J. Am. Chem. Soc. **1991**, *113*, 1313–1318

Reactions of 1,2-Dehydro-*o*-carborane with Dienes[1]

Tirthankar Ghosh, Henry L. Gingrich, Carolyn K. Kam, Edward C. Mobraaten, and Maitland Jones, Jr.*

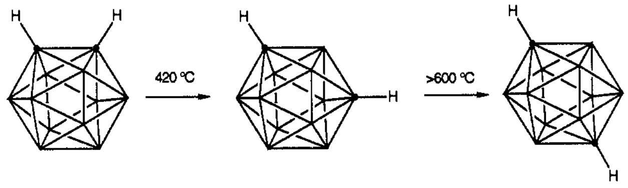
Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08544. *Received June 18, 1990*

Abstract: A carborane version of dehydrobenzene, 1,2-dehydro-*o*-carborane (**4**), has been generated from (2-bromo-*o*-carboranyl)lithium (**5**). This new intermediate undergoes the ene reaction as well as 2 + 2 and 2 + 4 cycloadditions. The 2 + 2 cycloaddition is nonstereospecific, whereas the 2 + 4 cycloaddition likely proceeds with retention of stereochemistry.

Introduction

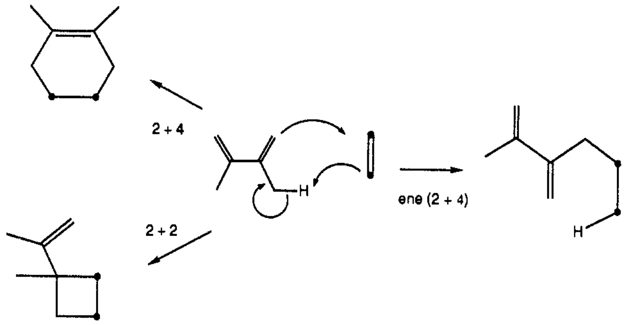
In one of the classic expriments of mechanistic organic chemistry, Roberts and co-workers demonstrated that a symmetrical intermediate must be formed when ^{14}C-labeled chlorobenzene is treated with potassium amide in liquid ammonia.[3] 1,2-Dehydrobenzene, or "benzyne", was soon trapped by all manner of species and has become a well-known member of the class of short-lived species called "reactive intermediates".[4] Dehydrobenzene itself has now been isolated and immobilized at low temperature,[5] and all manner of related dehydroaromatic molecules has been detected.[4] In this paper, we describe some reactions of a new and very different dehydroaromatic molecule, 1,2-dehydro-*o*-carborane.

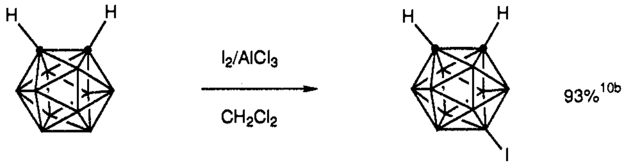
Besides benzenoid compounds, there is another class of aromatic molecules, the icosahedral carboranes, $B_{10}C_2H_{12}$. These molecules resemble benzenes in thermodynamic stability and, often, in chemistry as well.[6] *o*-Carborane (**1**) survives heating to several hundred degrees without apparent damage. At temperatures above 420 °C, quantitative rearrangement to *m*-carborane (**2**) occurs, and above $\sim$600 °C, a less efficient conversion to *p*-carborane (**3**) ensues.[7] The stability of benzene is of course the stuff of textbooks, but it, too, undergoes a thermal skeletal rearrangement, albeit only above 1100 °C.[8] In chemical reactivity, the classic test of aromaticity is the presence of the aromatic substitution reaction. Both benzene[9] and *o*-carborane[10] pass this test, as both react with a variety of electrophiles to give products in which the aromatic framework, two-dimensional in the case of benzene and three-dimensional for *o*-carborane, is preserved.



1, *o*-carborane **2**, *m*-carborane **3**, *p*-carborane

Scheme I. Two Concerted (Ene, 2 + 4) Pathways and the Stepwise 2 + 2 Pathways for Reaction of a Diene and an Ene





The reasons for the overall similarities in stability and reactivity in these two seemingly different molecules probably lie in their comparable molecular orbital systems. Benzene has six π molecular orbitals, three bonding and three antibonding.[9] The six available π electrons nicely fill the bonding set, leaving the antibonding molecular orbitals empty. The orbital system for **1** is more complicated, yet fundamentally similar. Each boron and carbon contributes one sp hybrid orbital directed radially toward the center of the cage and two p orbitals directed tangentially along the surface of the icosahedron. The result is a system of 13 bonding and 23 antibonding molecular orbitals.[11] Each boron contributes three electrons, each carbon contributes four, and the 12 hydrogens provide one each for a total of 50. Of these, 24 are used in making the 12 σ bonds to hydrogen leaving 26, exactly the proper number to fill perfectly the available bonding molecular orbitals. Just as benzene represents an exceedingly effective use of delocalized two-electron π bonds, so *o*-carborane is an example of the stability that can result from delocalization using only three-center, two-electron bonding. This method is an efficient way of holding atoms together if there are not enough electrons available for the more familiar two-center, two-electron bonds. Extraordinarily stable systems can be produced by use of either bonding scheme.

---

(1) Support of this work by the National Science Foundation (Grant CHE 8800448) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. Part of this work is taken from the AB Thesis of C.K.K., Princeton University, 1987, and another portion has been previously communicated.[2] 1,2-Didehydro-*o*-carborane is the more correct name for the title compound.

(2) Gingrich, H. L.; Ghosh, T.; Huang, Q.; Jones, M., Jr. *J. Am. Chem. Soc.* **1990**, *112*, 4082.

(3) Roberts, J. D.; Simmons, H. E., Jr.; Carlsmith, L. A.; Vaughan, C. W. *J. Am. Chem. Soc.* **1953**, *75*, 3290.

(4) (a) For the definitive exposition of the chemistry of dehydrobenzene, see: Hoffmann, R. W. *Dehydrobenzene and Cycloalkynes*; Academic: New York, 1967. (b) Shorter, but useful, treatments can be found: Wentrup, C. *Reactive Molecules*; Wiley: New York, 1984. Gilchrist, T. L.; Rees, C. W. *Carbenes, Nitrenes, and Arynes*; Appleton, Century, Crofts: New York, 1969. (c) Updates can be found in the now-defunct series: *Reactive Intermediates*; Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, 1978, 1981, 1985.

(5) Chapman, O. L.; Mattes, K.; McIntosh, C. L.; Pacansky, J.; Calder, G. V.; Orr, G. *J. Am. Chem. Soc.* **1973**, *95*, 6134. Chapman, O. L.; Chang, C.-C.; Kolc, J.; Rosenquist, N. R.; Tomioka, H. *J. Am. Chem. Soc.* **1975**, *97*, 6586.

