the latter are oxidized further. However, benzylic amines are prepared in excellent yield.

A typical procedure follows. The reagent **1** is conveniently prepared by dissolution of *I,I*-diacetoxyiodobenzene[11] (Aldrich) in trifluoroacetic acid and crystallization [mp 124–126 °C (lit.[12] 119–122, 122–124 °C)], taking only the first crop of crystals (53% yield). The amide to be rearranged (typically 4 mmol) is added to a solution of 1.5 equiv of **1** in 12 mL of acetonitrile–water (1:1 v/v) and is stirred at room temperature. The reaction time depends on the migrating group in the reaction; hexanamide required 5.5 h for complete reaction, whereas cyclohexanecarboxamide required only 2.25 h for reaction. These minimum reaction times were determined by actual product isolation. The reaction mixture is then diluted with 75 mL of water, acidified with 8 mL of concentrated HCl, and the iodobenzene and unreacted **1** are then extracted into ether. The ether layer is back-extracted with 20 mL of 10% HCl solution, and the combined aqueous layers are concentrated to yield the amine hydrochloride which, in the cases studied here, can be recrystallized from ethanol–ether. Alternately, nonvolatile amines could be isolated in free base form by extraction into ether from the aqueous layer, which has been made basic with NaOH.

Further studies of the functional group compatibility and the mechanism of this reaction are in progress.

References and Notes

(1) (a) We gratefully acknowledge support of this work by the National Institute of General Medical Sciences (GM 25143) and the National Science Foundation (CHE 77-22493). We also acknowledge the helpful comments of Professor H. E. Baumgarten cited below in ref 6 and 9c. (b) Undergraduate Research Participant, Summer, 1978.
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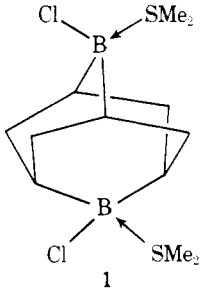
Received January 16, 1979

2,6-Diboraadamantane, a Novel Structure with Unusual Characteristics, via Cyclic Dihydroboration of 1,3,5,7-Cyclooctatetraene

Summary: Cyclic dihydroboration of 1,3,5,7-cyclooctatetraene with monochloroborane–methyl sulfide yields 2,6-dichloro-2,6-diboraadamantane, easily reduced to the corresponding dihydrido derivative with unexpected properties.

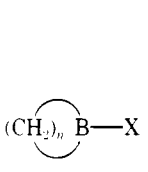
Sir: The cyclic dihydroboration of 1,3,5,7-cyclooctatetraene with the newly discovered reagent, monochloroborane–methyl sulfide ($H_2BCl{\cdot}SMe_2$),[1] gives an exclusively polymeric material which, on thermal depolymerization under reduced pressure, affords 2,6-dichloro-2,6-diboraadamantane in the form of its methyl sulfide adduct (**1**). This represents a novel



1

construction of a tricyclic molecule, the adamantane ring system, from a monocyclic precursor in a simple two-step reaction. The chemical properties of this tricyclic organoborane proved unexpected, indicating the need for a better understanding of the chemical effects of such structures.

A number of boraheterocycles have been conveniently prepared in the past via cyclic hydroboration of dienes and trienes.[2] These include boracycloalkanes (**2**), borabicyclanes (**3, 4**), and even a boratricyclane (**5**).[2] Moreover, it has proved



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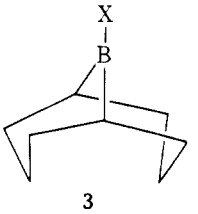

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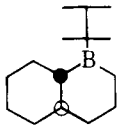

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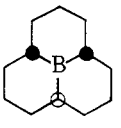
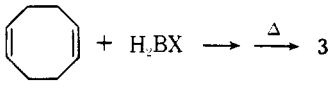


5

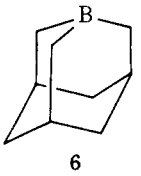
possible to achieve the transannular dihydroboration of 1,5-cyclooctadiene to synthesize 9-borabicyclo[3.3.1]nonane (9-BBN)[3] and its *B*-halo derivatives[4] by such cyclic hydroborations (eq 1).



