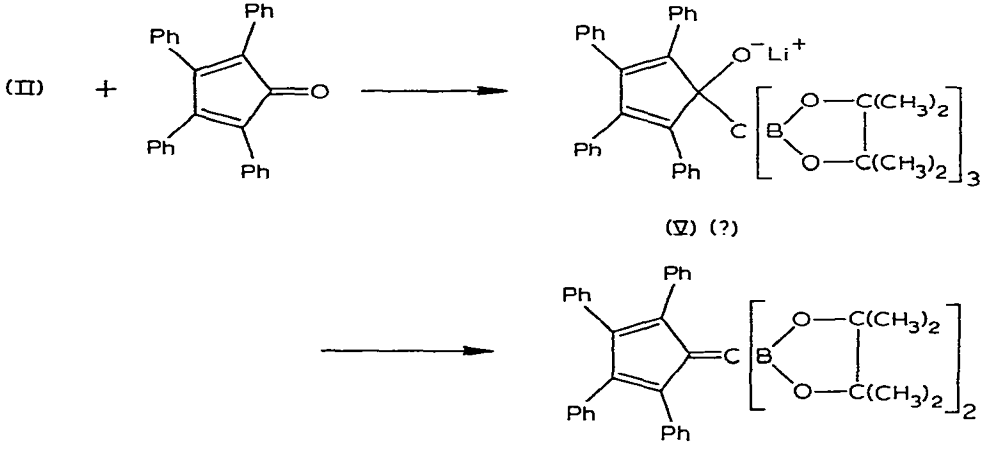


(IV)

Even though an excess of chlorotrimethylsilane was used , the yield of (IV) was low and considerable amounts of the degradation products $HC(BO_2C_2Me_4)_3$ and $H_2C(BO_2C_2Me_4)_2$ as well as the unchanged starting material $C(BO_2C_2Me_4)_4$ were recovered. The triborylmethane $HC(BO_2C_2Me_4)_3$ by itself might represent protonation of the anion (II) by accidental moisture introduced into the large volume of anhydrous tetrahydrofuran used as solvent at some stage after the butyllithium had all reacted, but the formation of the diborylmethane $H_2C(BO_2C_2Me_4)_2$ by this route seems questionable. The protonation process cannot be too rapid, but must allow time for $HC(BO_2C_2Me_4)_3$ to transfer a boronic ester group to $^-C(BO_2C_2Me_4)_3$, resulting in disproportionation to $C(BO_2C_2Me_4)_4$ and $^-HC(BO_2C_2Me_4)_2$, which on protonation yields $H_2C(BO_2C_2Me_4)_2$. Thus, we feel that the protonated products are not evidence of faulty laboratory technique, but that the triborylmethide anion (II) can abstract a proton from tetrahydrofuran or perhaps chlorotrimethylsilane, and that this side reaction competes effectively with the desired formation of (IV), in accord with the more recent evidence for the very strong basicity of these anions [5].

The tetraphenylcyclopentadienone derivative

If the reaction of cyclopentadienone, which is red, with the triborylmethide anion (II) produced a stable intermediate (V), which would be colorless, and the subsequent β-elimination to form the brown fulvene (VI) were slow, the changes should be plainly visible.



(V) (?)

(VI)

The dropwise addition of a solution of tetraphenylcyclopentadienone to a preparation of the anion (II) at −78° results in decolorization for about the first 5% of the reaction. After that, the solution changes to the brownish color characteristic of the fulvene (VI). It is probable that the butyllithium, even though in ~5% excess of 1/1, is all consumed by boronic ester (to form $Bu_2^-BO_2C_2Me_4$) prior to the addition of the tetraphenylcyclopentadienone and that the colorless phase of the reaction does represent accumulation of (V) [or a derivative of (V) having the alkoxide group coordinated with a boronic ester group either intra- or inter-molecularly], but there is no conclusive proof for (V). It should be noted that the conditions used for this reaction are much milder than those used previously for the condensation of ketones with the anion (II). Reactivities may differ, but it appears probable that the β-elimination step required in these condensations normally occurs rapidly and does not require acidification to accomplish.