(6) (a) Olah, G. A.; Surya Prakash, G. K.; Williams, R. E.; Field, L. D.; Wade, K. *Hypercarbon Chemistry*; Wiley: New York, 1987. (b) Muetterties, E. L. *Boron Hydride Chemistry*; Academic: New York, 1975. (c) Grimes, R. N. *Carboranes*; Academic: New York, 1970. (d) Onak, T. *Organoborane Chemistry*; Academic: New York, 1975.

(7) Wu, S.-h.; Jones, M., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 5373. Edvenson, G. M.; Gaines, D. F. *Inorg. Chem.* **1990**, *29*, 1210.

(8) Scott, L. T. *Acc. Chem. Res.* **1982**, *15*, 52. Scott, L. T.; Roelofs, N. H.; Tsang, T.-H. *J. Am. Chem. Soc.* **1987**, *109*, 5456.

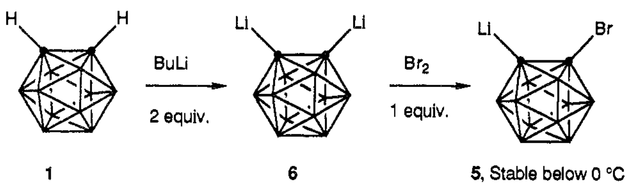
(9) Loudon, G. M. *Organic Chemistry*, 2nd ed.; Addison-Wesley: New York, 1988; Chapter 16.

(10) (a) Zakharkin, L. I.; Pisareva, I. V.; Bikkineev, R. K. *Bull. Akad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*) **1977**, 577. (b) Andrews, J. S.; Zayas, J.; Jones, M., Jr. *Inorg. Chem.* **1985**, *24*, 3715. (c) Albagli, D.; Zheng, G.-x.; Jones, M., Jr. *Inorg. Chem.* **1986**, *25*, 129 and references therein.

(11) Reference 6a, pp 92–94.

0002-7863/91/1513-1313$02.50/0

Scheme II. Formation of **5**, the Precursor to **4**



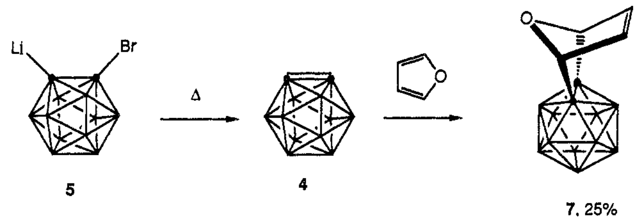
Of course there are differences as well as similarities. For example, in benzenoid molecules there is special reactivity associated with the α, or benzyl, position. Orbitals at the α position are efficiently coupled to the π orbitals of the ring. Charge is spread to ring positions through orbital overlap, as is a single electron. Not so with the carboranes. The chemistry of the "benzylic" position is not nearly as well developed as with the classically aromatic benzenes, but it seems clear that there is no efficient connection between the cage and an external orbital. An excellent illustration of this comes from a comparison of triplet phenylcarbene and triplet *o*-carboran-1-ylcarbene. Hutton, Roth, and Chari used the zero-field splitting parameter D to estimate a spin density $\rho = 0.9$ on the α carbons of a pair of *o*-carboranylcarbenes.[12] By contrast, triplet phenylcarbene has a much lower spin density on the divalent carbon; $\rho = 0.51$.[12,13]

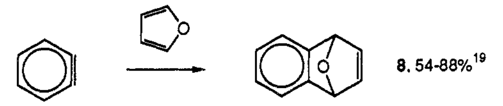
In this paper we describe some reactions of 1,2-dehydro-*o*-carborane (**4**), a three-dimensional relative of dehydrobenzene, and compare reactions of the two species with dienes. Dienes present a variety of possibilities for reaction. For example, 2 + 4 (Diels–Alder) and 2 + 2 cycloaddition reactions are both available and should proceed by different mechanisms if the dictates of orbital symmetry are obeyed.[14] As long as the HOMO of the ene partner is symmetric, the six-electron 2 + 4 cycloaddition may be concerted, whereas the 2 + 2 cycloaddition may not. In addition, a second 2 + 4 process, the ene reaction, is possible for many dienes. In the ene reaction the two electrons of a C–H σ bond take the place of a pair of π electrons in the classical Diels–Alder process (Scheme I).[15] We hoped that dienes might reveal both broad similarities and/or differences between the two species. In addition, we hoped to see more delicate differences as revealed by differing selectivities among the three available reactions. The first serious problem was to find a way to generate **4**.

4, 1,2-dehydro-*o*-carborane

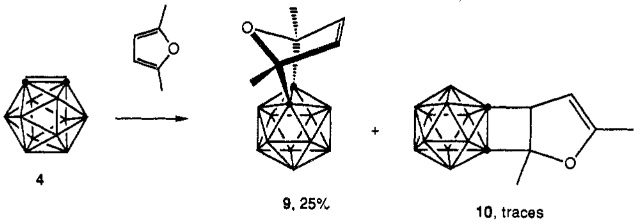
Formation and Reactions of 1,2-Dehydro-*o*-carborane. Dehydroaromatic molecules can be formed in a variety of ways, many of which may eventually find counterparts in sources of **4**. One of the earliest uses the elimination of halide from an α-halo anion generated at low temperature.[16] At −130 °C (α-bromophenyl)lithium can be intercepted,[17] but even at −100 °C bromide is lost.[18] Accordingly, in our initial attempts to mimic this procedure we foolishly ran our reactions at very low temperature, failing to account for the likely increased stability of **5**, the carborane version of (α-bromophenyl)lithium. Decent yields of products are not obtained from **5** unless the reactions are run above room temperature. An effective procedure first forms the dianion **6** by deprotonation of *o*-carborane with 2 equiv of butyllithium.

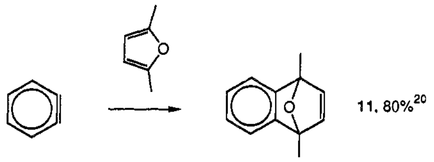
Precipitated **6** is then treated with 1 equiv of bromine at 0 °C to form the soluble bromo anion **5** (Scheme II). Addition of 10 equiv of furan to the solution of **5** followed by reflux in ether leads to adduct **7** in 25% isolated yield. The analogous reaction of dehydrobenzene, generated in a variety of ways, leads to an adduct **8** in 54–88% yield.[19] We see no evidence of isomeric products in the reaction of **4**, and there is no mention of such molecules in the dehydrobenzene literature.[19]





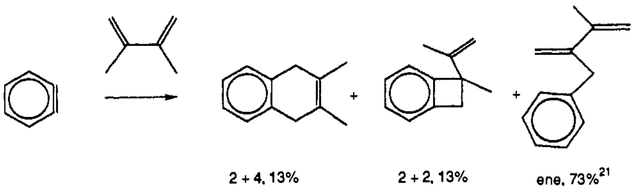
Other furans react similarly. For example, 2,5-dimethylfuran yields an adduct **9** in 25% yield. In this case, we are able to see traces of a compound thought to be the 2 + 2 adduct **10**, but we were not successful in separating this material from **9**. Dehydrobenzene also adds to 2,5-dimethylfuran to give **11** in ca. 80% yield.[20] No mention of a 2 + 2 product is made, but one should not make much of this apparent small difference. There is very little **10** formed in the reaction with **4**, and it would have been very easy in 1963 to miss traces of an analogous material.





