Reactions of 1,2-Dehydro-*o*-carborane with Thiophenes. Cycloadditions and an Easy Synthesis of “Benzo-*o*-carboranes”[1]

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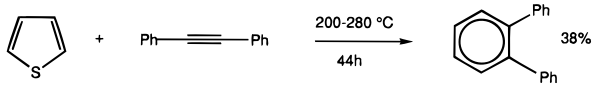
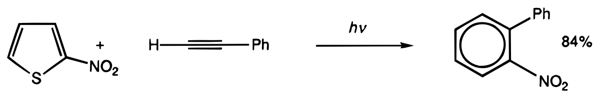
Cycloaddition reactions of 1,2-dehydro-*o*-carborane with thiophene, 2,5-dimethylthiophene, 2,5-dimethylfuran, [8](2,5)thiophenophane, and [8](2,5)furanophane are investigated. In all cases, except the reaction with the thiophenophane, both $4 + 2$ and $2 + 2$ cycloadducts are formed, with the $4 + 2$ product dominating. The $4 + 2$ adducts of the thiophenes are not stable but extrude sulfur under the reaction conditions to give “benzo-*o*-carboranes”.

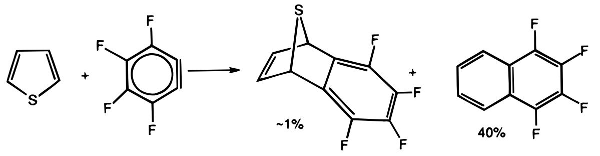
Diels−Alder reactions of simple thiophenes, once thought not to occur, are now known to take place with a wide variety of dienophiles, usually with concomitant loss of sulfur. For example, dicyanoacetylene adds to a variety of thiophenes to produce 1,2-dicyanobenzenes in 8−51% yield.[3] Even less reactive dienophiles have been shown to react with thiophene or its 2,5-dimethyl derivative at modestly elevated temperatures to give benzenes in 2−56% yield.[4] In all of these cases, a nonisolable bicyclic intermediate was reasonably postulated. Highly benzosubstituted thiophenes had been shown to undergo this reaction as early as 1939.[5]

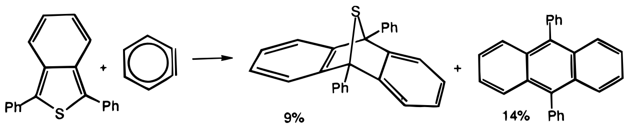


This cycloaddition−desulfurization reaction is also known to proceed photochemically, and very recently it was shown that the regiochemistry of the reaction can be explained through the usual HOMO/LUMO analysis.[6]



As early as the 1960s, it was known that very reactive dienophiles such as benzynes underwent the Diels−Alder reaction with simple thiophenes. In each case, small amounts of the $4 + 2$ adduct, generally suspected of being an intermediate in all the other reactions, were isolated.[7,8]





These early observations have now been extended several times. Among the important findings was that monocyclic thiophenes reacted with benzyne itself and not only with fluorinated arynes.[9] It was also shown that small amounts of $2 + 2$ addition and ene reaction were occurring in addition to the more prominent $4 + 2$ Diels−Alder reactions.[9d]

The *o*-carboranes are icosahedral clusters of two adjacent carbons and ten borons, held together in what must be the ultimate expression of three-center, two-electron bonding. Each vertex of the icosahedron bears a σ-bonded hydrogen. Like their more conventional cousins, the benzenes, the icosahedral carboranes are thermodynamically very robust and undergo aromatic substitution reactions with many electrophiles.[10] As

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(2) Department of Education Fellow, 1993−4.

(3) Helder, R.; Wynberg, H. *Tetrahedron Lett.* **1972**, 605. See also: Helder, R. Thesis, Rijks Universiteit Groningen, The Netherlands, 1974. Quoted in: Kane, V. V.; de Wolf, W. H.; Bickelhaupt, F. *Tetrahedron* **1994**, *50*, 4575. Nakayama, J.; Kuroda, K. *J. Am. Chem. Soc.* **1993**, *115*, 4612.

(4) Kuhn, H. J.; Gollnick, K. *Chem. Ber.* **1973**, *106*, 674.

(5) Clapp, D. B. *J. Am. Chem. Soc.* **1939**, *61*, 2733.

(6) D’Auria, M. *Tetrahedron Lett.* **1995**, *36*, 6567.

