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Preliminary communication

DEGENERATE AND NONDEGENERATE REARRANGEMENTS OF THE 7-BORABICYCLO[2.2.1]HEPTADIENE SYSTEM: TWOFOLD [1,3] SUPRAFACIAL SIGMATROPIC MIGRATIONS AND ANIONIC [1,2] CARBON—BORON SHIFTS*

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Summary

Two notable skeletal rearrangements of the 7-borabicyclo[2.2.1]heptadiene system (III) have been uncovered: (1) a facile, degenerate, net twofold [1,3] suprafacial sigmatropic migration of the 7-substituted boro group, observable by NMR spectroscopy when the carbon centers of the borole (I) and alkyne (II) bear suitable groups; and (2) a nondegenerate, anionic [1,2] aryl shift from carbon to boron, converting the 7,7-dimethylborate salt of III into an aryl(dimethyl)pentaarylborate salt. Thus, the degenerate rearrangement was revealed when pentaphenylborole (Ia) was allowed to react with di-*p*-tolylacetylene (IIb) at 25°C; the resulting 7-borabicyclo[2.2.1] heptadiene (III) formed displayed NMR methyl signals characteristic of *p*-tolyl groups located at both C^5 and C^6, as well as C^4 and C^5. Similarly, the nondegenerate, disruptive anionic isomerization of the 7,7-dimethylborate salt of IIIe or IVe was found to involve migration of either phenyl or *p*-tolyl groups from carbon to boron, showing that both phenyl (IIIe) and *p*-tolyl groups (IVe) were located at the bridgeheads in the precursors to VI.

Since the 7-borabicyclo[2.2.1] heptadiene system (III) has recently become readily accessible by the Diels—Alder addition of alkynes (II) to boroles [2,1] (I), we have sought to learn whether such a bicyclic organoborane might resemble the highly reactive, isoelectronic 7-norbornadienyl cation [3]. Previous studies had already shown that heptaphenyl-7-borabicyclo[2.2.1] heptadiene (IIIa) undergoes a thermal [1,3] suprafacial sigmatropic rearrangement, followed by disrotatory ring-opening to yield the

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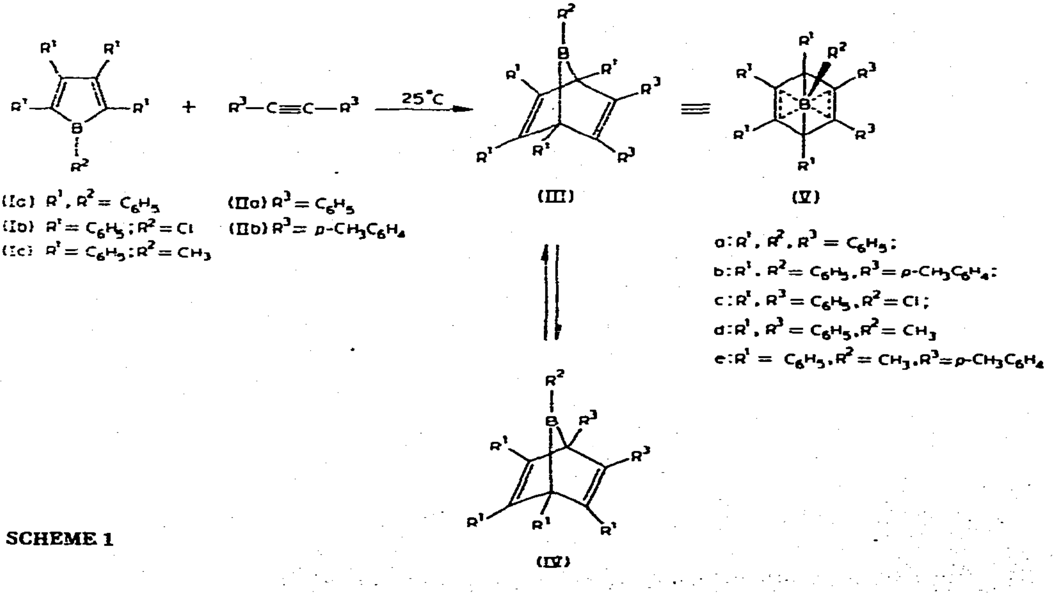
*Part XIV of the series Rearrangements of Organometallic Compounds, as well as Part V of the series Boraaromatic Systems (previous Part ref. 1).

borepin [1]. We now wish to report the further discovery of both degenerate and nondegenerate rearrangements of III, which strongly bear out the chemical analogy between III and the 7-norbornadienyl cation.