Although yields from dehydrobenzene are higher than from 1,2-dehydro-*o*-carborane, the reactivities of the two species seem roughly comparable within the confines of the rather narrow differences possible so far: Diels–Alder addition is strongly preferred to 2 + 2 addition. There is no sign of ene reaction for either intermediate in their reactions with 2,5-dimethylfuran. Presumably, the benefits of concerted formation of two bonds make 2 + 4 reaction preferred to 2 + 2, and the necessarily cis nature of the diene gives the 2 + 4 process an advantage over the ene reaction.

A more versatile trapping agent such as 2,3-dimethyl-1,3-butadiene provides avenues for all three reactions in a mobile, nonaromatic system. Dehydrobenzene is known to undergo all three, with the ene process strongly preferred.[21]



---

[12] Hutton, R. S.; Roth, H. D.; Chari, S. *J. Phys. Chem.* **1981**, *85*, 753.

[13] Trozzolo, A. M.; Murray, R. W.; Wasserman, E. *J. Am. Chem. Soc.* **1962**, *84*, 4990.

[14] Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Academic: New York, 1970.

[15] For an early review, see: Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 556.

[16] Reference 4a, pp 43–44.

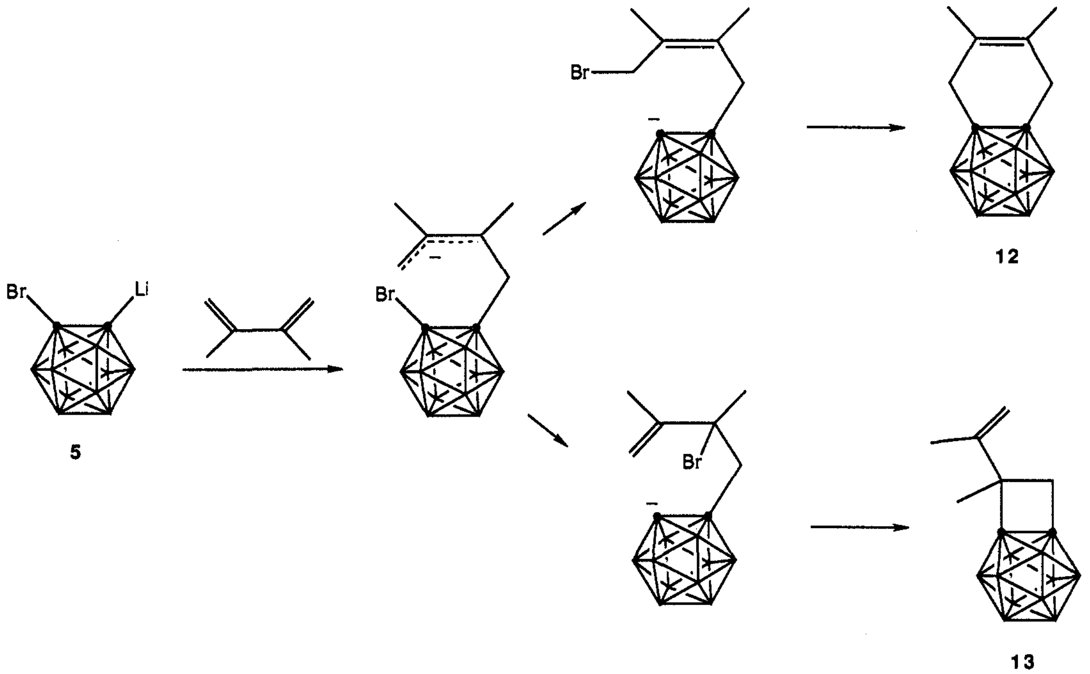
[17] Hart, F. A. *J. Chem. Soc.* **1960**, 3324.

[18] Gilman, H.; Gorsich, R. D. *J. Am. Chem. Soc.* **1956**, *78*, 2217.

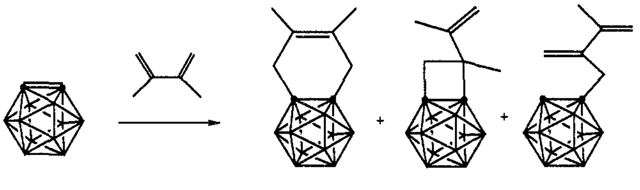
[19] Reference 4a, pp 214–215.

[20] Friedman, L.; Logullo, F. M. *J. Am. Chem. Soc.* **1963**, *85*, 1549.

Scheme III. Bromo Anion **5** as a Potential Intermediate in the Formation of Cycloadducts **12** and **13**



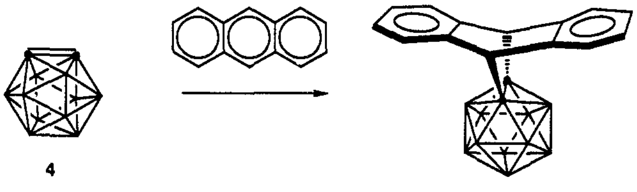
1,2-Dehydro-*o*-carborane is remarkably similar to didehydrobenzene in its reactions with this molecule. The three possible processes, 2 + 4 and 2 + 2 cycloadditions and ene reaction, all occur, giving adducts **12–14**. As for dehydrobenzene, it is the ene product that dominates. Perhaps there is a slightly greater tendency toward 2 + 2 addition for the carborane, but no important differences can be found.



|yield (relative %)| **12**, 3% (8%) **13**, 7% (18%) **14**, 30% (74%)

Diels–Alder reaction requires the s-cis arrangement of double bonds, obligatory for the furans, but variable in acyclic dienes. Squillacote and co-workers have estimated the ΔG between the favored s-trans and less stable s-cis forms of 2,3-dimethyl-1,3-butadiene at 1.7 kcal/mol ± 30%,[22] which corresponds to >95% s-trans isomer at room temperature equilibrium. As the ene reaction should have no great dependence on the planarity of the diene, it becomes favored as the amount of *s-cis*-diene diminishes.