(7) Callender, D. D.; Coe, P. L.; Tatlow, J. C. *J. Chem. Soc., Chem. Commun.* **1966**, 143. See also: Callender, D. D.; Coe, P. L.; Tatlow, J. C.; Uff, A. J. *Tetrahedron* **1969**, *25*, 25. Coe, P. L.; Pearl, G. M.; Tatlow, J. C. *J. Chem. Soc. C* **1971**, 604.

(8) Wittig, G.; Knauss, E.; Niethammer, K. *Liebigs Ann. Chem.* **1960**, *630*, 10.

(9) (a) Fields, E. K.; Meyerson, S. *J. Org. Chem.* **1969**, *34*, 2475. (b) Reinecke, M. G.; Newsom, J. G.; Chen, L.-J. *J. Am. Chem. Soc.* **1981**, *103*, 2760. (c) Del Mazza, D.; Reinecke, M. G. *J. Org. Chem.* **1988**, *53*, 5799. (d) Reinecke, M. G.; Del Mazza, D. *J. Org. Chem.* **1989**, *54*, 2142.

(10) (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. Bregadze, V. I. *Chem. Rev.* **1992**, *92*, 209.

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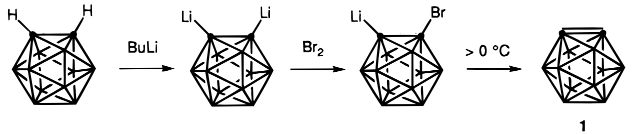
part of our investigation of the reactions of carborane-based reactive intermediates, we found a way to remove the two hydrogens attached to carbon to generate 1,2-dehydro-*o*-carborane (**1**) and have reported on many of its reactions.[11]

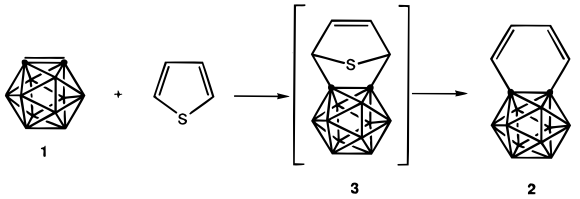


o-carborane. The dots represent the carbons, and all other vertices are borons. There is a hydrogen attached to every vertex atom.

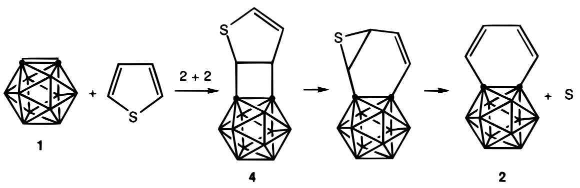
Despite the long carbon−carbon bond (the carbon−carbon distance in *o*-carborane itself is 1.63 Å[12]), intermediate **1** is a reactive but essentially normal π system, with the same HOMO/LUMO symmetry as ethylene or benzyne.[13]

In this paper, we report the reactions of 1,2-dehydro-*o*-carborane (**1**) with thiophenes. Although we have found the reactions with thiophene itself and 2,5-dimethylthiophene to resemble the comparable reactions of benzyne, in other cases, notably [8](2,5)thiophenophane, the reaction takes a more complicated and frustrating path.

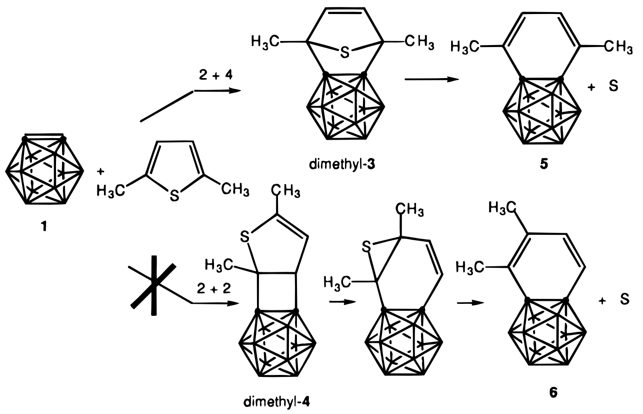
Addition to thiophene gives compound **2** in 19% yield. This exquisite compound was first made in 1968 by Matteson and his collaborators by a double displacement of 1,2-dilithio-*o*-carborane on 1,4-dibromobut-2-ene, followed by an oxidation procedure.[14] Our reaction constitutes an extremely simple route to these compounds in which a 1,3-diene is appended to the icosahedron in a union that might well be regarded as miscegenetic. We assumed that an intermediate of structure **3** was first formed but were unable to isolate it.