(1)

X = H, Cl, Br, I

Recently, the successful syntheses of 1-boraadamantane (**6**) and 2-boraadamantane (**7**) have been achieved by a series



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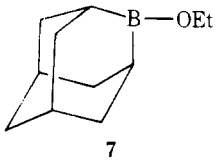

7

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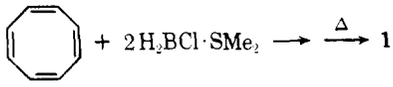
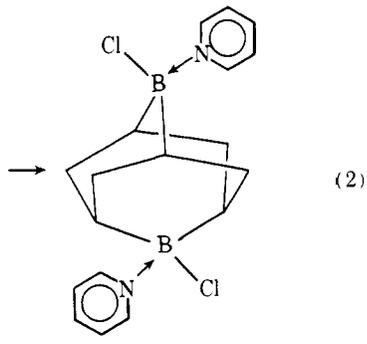
of steps involving both the hydroboration and allylboration reactions.[5,6] However, the synthesis of such cage-like structures by a simple cyclic hydroboration has not been achieved. Such a process would make possible a more simple, more direct route to these structures. Accordingly, we undertook to explore the double cyclic hydroboration of 1,3,5,7-cyclooctatetraene (COT) as a possible route to the 2,6-diboraadamantane ring system.

Although monochloroborane etherate ($H_2BCl{\cdot}OEt_2$) has proven to be a versatile reagent for the conversion of α,ω-acyclic dienes into 1-chloroboracyclanes,[7] the hydroboration of COT with this reagent is slow and is accompanied by the cleavage of ether. However, $H_2BCl{\cdot}SMe_2$ hydroborates COT cleanly, leading exclusively to a polymeric material. On distillation under reduced pressure, depolymerization occurs and the methyl sulfide adduct of 2,6-dichloro-2,6-diboraadamantane, **1**, is obtained in high yield (eq 2).[8] Pyridine readily displaces SMe_2 from **1**, forming the dipyridine adduct (**8**) in quantitative yield.

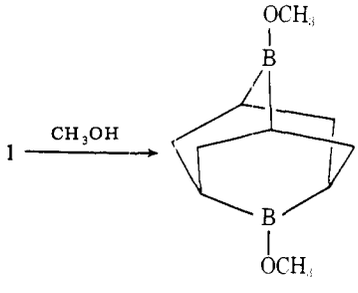




(2)

8

Methanolysis of **1** affords 2,6-dimethoxy-2,6-diboraadamantane (**9**), which undergoes a redistribution reaction with $H_3B{\cdot}SMe_2$ in THF,[9] producing the bis(THF) adduct of 2,6-diboraadamantane (**10**) (eq 3). This complex (**10**) can be



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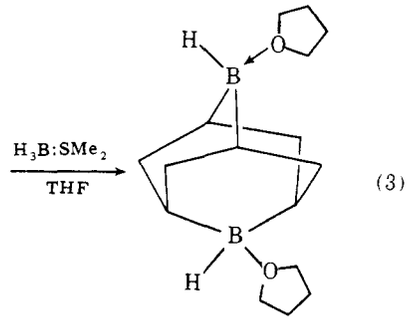
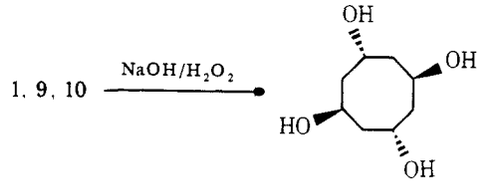


(3)

10

conveniently recrystallized from a mixture of pentane and CH_2Cl_2. It is interesting to note that THF is tightly bound to boron in **10**, whereas the structurally similar molecule, 9-BBN, does not form a stable isolable complex with THF, but engages in a mobile equilibrium. It is evident that the Lewis acid properties of the boron substituents are greatly enhanced in the diboraadamantane structure (**10**). No reason for this phenomenon can be given at this time. However, it is suggestive of the marked changes caused by incorporating boron into cage structures, a fascinating phenomenon.[10]

Oxidation of **1**, **9**, and **10** with alkaline hydrogen peroxide gives 1,5-*cis*-3,7-*trans*-cyclooctatetraol (**11**) (eq 4). The



(4)

11

structures of all the new compounds (**1**, **8–10**) have been established on the basis of ^1H NMR and mass spectral data. The assigned structure of **11** is supported by ^1H NMR and ^{13}C NMR analyses.

The following experimental procedures are representative.