Dehydrobenzene adds quite well to extended aromatic systems, and here, too, the corresponding reaction of 1,2-dehydro-*o*-carborane can be found. With anthracene as substrate, didehydrobenzene produces trypticene in 30% yield.[23] Dehydrocarborane **4** gives the beautiful analogue of trypticene, **15**, in 19% yield. Sadly, **15** appears not to be a useful neutral alternate source of **4**. Although we have been able to detect anthracene on flash vacuum pyrolysis of **15**, neither thermal nor photochemical reactions give detectable amounts of adducts of **4**.

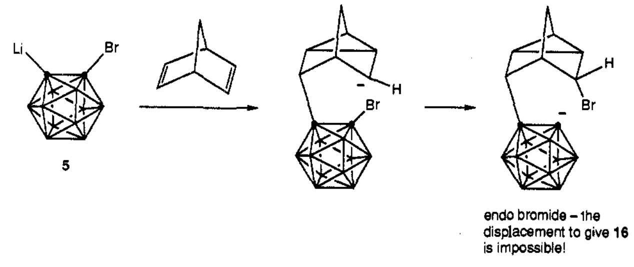


4

15, 19%

(dehydrobenzene, 30%)[23]

Scheme IV. In This Case the Mechanism of Scheme III Cannot Operate, yet the Product Is Formed in Good Yield. The Case for the Intermediacy of **4** Is Strengthened.



endo bromide – the displacement to give **16** is impossible!

Is 1,2-Dehydro-*o*-carborane Really an Intermediate? Throughout the previous section it has been assumed that the dehydro compound **4** was responsible for the products. Although **4** is surely the "obvious" intermediate, it remains to examine other possibilities. Compounds **5** and **6**, the two intermediates of Scheme II, come quickly to mind. Could either the dianion of *o*-carborane **6** or the α-bromo anion **5** be involved in the reactions? The dianion can be easily eliminated as no products are produced in the absence of bromine. The α-bromo anion **5** poses a more difficult problem, as reasonable mechanisms can be written for the formations of the 2 + 4 and 2 + 2 cycloadducts by use of this intermediate. In the best variation, an endothermic addition to the diene is followed by transfer of bromide from the carborane to a diene carbon. A final closure can occur to give either overall 2 + 4 or 2 + 2 addition (Scheme III). In an attempt to thwart the putative transfer of bromine, we examined the reaction with norbornadiene. Dehydrobenzene reacts with this substrate to give both homo 2 + 4 and 2 + 2 addition.[24] Our procedure leads to three products, **16–18**, in a 7:1 ratio. We were not able to separate **17** and **18**, but ^{1}H NMR spectroscopy showed that they were formed in an approximately 1:1 ratio. The mechanism of Scheme III cannot

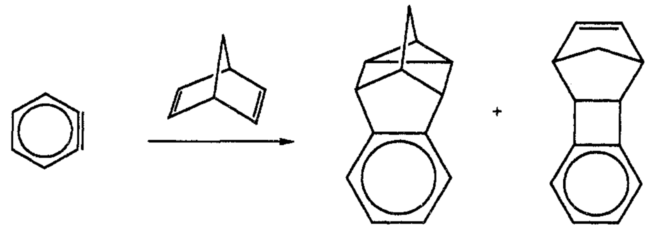
---

(21) Wittig, G.; Dürr, H. *Liebigs Ann. Chem.* **1964**, *672*, 55.

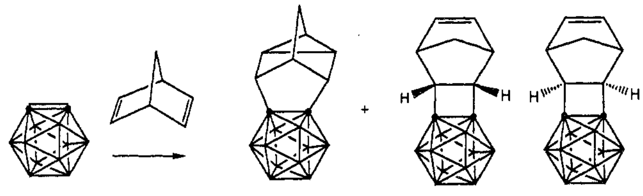
(22) Squillacote, M. E.; Semple, T. C.; Mui, P. W. *J. Am. Chem. Soc.* **1985**, *107*, 6842.

(23) Wittig, G.; Hoffmann, R. W. *Chem. Ber.* **1962**, *95*, 2718.

(24) Reference 4a (p 235) quotes the following reference: Friedman, L.; Rice, R. L. quoted by Lugullo, F. M. Ph. D. Thesis, 1965.



30 relative %[24] 70 relative %[24]



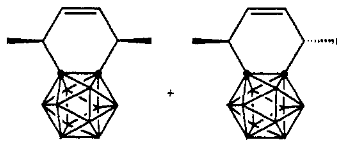
4 **16**, 87 relative % **17** + **18** 1:1, 13 relative %

give **16** as the transfer of bromine in the penultimate step requires a front-side S_N2 reaction (Scheme IV). Even if some other coupling reaction is postulated for this step, the endothermicity of the initial addition step in the addition to norbornadiene seems prohibitively high. To analyze this, we take into account three factors: (1) the stability of the anion as measured by the pK_a change, (2) the strain energy change, and (3) the ΔH change as a π bond is "traded" for a σ bond. The pK_a of carborane itself is ~20,[25] and we use that value for 1-bromo-*o*-carborane as well. We estimate the pK_a of methylcyclopropane as >55.[26] Both of these estimates are conservative. The bromine is certain to increase the acidity of an adjacent C–H bond, and 55 may be a low estimate for the methyl group of a simple hydrocarbon.[26] Using eq 1,[27] we calculate an energy change of +48 kcal/mol for factor

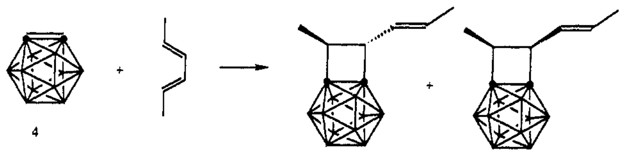
$$\Delta G = 2.3RT\Delta pK_a \qquad (1)$$

1. The strain energy difference between norbornadiene and nortricyclene is calculated to be +12 kcal/mol,[28] and we take −30 kcal/mol for the difference between a diene π bond and a σ bond. The net result is a calculated endothermicity of 30 kcal/mol. Even if this calculation is optimistic by a factor of 2–3, the bromo anion **5** seems a most improbable intermediate.

Nature of the Intermediate. The exo-ring π bond of benzyne was characterized as "normal", if reactive, through an examination of the stereochemical outcome of the 2 + 4 and 2 + 2 cycloaddition reactions.[29] The Diels–Alder reaction was found to be stereospecific and the 2 + 2 cycloaddition nonstereospecific, just as orbital symmetry requires of a bond in which the usual phase relationships in the HOMO (symmetrical) and LUMO (unsymmetrical) obtained. Our plan was to use the same technique for **4**. Although the product spectrum from 2,3-dimethyl-1,3-butadiene was remarkably similar for the two intermediates, this was not the case when *trans,trans*-2,4-hexadiene was used. In the reaction with benzyne, the 2 + 4 product dominates, as 2 + 2 and ene reactions lead only about 15% of the product mixture.[29] Although all three reactions occur between **4** and this diene, it is the 2 + 2 reaction that is the major process.