However, the presumption of the presence of **3** is premature. As mentioned earlier, thiophenes are known to undergo 2 + 2 cycloadditions to give compounds containing the bicyclo[3.2.0] framework, and such compounds can rearrange to six-membered rings.[9d,15] Thus, a mechanism of the following kind, in which a 2 + 2 adduct, **4**, is an intermediate, must be considered for the formation of **2**:

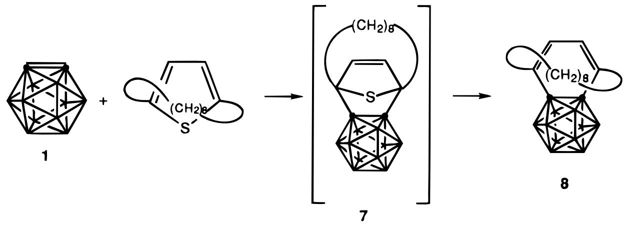


Reaction with 2,5-dimethylthiophene settles the issue. A dimethyl-**3** must give the product **5**, with only a single methyl signal in the ^{1}H NMR spectrum, whereas a mechanism proceeding through a dimethyl-**4** must give **6**, a compound with two different methyl groups. In fact, only **5** is formed, in 15% yield after crystallization from aqueous ethanol.



So, the mechanism involving a 4 + 2 Diels−Alder reaction and an intermediate of structure **3** is correct. A close examination of the ^{1}H NMR spectrum of the crude reaction mixture leading to **5** reveals a small amount of another product, whose structure is probably that of the sulfur-containing 2 + 2 adduct (vide infra). Nonetheless, by far the major process is a straightforward Diels−Alder 4 + 2 cycloaddition that, like the many reactions carried out by others, was followed by extrusion of sulfur.

Therefore, it seemed reasonable that addition to [8](2,5)-thiophenophane would lead to an unstable intermediate (**7**) and thus to the [8]cyclophane **8**.



Such new cyclophanes seemed of interest as potential probes of the aromaticity, or, more likely, lack thereof, of the carbocyclic ring.[16] Accordingly, [8](2,5)thiophenophane, synthesized by the method of Helder and Wynberg,[17] was allowed to react with **1** under conditions similar to those used for the simpler thiophenes. Preparative gas chromatography led to a single adduct of the proper molecular weight for **8**. However, the ^{1}H NMR spectrum gave us pause. In particular, there were two separate vinyl hydrogens, and these did not coalesce up to 85 °C. This could be the case in **8** were the eight-carbon bridge to be locked in an "S"-shaped conformation. However, this is clearly not the situation in the rather closely related [8](1,4)-naphthalenophane (**9**) made some years ago by Wiberg and

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[11] (a) Gingrich, H. L.; Ghosh, T.; Huang, Q.; Jones, M., Jr. *J. Am. Chem. Soc.* **1990**. *112*, 4082. (b) Ghosh, T.; Gingrich, H. L.; Kam, C. K.; Mobraaten, E. C.; Jones, M., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 1313. (c) Huang, Q.; Gingrich, H. L.; Jones, M., Jr. *Inorg. Chem.* **1991**, *30*, 3254. (d) Gingrich, H. L.; Huang, Q.; Morales, A. L.; Jones, M., Jr. *J. Org. Chem.* **1992**, *57*, 3803. (e) Cunningham, R. J.; Bian, N.; Jones, M., Jr. *Inorg. Chem.* **1994**, *33*, 4811. (f) Ho, D. M.; Cunningham, R. J.; Brewer, J. A.; Bian, N.; Jones, M., Jr. *Inorg. Chem.* **1995**, *34*, 5274.

[12] Ott, J. J.; Gimarc, B. M. *J. Comput. Chem.* **1986**, *7*, 673.

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

[14] Hota, N. K.; Matteson, D. S. *J. Am. Chem. Soc.* **1968**, *90*, 3570. Matteson, D. S.; Hota, N. K. *J. Am. Chem. Soc.* **1971**, *93*, 2893. See also: Matteson, D. S.; Davis, R. A. *Chem. Commun.* **1970**, 669 (for a related "naphthocarborane"). Wu, S.; Jones, M., Jr. *Inorg. Chem.* **1988**, *27*, 2005 (for a carbon−boron-bridged "naphthalene").