For the preparation of **1**, a 250-mL reaction flask fitted with a reflux condenser was charged with 22.1 mL of $H_2BCl{\cdot}SMe_2$ (210 mmol, 5% excess) in 75 mL of CH_2Cl_2 under nitrogen and 11.26 mL of COT (100 mmol) was added dropwise with vigorous stirring at 25 °C. Following completion of the addition, the reaction mixture was heated under reflux for 6 h. Then the solvent was removed under vacuum, and the product was both depolymerized and distilled by heating under reduced pressure (0.4 mm, oil-bath temperature 180–200 °C). At the end of this operation, the solid that had crystallized in the condenser was melted and allowed to flow into the collection flask. Recrystallization of the product from a mixture of CH_2Cl_2, pentane, and 14.6 mL (200 mmol)[8] of SMe_2 affords 19.0 g (58% overall yield) of colorless crystalline solid: mp 167–168 °C; ^1H NMR ($CDCl_3$), sharp singlet at δ 2.23 (12 H, SMe_2 protons), broad peak at δ 2.07 (8 H, methylene groups), and another broad peak at δ 1.03 (4 H, methine protons); ^{11}B NMR, single resonance at δ 13.9.[11]

To obtain **9**, 2.65 g (8.2 mmol) of **1** was dissolved in 50 mL of CH_2Cl_2 and 1.42 mL (35 mmol, 100% excess) of methanol was added dropwise. After stirring for 1 h at 25 °C, the solvent, excess methanol, SMe_2, and HCl generated in the reaction were pumped off. The resulting solid was recrystallized from a mixture of CH_2Cl_2 and pentane to obtain 1.45 g (93% yield) of **9** as a colorless crystalline solid: mp 117–119 °C; ^1H NMR ($CDCl_3$), singlet at δ 3.75 (6 H, methoxy protons), an unresolved multiplet at δ 1.95 (8 H), and a broad peak at δ 1.28 (4 H); ^{11}B NMR, single resonance at δ 54.6.

The following procedure is representative for the preparation of **11**. To a solution of 5.8 g (17.8 mmol) of **1** in 100 mL of THF were added 25 mL of EtOH, 10 mL of water, and 3.2 g (80 mmol) of NaOH pellets with vigorous stirring. After the NaOH had dissolved, the flask was cooled to 0 °C and 20 mL of 30% H_2O_2 (160 mmol, 100% excess) was added dropwise, followed by stirring for 0.5 h at 0 °C, 1 h at 25 °C, and 6 h at 60–65 °C. The aqueous layer was saturated with anhydrous K_2CO_3, and the organic layer was separated. The solvent was pumped off and the resulting solid, on recrystallization from a mixture of ethanol and ether, afforded 1.1 g (35% yield) of colorless crystals: mp 204–206 ° C; ^1H NMR (D_2O), singlet at δ 4.6 (4 H, exchanged OH protons), a distorted quintet centered on δ 4.02 (4 H, J = 6 Hz, methine protons), and a distorted triplet centered on δ 1.85 (8 H, J = 6 Hz, methylene protons); ^{13}C NMR (D_2O), two types of carbons at δ 64.57 and δ 43.98.

The THF complex of 2,6-diboraadamantane, **10**, was prepared as follows. To a suspension of 5.4 g (28 mmol) of **9** in 40 mL of THF was added at 25 °C 1.0 mL (19 mmol) of $H_3B{\cdot}SMe_2$ with stirring. After 2 h, the solvent was pumped off, and the resulting solid was recrystallized from a mixture of CH_2Cl_2 and pentane to obtain 5.9 g (76% yield) of the bis(THF) complex: mp 145–147 °C; ^1H NMR ($CDCl_3$), multiplet centered on δ 4.3 (8 H, α protons of THF), another multiplet at δ 2.1 (8 H, β protons of THF), unresolved peak at δ 1.83 (8 H, methylene groups), and a broad peak at δ 0.85 (4 H, methine protons); ^{11}B NMR, single resonance at δ 21.5.

This study clearly illustrates the novelty of cyclic hydroboration in the synthesis of boraheterocycles. It describes the preparation and characterization of the 2,6-diboraadamantane ring system for the first time. The synthesis involves only two steps, representing a truly simple and novel construction of a tricyclic molecule from a monocyclic precursor.

Known organoborane conversion reactions are being examined for this 2,6-diboraadamantane system as a possible route to other adamantane derivatives. However, the chemical properties of the 2,6-diboraadamantane are themselves highly interesting and deserve exploration.

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(8) Some of the SMe_2 is lost during the thermal treatment. Therefore, it is necessary to add additional SMe_2 while recrystallizing **1**.
(9) The redistribution reaction between *B*-methoxy-9-BBN and $H_3B{\cdot}SMe_2$ gives 9-BBN dimer in quantitative yield. For details, see: Brown, H. C.; Kulkarni, S. U. *J. Organomet. Chem.*, **1979**, *168*, 281–293.
(10) Trialkylboranes (R_3B) in general do not form strong isolable complexes with Et_2O or THF, but the corresponding complexes of **6** have been prepared and characterized.[5]
(11) The ^1H and ^{11}B NMR chemical shifts are with reference to tetramethylsilane and $BF_3{\cdot}OEt_2$ respectively; the positive sign represents downfield from the reference.
(12) Graduate Research Assistant on Grant GM 10937-14 from the National Institutes of Health.