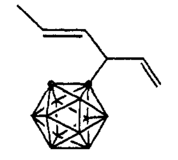


22, 90 % **23**, 10 %



4 **20**, 81 % **21**, 19 %

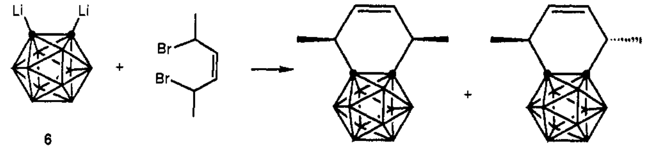
4+2	2+2	ene	
21	56	23	dehydro-*o*-carborane
85	5	10	benzyne[29]



19

Five compounds are formed in the reaction. There is a single product, **19**, derived from an ene reaction. Two other compounds, **20** and **21**, are cyclobutanes formed through a 2 + 2 cycloaddition. Fortunately, the single tertiary allylic hydrogen stands out clearly in the ^1H NMR spectra, and the coupling to the other cyclobutyl hydrogen could be determined. The major product **20** is assigned the trans stereochemistry and **21** the cis on the basis of the smaller coupling constant for **20** (**20**, J = 4.8 Hz; **21**, J = 8.0 Hz).[30] The 2 + 2 cycloaddition is nonstereospecific, as expected if **4** has a symmetrical HOMO.

There are two products of 2 + 4 cycloaddition (**22** and **23**), although this is not apparent at first. The two have fiendishly similar ^1H NMR spectra and are nearly impossible to separate by gas chromatography. Only a very slight difference in the chemical shift of the methyl groups appears. It took an independent synthesis of the two products before we became certain that there were indeed two adducts. Reaction of 1,2-dicarboranyllithium (**6**) with *cis*-2,5-dibromohex-3-ene[31] led to **22** and **23** in a 1:1 ratio, along with a small amount of **20**. With authentic adducts in hand it became easy to determine the ratio formed in the cycloaddition reaction as **22**:**23** = 9:1. It appears that the products of 2 + 4 cycloaddition are formed largely, but not completely, in a stereospecific fashion.



6 **22**, 50% **23**, 50%

As might be anticipated, the product mixture from reaction of **4** with *cis,trans*-2,4-butadiene is even more complicated. All of the products formed from the *trans,trans*-diene are expected, along with an additional ene product and two more 2 + 2 adducts. Preparative gas chromatography cleanly separates the 2 + 4 adducts **22** and **23** from the rest of the products, but the other compounds are obtained only as mixtures. All of the products isolated earlier from the *trans,trans*-diene are present along with molecules that can be reasonably assigned the structures expected for the additional compounds. We were unable to obtain these pure, however, and will concentrate upon **22** and **23**. Once again, a 9:1 ratio of the two is isolated, but in this case it is the trans isomer **23** that is the favored product.

---

[25] Shatenshtein, A. I.; Zakharkin, L. I.; Petrov, E. S.; Yakovleva, E. A.; Yakushin, F. S.; Vukmirovich, Z.; Isaeva, G. G.; Kalinin, V. N. *J. Organomet. Chem.* **1970**, *23*, 313.

[26] A value of >70 has been estimated for isobutane. Breslow, R.; Goodin, R. *J. Am. Chem. Soc.* **1976**, *98*, 6076. Methane itself is probably more acidic; pK_a = 58.7 ± 5. Jaun, B.; Schwarz, J.; Breslow, R. *J. Am. Chem. Soc.* **1980**, *102*, 5741. The methyl group of 2,2,3,3-tetramethylcyclopropane is less acidic than the ring hydrogens, and there appears to be no special stability associated with the cyclopropylcarbinyl anion. Streitwieser, A. Private communication.

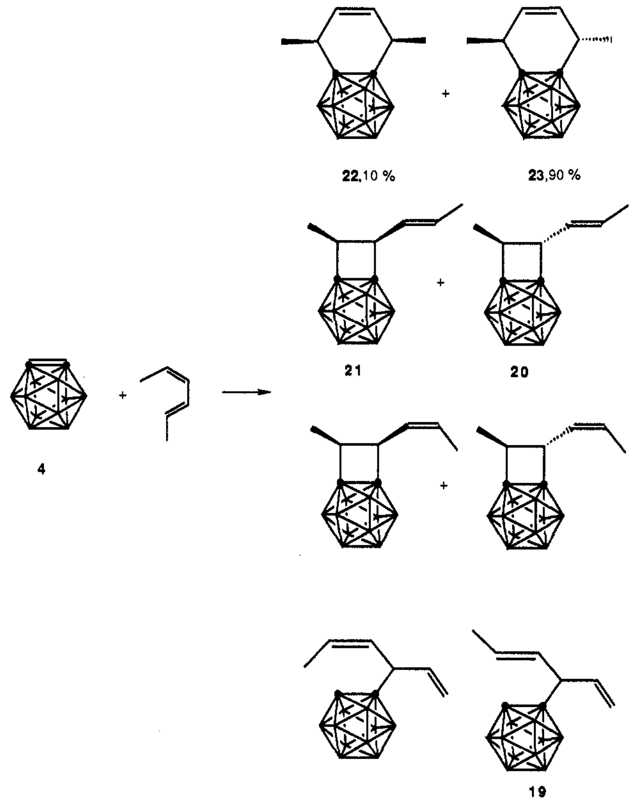
[27] Klumpp, G. W. *Reactivity in Organic Chemistry*; Wiley: New York, 1982; p 371.

[28] Schleyer, P. v. R.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377.

[29] Jones, M., Jr.; Levin, R. H. *J. Am. Chem. Soc.* **1969**, *91*, 6411.

[30] In mobile cyclobutyl systems, cis and trans coupling constants can be close. Bovey, F. A. *Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; Academic: New York, 1988; pp 200, 201. However, in these rigid molecules the Karplus curve should hold more strictly. *Ibid.* pp 194–7. Karplus, M. *J. Am. Chem. Soc.* **1963**, *85*, 2870.

[31] Müller, P.; Rodriguez, D. *Helv. Chim. Acta* **1985**, *68*, 975.



The reactions of **4** and dehydrobenzene with these two dienes are similar in some respects, but differ in two ways. For both intermediates there is much less ene reaction with *trans,trans*-2,4-hexadiene than with 2,3-dimethyl-1,3-butadiene. Dehydro-*o*-carborane is otherwise consistent in its reactions with the two dienes, as the relative importance of 2 + 2 and 2 + 4 cycloadditions is essentially the same, 73% and 69% 2 + 2 reaction, respectively. By contrast, dehydrobenzene prefers 2 + 4 reaction with *trans,trans*-2,4-hexadiene by a wide margin.