[15] See, for example: Reinhoudt, D. N.; Trompenaars, W. P.; Geevers, J. *Tetrahedron Lett.* **1976**, 4777. Reinhoudt, D. N.; Kouwenhoven, C. G. *Tetrahedron* **1974**, *30*, 2093. Benders, P. H.; Reinhoudt, D. N.; Trompenaars, W. P. *Thiophene and Its Derivatives*; Gronowitz, S., Ed.; Wiley: New York, 1985; Chapter X.

[16] Ho, D. M.; Cunningham, R. J.; Brewer, J. A.; Bian, N.; Jones, M., Jr. *Inorg. Chem.* **1995**, *34*, 5274.

[17] Helder, R.; Wynberg, H. *Tetrahedron* **1975**, *31*, 2551. There are several routes to this compound, but this one is by far the best.

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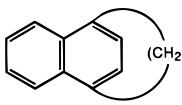
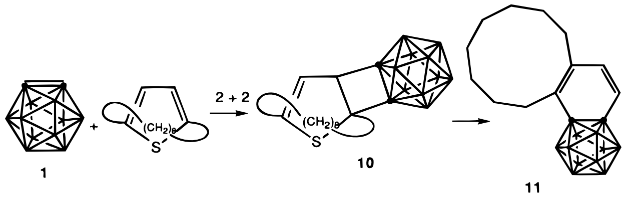
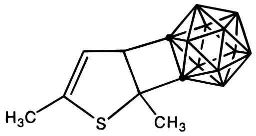


O'Donnell.[18] Therefore it was obvious that we had to look closely at the structure of the putative **8**. The plot thickened somewhat when we were able to crystallize **10**, the primary, sulfur-containing, adduct, from the crude reaction mixture. The ^{1}H NMR spectrum of **10** was clearly not that of a 4 + 2 adduct but fit well for the much less symmetrical 2 + 2 adduct. Of particular significance are two 1 H signals at δ 4.25 (tertiary allylic hydrogen) and 5.2 (vinyl hydrogen). Preparative gas chromatography of **10** led only to the desulfurized compound **11**. It now seemed highly likely that addition had taken place in 2 + 2 fashion to give **10** and then, upon loss of sulfur, not **8** but **11**. Clearly, **11** would show the observed pair of one-hydrogen signals at all temperatures. Recrystallization of **11** from isopropyl alcohol led to a sample suitable for analysis by X-ray diffraction. Figure 1 shows a view of the X-ray-derived structure along with the numbering for **11**. Tables 1 and 2 give the crystallographic data and the atomic coordinates for **11**. A preliminary X-ray determination was also made of the structure of **10**, confirming that it is the product of a 2 + 2 addition.[19]



Despite the dominance of 4 + 2 addition in the reaction of **1** with 2,5-dimethylthiophene, reaction with the thiophenophane has taken another course. Indeed, in this case there is no evidence for 4 + 2 addition, even in the crude reaction mixture, which shows an approximately 2:1 mixture of **10** and **11** as determined by matching peaks with those of the pure compounds. Perhaps the mechanistic turnabout is not as dramatic as it seems. For example, in the reaction of **1** with 2,5-dimethylthiophene, the major adduct, **5**, formed by 4 + 2 cycloaddition followed by loss of sulfur, was isolated by column chromatography. Analysis of the other chromatography fractions by ^{1}H NMR spectroscopy and GC/MS showed very small amounts of a compound almost certainly **12**, the 2 + 2 adduct.



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This judgment is based on the appearance of peaks for the tertiary and vinylic hydrogens of **12** in almost exactly the same positions as the known related hydrogens of **10** (**10**, δ 5.2, 4.25; **12**, δ 5.16, 4.20). In 2,5-dimethylthiophene, both 4 + 2 and 2 + 2 cycloadditions occur, with the 4 + 2 reaction dominating by no more than a few kilocalories per mole. In [8](2,5)-thiophenophane, the situation changes, and 2 + 2 cycloaddition becomes dominant. Although this may seem strange, it would take only the change of a few kilocalories per mole in the two processes to effect such a turnabout.