Experimental

Trimethylsilyltris(tetramethylethylenedioxyboryl)methane (IV)

A solution of 10.0 g (19.2 mmoles) of tetrakis(tetramethylethylenedioxyboryl)methane (I) in 150 ml of anhydrous tetrahydrofuran (which had been distilled from lithium aluminum hydride) was cooled with a dry ice/acetone bath and stirred under argon during the dropwise addition of 12 ml (19.2 mmoles) of 1.6 *M* butyllithium in hexane over a period of 30 min. The mixture was then stirred 24 h at −78°. A solution of 5 ml of chlorotrimethylsilane in 50 ml of tetrahydrofuran was added to the cold, stirred mixture over a period of 1 h and the mixture was kept at −78° for 48 h. The solvent was removed under vacuum and the solid residue was treated with 200 ml of benzene. The lithium chloride was filtered and the benzene solution was concentrated. Distillation yielded 3.2 g of impure pinacol ester of butaneboronic acid, $C_4H_9BO_2C_2Me_4$, b.p. up to 70°/1 mmHg, which was partially purified by gas chromatography. (Found: C, 65.19; H, 11.57; B, 5.41. $C_{10}H_{21}BO_2$ calcd.: C, 67.37; H, 10.80; B, 5.51%.) The waxy residue was partially purified by molecular distillation at 70—100°/0.1 mmHg, yield 1.2 g, and was then chromatographed on acid-washed alumina with 10% benzene in hexane. The yield of $Me_3SiC(BO_2C_2Me_4)_3$ (m.p. 138—140°) was 0.75 g. NMR (CCl_4 , external TMS): δ 0.02 (s, 0, $SiCH_3$) and 1.16 ppm (s, 36, CCH_3). Mass spectrum: base peak *m/e* 450 (*M*—16); *m/e* 451, 19%; *m/e* 449, 56%; *m/e* 448, 5%; *m/e* 452, 2%. (Found: C, 56.68; H, 9.86; B, 6.68; Si, 5.67. $C_{22}H_{45}B_3O_6Si$ calcd.: C, 56.81; H, 9.73; B, 6.96; Si, 6.03%.) The remaining 5.3 g of residue from the molecular distillation was subjected to gas chromatography and found to contain $C(BO_2C_2Me_4)_4$, $HC(BO_2C_2Me_4)_3$, and $H_2C(BO_2C_2Me_4)_2$ in the approximate ratio 1/2/4 by comparison of the retention times with those of authentic samples. The authentic sample of $H_2C(BO_2C_2Me_4)_2$ was prepared from pinacol and $H_2C[B(OMe)_2]$ [7] and showed the expected CH_2 peak in the NMR. The other compounds have been reported previously [1, 8].

1,1-Bis(tetramethylethylenedioxyboryl)-2,3,4,5-tetraphenylfulvene (VI)

The anion (II) was prepared as described in the preceding experiment, except that 300 ml of tetrahydrofuran was used with 10 g of (I). After 18 h at —78°, a solution of 7.4 g of tetraphenylcyclopentadienone in tetrahydrofuran was added dropwise over a period of 4 h. The red color of the tetraphenylcyclopentadienone was discharged during about the first 5% of the addition, and the mixture took on the brown color of the product (VI) after that. The mixture was stirred 48 h at —78°, then warmed to room temperature and treated with 2.5 ml of chlorodimethoxyborane. The solvent was removed under vacuum and the dark residue was treated with 300 ml of benzene and filtered to remove lithium chloride. The benzene was evaporated under vacuum and the residue (about 12 g) was washed three times with 50 ml of hexane and then chromatographed on acid-washed alumina with hexane and benzene as the eluting solvents. The yield of the fulvene (VI) was 4.8 g (39%); m.p. 267—268°. UV-visible spectrum: λ_{max} 458 nm. IR(CCl_4): 1610 cm^{-1} (C=C). NMR (CCl_4): δ 1.16 (s, 24, CH_3), 6.91 (m, 4, phenyl), 7.23 (m, 6, phenyl), and 7.43 ppm (s, 10, phenyl). (Found: C, 79.26; H, 7.09; B, 3.59. $C_{42}H_{44}B_2O_4$ calcd.: C, 79.51; H, 6.99; B, 3.41%.)

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