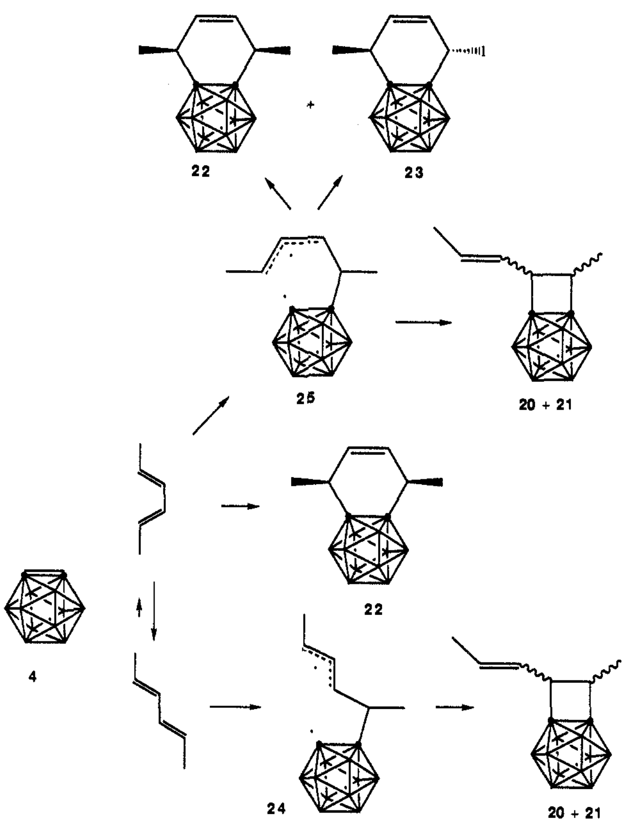
The most important difference for us is the apparent lack of stereospecificity in the 2 + 4 reaction. We think this difference springs simply from the relative importance of the 2 + 2 reaction for 1,2-dehydro-*o*-carborane. This reaction has been shown to be stepwise for dehydrobenzene,[29,32] and our data for **4** reveal a similar course of reaction. There is ~90% retention of stereochemistry in the 2 + 4 cycloaddition reactions of **4** with both *trans,trans*-2,4-hexadiene and *cis,trans*-2,4-hexadiene. Stepwise 2 + 2 additions of both **4** and dehydrobenzene thoroughly scramble stereochemical relationships, and do not induce the modest deviations from stereospecificity seen in these 2 + 4 reactions. Stepwise addition to a diene surely takes place mostly through the favored s-trans form and thus produces an intermediate **24** destined for 2 + 2 formation and prevented from forming any 2 + 4 product. However, stepwise addition to the minor s-cis form of the diene gives an intermediate **25** that can eventually close to 2 + 2 and both 2 + 4 products. Our mechanistic suggestions are shown in Scheme V.

In sum, we see an intermediate best formulated as a "normal" dehydro compound, possessing a symmetrical HOMO and unsymmetrical LUMO. There are differences between dehydro-*o*-carborane and dehydrobenzenes in the details of reaction preferences, conceivably largely dependent upon the increased steric demands of **4**, but an overall view of reactivity shows the two to be quite similar.

Experimental Section

Melting points were determined on a Thomas Hoover Uni-melt capillary melting point apparatus and are uncorrected. Infrared spectra were run on a Perkin-Elmer Model 1310 infrared spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were obtained on a General Electric QE 300 spectrometer at 300 and 75.0 MHz, respectively. ^{11}B NMR spectra were recorded on a Bruker WM 250 spectrometer at 80 MHz, with chemical shifts referenced to external boron trifluoride etherate. Precise masses were measured on a KRATOS MS 50 RFA high-resolution mass spectrometer. The elemental analysis was performed by Robertson Laboratories, Inc., Madison, NJ.

Scheme V. Mechanistic Pathways Followed by **4**



General Procedure for the Generation and Trapping of 1,2-Dehydro-*o*-carborane (4). To a solution of 2.5 M BuLi (4 mL, 10 mmol) in ether (10 mL) cooled by an ice bath was added a solution of *o*-carborane (Dexsil, 720 mg, 5 mmol) in ether (10 mL). The resulting curdy white precipitate was stirred at room temperature for 2 h. The mixture was again cooled by an ice bath, and bromine (800 mg, 5 mmol) was added dropwise with vigorous stirring to form **5**. After 15 min, a solution of the diene (10–20 mmol) in ether was added. The solution was heated under reflux for 16 h. After being cooled, the dark brown solution was poured into cold water and the ether layer separated. This was washed with brine and dried over $MgSO_4$. Removal of the ether under reduced pressure gave the crude product, which was purified by preparative gas chromatography (PGC) and/or column chromatography.

Trapping of 1,2-Dehydro-*o*-carborane (4) with Furan. Isolation of the Diels–Alder adduct 7. A solution of *o*-carborane (1.44 g, 10.0 mmol) in anhydrous ether (10 mL) was added dropwise to a stirred solution of 2 M butyllithium in pentane (10.0 mL, 20.0 mmol) and anhydrous ether (10 mL) at 0 °C under an argon atmosphere. Upon completion of this addition, the reaction mixture was allowed to stir at room temperature for 1 h. The reaction mixture was then cooled to 0 °C, and bromine (1.60 g, 10.0 mmol) was added dropwise with stirring. The mixture was then allowed to stir at 0 °C for an additional 30 min. A solution of furan (6.81 g, 100 mmol) in anhydrous ether was added dropwise to the stirred reaction mixture still at 0 °C. Following this addition, the reaction mixture was allowed to stir at room temperature for 1 h and was then heated at reflux with stirring for 24 h. After being cooled, the reaction mixture was treated with water (15 mL) and the organic layer separated. The dried ($MgSO_4$) organic layer was evaporated at reduced pressure to give a viscous, dark brown oil. This material was chromatographed over silica gel, eluting initially with hexanes, followed by 5:95 ether/hexanes to yield a solid, which was recrystallized from hexanes to afford the Diels–Alder adduct **7** as colorless needles (0.52 g, 25%): mp 118.5–119.5 °C; IR (film) 2685, 2665, 2600, 2540, 1300, 1080, 1010, 875 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.1–4.3 (br m, 10 H, B*H*), 5.23 (s, 2 H), 6.65 (s, 2 H); ^{13}C NMR ($CDCl_3$, 75.0 MHz) δ 78.6, 81.7, 139.2; ^{11}B

---

[32] Tabushi, I.; Oda, R.; Okazaki, K. *Tetrahedron Lett.* **1968**, 3743. Wasserman, H. H.; Solodar, A. J.; Keller, L. S. *Tetrahedron Lett.* **1968**, 5597. Friedman, L.; Osiewicz, R. J.; Rabideau, P. W. *Tetrahedron Lett.* **1968**, 5735. Atkin, R. W.; Rees, C. W. *J. Chem. Soc., Chem. Commun.* **1969**, 152.