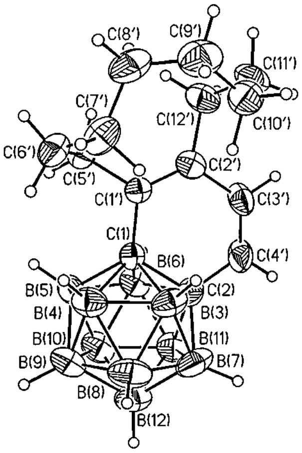

Figure 1. The X-ray-derived structure of **11**.

Table 1. Crystallographic Data for Compound **11**

space group	*Pn* (No. 7)	formula	$C_{14}H_{28}B_{10}$
a, Å	7.1086(4)	fw	304.46
b, Å	9.7055(7)	*Z*	2
c, Å	13.2338(11)	ρ_{calcd}, g/cm^3	1.108
β, deg	91.784(6)	*T*, K	230(2)
V, Å^3	912.59(11)	λ(Mo Kα), Å	0.710 73
$R(F)$,^{a} $R_w(F^2)$^{b}	0.044, 0.085	μ, mm^{-1}	0.054

^{a} $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w(F^2) = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for Compound **11**

	x	*y*	*z*	*U*(eq)^a
C(1)	2543(3)	1275(3)	2468(2)	35(1)
C(2)	2934(4)	248(3)	3446(2)	44(1)
B(3)	854(5)	54(3)	2750(3)	50(1)
B(4)	1500(5)	352(4)	1497(3)	52(1)
B(5)	3932(5)	757(4)	1485(3)	48(1)
B(6)	4834(5)	713(4)	2739(3)	45(1)
B(7)	2142(6)	−1387(4)	3203(3)	63(1)
B(8)	1264(6)	−1367(4)	1957(3)	63(1)
B(9)	3147(6)	−912(4)	1158(3)	60(1)
B(10)	5199(5)	−697(4)	1941(3)	56(1)
B(11)	4596(5)	−980(4)	3204(3)	52(1)
B(12)	3551(5)	−1998(4)	2228(3)	59(1)
C(1′)	2135(3)	2756(2)	2700(2)	34(1)
C(2′)	2027(4)	3166(3)	3675(2)	42(1)
C(3′)	2347(4)	2218(3)	4520(2)	51(1)
C(4′)	2788(4)	907(3)	4424(2)	57(1)
C(5′)	2004(4)	3738(3)	1810(2)	46(1)
C(6′)	175(5)	3754(3)	1153(2)	58(1)
C(7′)	−1621(4)	3747(4)	1745(2)	56(1)
C(8′)	−1986(5)	5112(4)	2316(3)	67(1)
C(9′)	−3011(6)	4953(4)	3292(3)	74(1)
C(10′)	−1993(5)	4123(3)	4104(3)	60(1)
C(11′)	−229(5)	4738(4)	4595(3)	59(1)
C(12′)	1586(5)	4627(3)	4005(3)	54(1)

^{a} *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Indeed, the dominant reaction changes yet again when [8]-(2,5)furanophane is used in place of [8](2,5)thiophenophane. We showed earlier that **1** reacts with 2,5-dimethylfuran mainly by 4 + 2 reaction, although very small amounts of the 2 + 2 adduct could be isolated.[11b] Unlike the sulfur case, this time the cyclophane mimicks the unbridged compound. Addition of **1** to [8](2,5)furanophane gives a greater than 4:1 ratio of 4 + 2 (**13**) and 2 + 2 (**14**) adducts. These compounds are difficult

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(18) Wiberg, K. B.; O'Donnell, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 6660.

(19) Crystal data for **10**: monoclinic, $P2_1/c$ (No. 14), a = 12.773(2) Å, b = 12.837(2) Å, c = 11.925(2) Å, β = 94.46(1)°, V = 1949.3(6) Å^3, Z = 4. Because of disorder and unsatisfactory refinement, connectivity and conformation were confirmed but final crystallographic results are not being reported at this time.