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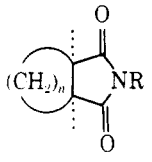
Received January 8, 1979

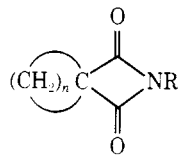
Norrish Type I Reaction of Aliphatic Cyclic Imides. General Reaction Pattern, Competition with Type II Processes, and Some Synthetic Applications[1]

Summary: Aliphatic cyclic imides generally undergo Norrish type I reaction (α-cleavage) to form ene formimides, which, if the formimide and the olefin are conjugated, may lead to azetidinediones.

Sir: Extensive studies of photoreactions of cyclic imides have been described,[2] mainly involving Norrish type II reaction[2] and Paterno–Büchi reaction.[2,3] While these reactions are evidently analogous to those of simpler carbonyl compounds,[2] Norrish type I reaction (α-cleavage), one of representative photoreactions of the carbonyl system,[4] has not been studied except a very few examples.[2,5] We now wish to report that aliphatic cyclic imides undergo Norrish type I reaction generally to form ene formimides, and that, when the formimide and the olefin are conjugated with each other in the product, namely with certain succinimides as starting substrates, secondary transformation follows to give azetidinediones.[6]

The occurrence of type I reaction has been observed for *N*-ethylcamphorimide with ene formimide and ene carboxamide as products.[5d] Further, irradiation of **1a**, a succinimide



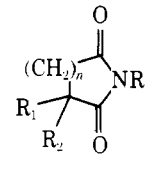


1a, n = 4; R = C_2H_5
b, n = 4; R = H
c, n = 4; R = CH_3
d, n = 2; R = C_2H_5
e, n = 2; R = H
f, n = 2; R = CH_3

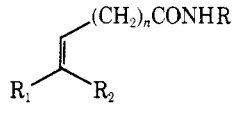
2a, n = 5; R = C_2H_5
b, n = 5; R = CH_3
c, n = 3; R = C_2H_5
d, n = 3; R = CH_3

with α,α'-disubstituents on the imide ring, gave the ring-expanded type II product in relatively poor yield,[5d] the results suggesting concomitant occurrence of some competing reactions such as type I reaction. Irradiation[7] of **1b** (cis) in 10 mM acetonitrile for 2 h gave 1-cyclohexenecarboxamide (40%), and the recovered **1b** (28%) turned out to be a mixture of cis and trans isomers (3:1) as determined by ^1H NMR,[8] indicating that α-cleavage of the (O=)C–C bond occurred and the recombination resulted in scrambling of the ring juncture of **1b**. Interestingly a similar reaction of **1c** gave a spiro azetidinedione **2b** (27%; mp 92–93 °C) in place of an enamide, and a stereochemical mixture of **1c** (36%; cis/trans = 2:3).[9] Careful reexamination of the photolysis of **1a** now gave, additionally, a homologous spiro azetidinedione **2a** (17%; mp 63–64 °C), and the recovered **1a** was a mixture (cis/trans = 1:1). Similar treatment of **1d** also afforded a spiro product **2c** (5%).

In order to see detailed structural requirements of the type I processes, photolysis of some unsymmetrically substituted imides **3** was examined. Irradiation of α-monosubstituted succinimides, **3a** and **3b**, afforded cis–trans mixtures of acrylamides **4a** (13%) and **4b** (10%), respectively. Similarly the



3a, n = 1; R_1 = CH_3; R_2 = R = H
b, n = 1; R_1 = R = CH_3; R_2 = H
c, n = 1; R_1 = R_2 = CH_3; R = H
d, n = 1; R_1 = R_2 = R = CH_3
e, n = 2; R_1 = R_2 = CH_3; R = H



4a, n = 0; R_1 = CH_3; R_2 = R = H
b, n = 0; R_1 = R = CH_3; R_2 = H
c, n = 0; R_1 = R_2 = CH_3; R = H
d, n = 0; R_1 = R_2 = R = CH_3
e, n = 1; R_1 = R_2 = CH_3; R = CHO
f, n = 1; R_1 = R_2 = CH_3; R = H

α,α-dimethylsuccinimides, **3c** and **3d**, gave the corresponding acrylamides **4c** (55%; mp 106–107 °C) and **4d** (40%; mp 77–78 °C), respectively. By contrast, irradiation of α,α-dimethylglutarimide **3e** gave rise to ene formimide **4e** (22%; mp 88–89.5

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