NMR ($CDCl_3$, 80 MHz) δ −2.68 (d, 3 B), −4.62 (d, 1 B), −11.56 (d, 1 B), −13.63 (d, 3 B), −16.95 (d, 2 B); precise mass for $C_6H_{14}{}^{11}B_8{}^{10}B_2O$, calcd 210.2048, found 210.2040.

Trapping of 1,2-Dehydro-*o*-carborane (4) with 2,5-Dimethylfuran. Isolation of the Diels–Alder Adduct 9. To a solution of **5** (5 mmol, prepared as in the General Procedure) in ether was added a solution of 2,5-dimethylfuran (2.0 g, 20.8 mmol) in ether (10 mL). The mixture was heated under reflux for 16 h. After workup as for **7**, the crude product was chromatographed over silica gel with hexane followed by hexane ether (85:15) as eluent. First to elute was pure **9** (250 mg), followed by a mixture of **9** and **10**. This was then subjected to PGC on a 10% OV-17 (5 ft × 1/4 in.) column at 180 °C. A fraction was obtained that contained a mixture of 9 and **10** in a 3:7 ratio.

9: mp 80–84 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.42 (s, 2 H), 1.00–3.30 (br m, 10 H, B*H*), 1.68 (s, 6 H); precise mass for $C_8{}^{11}B_8{}^{10}B_2H_{18}O$, calcd 238.2361, found 238.2366.

10: ^1H NMR (by subtracting the peaks for **9**) δ 4.60 (m, 1 H), 4.00 (m, 1 H), 1.00–3.30 (br m, 10 H, B*H*), 1.81 (d, *J* = 3 Hz, 3 H), 1.68 (s, 3 H).

Reaction of 1,2-Dehydro-*o*-carborane (4) with 2,3-Dimethyl-1,3-butadiene. Formation of 12–14. To a solution of butyllithium (4 mL of a 2.5 M solution in hexane, 10 mmol) in 10 mL of ether at 0 °C was added dropwise a solution of *o*-carborane (720 mg, 5 mmol) in 10 mL of ether. After the addition, the curdy white precipitate was stirred at room temperature for 1.5 h. The reaction mixture was cooled to 0 °C, and bromine (800 mg, 5 mmol) was added very slowly. To the resulting clear solution was added 2,3-dimethyl-1,3-butadiene (2 g, 24 mmol) as a solution in ether (10 mL). The reaction mixture was heated at reflux for 16 h and then quenched by pouring the mixture into ice–water. The ether layer was separated, washed with brine, and dried over $MgSO_4$. Removal of the ether under reduced pressure gave a dark liquid that was chromatographed over silica gel with hexane as eluent to obtain 550 mg (50%) of the three products as a mixture. This was then subjected to PGC at 160 °C on a 10% OV-17 column (5 ft × 1/4 in.). First to elute was **12**, followed by **14** and then **13**.

12: mp 75–77 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.96 (d, *J* = 3 Hz, 1 H), 4.74 (br s, 1 H), 3.13 (d, *J* = 11.7 Hz, 1 H), 2.68 (d, *J* = 11.7 Hz, 1 H), 1.20–3.00 (br m, 10 H, B*H*), 1.80 (s, 3 H), 1.60 (s, 3 H); precise mass for ${}^{11}B_{10}C_8H_{20}$, calcd 226.2495, found 226.2516.

14: ^1H NMR ($CDCl_3$, 300 MHz): δ 5.38 (s, 1 H), 5.12 (s, 1 H), 5.07 (m, 2 H), 3.60 (br s, 1 H), 3.27 (s, 2 H), 1.20–3.20 (br m, 10 H, B*H*), 1.95 (s, 3 H); precise mass for ${}^{11}Bg_8{}^{10}B_2C_8H_{20}$, calcd 224.2568, found 224.2570.

13: ^1H NMR ($CDCl_3$, 300 MHz): δ 2.90 (s, 4 H), 1.20–3.00 (br m, 10 H, B*H*), 1.63 (s, 6 H); precise mass for ${}^{11}B_8{}^{10}B_2C_8H_{20}$, calcd 226.2495, found 226.2481.

Trapping of 1,2-Dehydro-*o*-carbonate (4) with Anthracene. Isolation of the Diels–Alder adduct 15. A solution of *o*-carborane (1.44 g, 10.0 mmol) in anhydrous ether (10 mL) was added dropwise to a stirred solution of 2 M butyllithium in pentane (10.0 mL, 20.0 mmol) and anhydrous ether (10 mL) at 0 °C under an argon atmosphere. Upon completion of this addition, the reaction mixture was allowed to stir at room temperature for 1 h. The reaction mixture was then cooled to 0 °C, and bromine (1.60 g, 10.0 mmol) was added dropwise with stirring. The reaction mixture was then allowed to stir at 0 °C for an additional 15 min. To the resulting solution of cold (0 °C) 1-lithio-2-bromo-*o*-carborane (**5**) was then added all at once a slurry of anthracene (3.56 g, 20.0 mmol) in anhydrous ether (20 mL). Following this addition, the reaction mixture was allowed to stir at room temperature for 1 h and was then heated at reflux with stirring for 24 h. After being cooled, the reaction mixture was treated with water (15 mL). Excess anthracene was then collected by suction filtration and washed with ether (50 mL). The combined organic layers (from the filtrate) were separated, dried over $MgSO_4$, and evaporated at reduced pressure to give a dark brown semisolid. This material was chromatographed over silica gel, eluting with hexanes to afford a yellow solid that was recrystallized from ethyl acetate/hexanes to yield the Diels–Alder adduct **15** as colorless prisms (0.61 g, 19%): mp 246–247 °C; IR (film) 2680, 2600, 2575 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.0–3.4 (br m, 10 H, B*H*), 4.78 (s, 2 H), 7.18–7.28 (m, 8 H); precise mass for $C_{16}H_{20}{}^{11}B_8{}^{10}B_2$, calcd 320.2569, found 320.2529.

Trapping of 1,2-Dehydro-*o*-carborane (4) with Norbornadiene. Isolation of 16–18. To a solution of **5** (5 mmol, prepared as in the General Procedure) in ether was added a solution of norbornadiene (1.4 g, 15.2 mmol) in ether (5 mL). The reaction was heated at reflux for 16 h. After workup as for **7**, the crude product mixture was chromatographed over silica gel with hexane as eluent to give a colorless oil (230 mg) that was still a mixture of products. This mixture was then subjected to PGC on an OV-17 (5 ft × 1/4 in.) column. The temperature was varied from 160 to 210 °C. First to elute was *o*-carborane, followed by 1-bromo-*o*-carborane, 1-butyl-*o*-carborane, a mixture of **17** and **18**, and finally **16**. **16**: mp 150–152 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.12 (s, 2 H), 2.80 (s, 2 H), 1.82 (m, 2 H), 1.20–3.20 (br m, 10 H B*H*), 1.40 (d, *J* = 4.8 Hz, 2 H). Anal. Calcd for $C_9B_{10}H_{18}$: C, 46.13, H, 7.74. Found: C, 45.90, H, 7.47.