Thus, the degenerate rearrangement of the heptaaryl-7-borabicyclo[2.2.1]-heptadiene system became observable when pentaphenylborole (Ia) was allowed to react with di-*p*-tolylacetylene (IIa) at 25°C to yield the almost colorless adduct IIIb, assumed to be 1,2,3,4,7-pentaphenyl-5,6-di-*p*-tolyl-7-borabicyclo-[2.2.1]heptadiene. But the NMR spectrum of the purified and otherwise well-characterized product (crystallization from ether <25°C gave a product of proper mass spectrum (*P* of 650 and *P* − 1 in a ratio of 4:1) and NMR spectrum (aromatic/methyl peaks in a ratio of 5.5:1) displayed two sharp singlets at 2.78 and 2.60 ppm (C_2Cl_4 solution). The ratio of these methyl signals was temperature-dependent, varying from 3.0:1.0 at 47°C (the peak at 2.78 ppm being greater) to 2.0:1.0 at 98°C. Recording the spectrum at 120°C (C_2Cl_4 solution at 100 MHz with signal lock on internal $C_6H_5SiMe_3$) did result in partial merging, but not coalescence, of the signals. From this it may be estimated that $\Delta G^{\neq}$ for this isomerization is >20 kcal/mol. Although extended heating of bicyclic boron compounds, such as III, does cause isomerization to the borepin nucleus [1], during the NMR measurements no green fluorescence, characteristic of the borepin chromophore, was noted, Consequently, the development of two methyl signals in the NMR spectrum of the supposed IIIb indicates the occurrence of net, twofold [1,3] suprafacial sigmatropic migrations of the 7-phenylboro group in IIIb, which interconvert isomers IIIb and IVb, having vicinal *p*-tolyl groups at the 5,6- and 4,5-positions, respectively (Scheme 1). With the assumption that the proportion of IVb/IIIb at equilib-

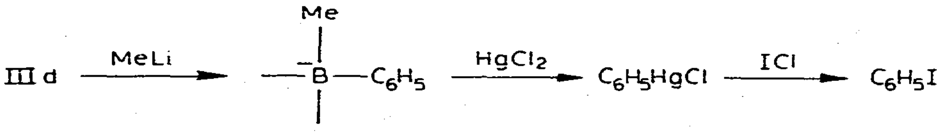


SCHEME 1

rium is governed only by probability factors[*], a ratio of 2:1 would be expected and such a value is observed at ca. 100°C. Further considerations of the possible role of electronic factors lead us to suggest that the electron-donating *p*-tolyl may be more stabilizing when attached to the vinylic carbons, C^5 and C^6, than when at a bridgehead, C^4. Such homoconjugation as indicated by structure V would be expected to favor isomer IIIb over isomer IVb, since *p*-tolyl groups would enhance the π-basicity of the C^5—C^6 double bond. The methyl signal ratio at 47°C and the temperature dependence of the ratio are in accord with the greater stability of IIIb and a ΔH of ca. 3 kcal/mol.

Corroboration that these systems interconvert was gained by the uncovering of a novel nondegenerate rearrangement of certain 7-methylboro derivatives of III. Thus, when 1-chloro- or 1-methyl-2,3,4,5-tetraphenylborole (Ib or Ic) was treated with diphenylacetylene, the corresponding adducts (IIIc or IIId) were formed in high yield. Subsequent treatment of either adduct with an excess of methyllithium in THF produced a dark green solution (VII). Brief heating and then work-up with D_2O led to the isolation of 80% of pentaphenylbenzene, which by NMR spectroscopy was shown to be deuterated at C^6 of the central ring. Then Ic was treated with di-*p*-tolylacetylene (IIb) and the resulting adduct IIe subjected to the foregoing methyllithium treatment; hydrolytic work-up furnished an 80% yield of pentaarylbenzenes, which by mass spectrometry were shown to be composed of ca. equal parts of triphenyldi-*p*-tolyl- and tetraphenyl-*p*-tolyl-benzenes and by NMR spectroscopy to contain at least three components.