17 and 18 (1:1 mixture of endo and exo): ^1H NMR ($CDCl_3$, 300 MHz) δ 6.85 (dd), 6.60 (dd), 3.70 (br) 3.60 (m), 3.20 (d), 3.10 (s) 2.90 (m), 1.40 (m), 1.20–3.20 (br, 10 H, B*H*); precise mass for $C_9{}^{11}B_8{}^{10}B_2H_{18}$, 234.2412, found 234.2402.

Trapping of 1,2-Dehydro-*o*-carborane (4) with *trans,trans*-2,4-Hexadiene. Isolation of 19–23. To a solution of **5** (5 mmol, prepared as in the General Procedure) in ether was added a solution of *trans-trans*-2,4-hexadiene (1.64 g, 20 mmol) in ether (5 mL). The solution was refluxed for 16 h. After workup as for **7**, the crude product was chromatographed over silica gel with pentane as eluent. First to elute was a mixture of 1-bromo-*o*-carborane, 1-butyl-*o*-carborane, and the five adducts (**19–23**, total weight 300 mg). Next to elute was unreacted *o*-carborane (80 mg). The first fraction was then subjected to PGC at 180 °C on a 3% SP-2250 (8 ft × 1/4 in.) column. First to elute was 1-bromo-*o*-carborane, followed by 1-butyl-*o*-carborane and then **21**, **19**, **20**, and a mixture of **22** and **23**.

19: ^1H NMR ($CDCl_3$, 300 MHz) δ 5.65 (m, 1 H), 5.33 (m, 1 H) 5.25 (dd, *J* = 13, 9 Hz, 1 H), 5.13 (d, *J* = 10 Hz, 1 H), 3.65 (br s, 1 H), 3.44 (m, 1 H), 1.70 (d, *J* = 7 Hz, 3 H), 1.40–2.80 (br m, 10 H, B*H*); precise mass for $C_8{}^{11}B_8{}^{10}B_2H_{20}$, calcd 224.2568, found 224.2499.

20: ^1H NMR ($CDCl_3$, 300 MHz) δ 5.57 (m, 2 H), 3.40 (dd, *J* = 4.8 Hz, 4.8 Hz, 1 H), 3.20 (dq, *J* = 7.0, 4.8 Hz, 1 H), 1.25 (d, *J* = 7 Hz, 3 H), 1.40–2.80 (br m, 10 H, B*H*); precise mass for $C_8{}^{11}B_8{}^{10}B_2H_{20}$, calcd 224.2568, found 224.2568.

21: ^1H NMR ($CDCl_3$, 300 MHz) δ 5.60 (m, 2 H), 3.80 (dd, *J* = 8.0, 8.0 Hz, 1 H), 3.50 (m, 1 H), 1.80 (d, *J* = 6.2 Hz, 3 H), 1.20 (d, *J* = 10 Hz, 3 H), 1.40–2.80 (br m, 10 H, B*H*); precise mass for $C_8{}^{11}B_8{}^{10}B_2H_{20}$, calcd 224.2568, found 224.2575.

22: ^1H NMR, ($CDCl_3$, 300 MHz) δ 5.45 (s, 2 H), 3.05 (q, *J* = 7 Hz, 2 H), 1.29 (d, *J* = 7 Hz, 6 H), 1.40–3.10 (br m, 10 H, B*H*).

23: ^1H NMR ($CDCl_3$, 300 MHz) δ 5.45 (s, 2 H), 3.05 (q, *J* = 7 Hz, 2 H), 1.28 (d, *J* = 7 Hz, 6 H), 1.40–3.10 (br m, 10 H, B*H*).

Trapping of 1,2-Dehydro-*o*-carborane (4) with *cis,trans*-2,4-Hexadiene. To a solution of **5** (5 mmol, prepared as in General Procedure) in ether was added a solution of *cis,trans*-2,4-hexadiene (1.64 g, 20 mmol) in ether (5 mL). The solution was refluxed for 16 h. After workup as for **7**, the crude product was chromatographed over silica gel with pentane as eluent. First to elute was a mixture of **22** and **23** (200 mg), followed by unreacted *o*-carborane (200 mg). The first fraction was then subjected to PGC at 170 °C on a 3% SP-2250 (8 ft × 1/4 in.) column. The last fraction to elute was a 9:1 mixture of **23** and **22**.

Preparation of 22 and 23. To a solution of 2.5 M BuLi (4 mL, 10 mmol) in ether (10 mL) at 5 °C was added a solution of *o*-carborane (720 mg, 5 mmol) in ether (10 mL). The mixture was warmed to room temperature and stirred for 1.5 h. To the white slurry was added a solution of *cis*-2,5-dibromohex-3-ene[31] (1.25 g, 5 mmol) in ether (10 mL). The solution was heated under reflux for 16 h. After workup, the crude product was chromatographed over silica gel with hexane as eluent. First to elute was a mixture of **22**, **23**, and **20** (400 mg, 30%), with the ratio of (**22** + **23**):**20** being 6. This fraction was then subjected to PGC on a 3% SP-2250 (8 ft × 1/4 in.) column at 180 °C. This gave pure **22** and **23** in a 1:1 ratio: precise mass for $C_8{}^{11}B_8{}^{10}B_2H_{20}$, calcd 224.2568, found 224.2546.

Registry No. 1, 16872-09-6; **4**, 127065-16-1; **5**, 127085-60-3; **7**, 127065-19-4; **9**, 131296-25-8; **10**, 131296-26-9; **12**, 127065-17-2; **13**, 127065-18-3; **14**, 127085-61-4; **15**, 127065-20-7; **16**, 131296-27-0; **17**, 131296-28-1; **18**, 131349-71-8; **19**, 131296-29-2; **20**, 131296-30-5; **21**, 131349-72-9; **22**, 131296-31-6; **23**, 131296-32-7; (*E,E*)-$H_3CCH{=}CHCH{=}CHCH_3$, 5194-51-4; (*E,Z*)-$H_3CCH{=}CHCH{=}CHCH_3$, 5194-50-3; (*Z*)-$H_3CCH(Br)CH{=}CHCH(Br)CH_3$, 100937-48-2; furan, 110-00-9; 2,5-dimethylfuran, 625-86-5; 2,3-dimethyl-1,3-butadiene, 513-81-5; anthracene, 120-12-7; norbornadiene, 121-46-0.