The loss of an aryl group during the treatment of IIId or IIIe with methyllithium was traced to a nondegenerate, anionic [1,2] migration of an aryl group from carbon to boron, possibly fostered by relief of ring strain in VI and aromatization in IX (Scheme 2). The presence of a phenylborate grouping in IX was established by a sequence of mercurideboronation and iododemercuration:



$$\text{III d} \xrightarrow{\text{MeLi}} -\overset{\text{Me}}{\underset{|}{\overset{|}{\text{B}^{-}}}}-C_6H_5 \xrightarrow{\text{HgCl}_2} C_6H_5HgCl \xrightarrow{\text{ICl}} C_6H_5I$$

As shown in Scheme 2, the formation of IX arises from the 1,2-shift of an aryl group originally situated at a bridgehead. Therefore, the migration of both phenyl and *p*-tolyl groups when IIIe is subjected to methyllithium would be consistent with the simultaneous presence of IIIe and IVe. Accordingly, these results indicate that the net twofold [1,3] sigmatropic rearrangement shown in Scheme 1 has interconverted IIIe and IVe, before the [1,2] anionic

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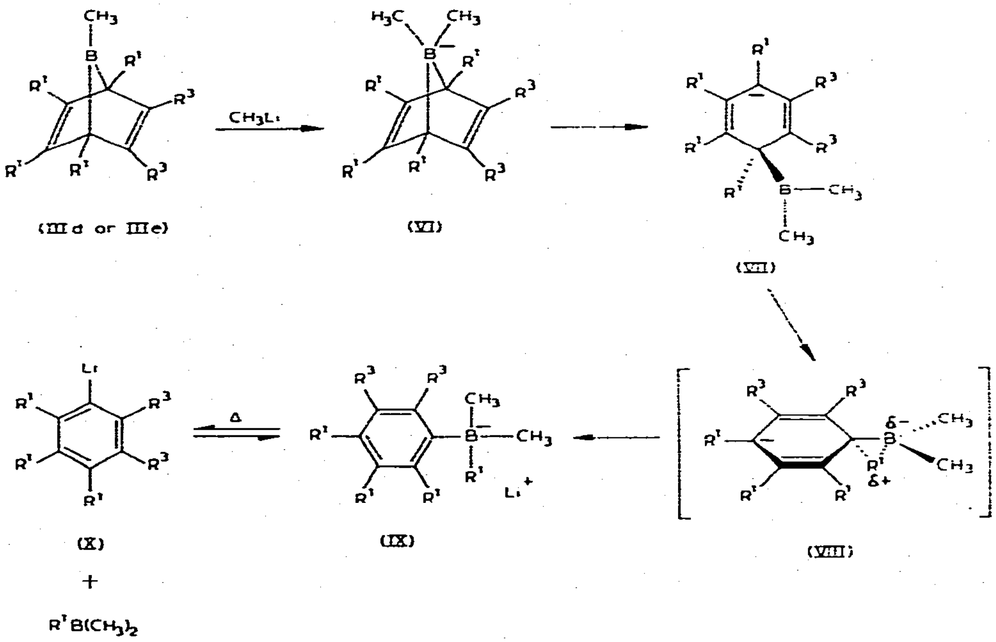
[*] In arriving at the expected ratio of 2:1, the following, reasonable assumptions are made: (a) *p*-tolyl groups attached to olefinic carbon would occur downfield from *p*-tolyl groups attached to saturated, bridgehead carbon centers; and (b) the olefinically bonded *p*-tolyl groups in IIIb and IVb would give coincident signals. Finally, structure IV is statistically favored by 2:1 over structure III.



rearrangement disrupts the bicyclic intermediate VI and leads to IX*.

The rearrangements of III rather closely resemble those of the 7-norbornadienyl cation, where [1,3] sigmatropic rearrangements and conversions to tropylium salts and toluene derivatives have been observed [3]. As to any electronic evidence for the bishomoconjugation ascribed to the 7-norbornadienyl cation, the electronic spectrum of IIIa is of interest: in ether this compound has its long-wavelength absorption at 318 nm, whereas its pyridine adduct has as its longest-wavelength absorption only a shoulder at 273 nm. Since *cis*-stilbene absorbs at 280 nm, the bathochromic shift in IIIa over that of *cis*-stilbene units seems reasonably to stem from an electronic interaction between tricoordinate boron and the 2,3-diphenyl-substituted double bonds of IIIa. Such an interaction can be viewed as that of a bishomoboracyclopropene (cf. V) [4].

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*In designating the degenerate interconversion of III and IV as a net twofold [1,3] sigmatropic rearrangement, no conclusion is intended as to its path. One could envisage a simultaneous pair of 1,3-shifts, or two, stepwise 1,3-shifts. Because of the ultimate formation of borepins from such adducts as III, however, we tend to favor the stepwise path. The assumed 7-borabicyclo-[4.1.0] heptadiene intermediate apparently undergoes a further 1,3-shift to re-form III or IV more rapidly than the ring-opening leading to the borepin.

References

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