Table 3. Enthalpy of Reaction for the Addition of Acetylene to Cyclic Dienes

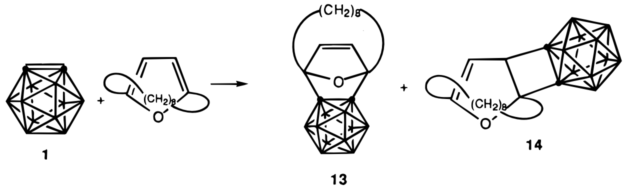
substrate	4 + 2	2 + 2	diff	cor diff
Acetylene Series				
2,5-dimethylfuran	−6.1	−9.9	−4	∼0
2,5-dimethylthiophene	−4.4	−12.8	−8	−4
[8](2,5)furanophane	−3.8	−1.7	+2	+6
[8](2,5)thiophenophane	+6.9	−9.9	−17	−13
1,2-Dehydro-*o*-carborane Series				
2,5-dimethylfuran	−67.9	−76.0	−8	
2,5-dimethylthiophene	−49.6	−67.0	−17	
[8](2,5)furanophane	−67.2	−79.1	−12	
[8](2,5)thiophenophane	−46.0	−72.7	−27	

Table 4. Strain Energies of Starting Cyclophanes and Their Addition Products[a]

	[8](2,5)cyclophane	4 + 2 adduct	2 + 2 adduct
Acetylene Series			
S	19.7	30.4	12.1
O	13.1	14.8	10.3
1,2-Dehydro-*o*-carborane Series			
S	19.7	23.3	14.0
O	13.1	13.0	10.1

[a] These numbers are calculated as differences from a strainless reference. For example, for [8](2,5)thiophenophane (AM1 $\Delta H_f = -3.6$ kcal/mol), a strainless energy is calculated from that of 2,5-dipentylthiophene (AM1 $\Delta H_f = -40.7$ kcal/mol) minus that of ethane (AM1 $\Delta H_f = -17.4$ kcal/mol. Thus we calculate $-3.6 - (-40.7 + 17.4) = 19.7$ kcal/mol.

to separate, but the composite ^{1}H NMR spectrum is easily dissected by use of the signals for the hydrogens attached to the double bonds.



Of course, the question now arises as to why the reaction with [8](2,5)furanophane takes place mainly in 4 + 2 fashion, whereas addition to the seemingly closely related [8](2,5)-thiophenophane is dominated by 2 + 2 cycloaddition. We modeled this reaction by using the AM1 method[20] to examine computationally the cycloadditions of acetylene and 1,2-dehydro-*o*-carborane with four dienes, 2,5-dimethylfuran, 2,5-dimethylthiophene, and the two [8](2,5)cyclophanes. In Table 3, columns 2 and 3 list reaction enthalpies for the 4 + 2 and 2 + 2 cycloadditions, column 4 tabulates the enthalpy differences between the products of the two reactions, and column 5 gives the differences for the acetylene series corrected by the approximately 4 kcal/mol by which AM1 underestimates the energy difference between norbornadiene and bicyclo[3.2.0]-hepta-2,6-diene.[21] No analogous thermochemical calibration points are available for the carborane-containing compounds.

It is noteworthy that the 2 + 2 adducts are calculated to be the thermodynamically preferred products in all but one of these additions. That the 4 + 2 products compete at all is presumably a result of lower reaction barriers for the orbital symmetry allowed 4 + 2 than for the forbidden 2 + 2 processes. Among the acetylene reactions, the last one, cycloaddition to [8](2,5)-thiophenophane, shows by far the strongest preference for the 2 + 2 product, as a result of the sharp strain energy (SE) increase brought on by 4 + 2 addition ($\Delta SE = +10.7$ kcal/mol) and the 2 + 2 product's relaxed bridge geometry ($\Delta SE = -7.6$ kcal/mol), reminiscent of the hyperstable olefin bicyclo[7.2.2]tridec-9-ene.[22] These computational findings for acetylene match the dehydrocarborane experimental results reasonably well; the first three reactions produce both adducts, whereas the fourth process is dominated by 2 + 2 addition.

Though the relative trends are sensible, acetylene is a poor model for the highly reactive dehydro-*o*-carborane because the cycloaddition exothermicities are greatly underestimated, as seen in Table 4. Preliminary analysis of dehydro-*o*-carborane using density functional methods indicates that its 4 + 2 cycloaddition to 2,5-dimethylthiophene is about 40 kcal/mol exothermic.[23] So, the poor 4 + 2 vs 2 + 2 discrimination seen experimentally is easily understood, despite the large product energy differences calculated. These highly exothermic reactions should have early transition states and therefore little selectivity. Nonetheless, some of the large energy differences must be manifested in the transition states leading to the products and thus affect the rates of the possible reactions.

Why does the introduction of an octamethylene bridge affect the cycloadditions of the thiophenophane and the furanophane so differently? The answer lies in the strain energy changes that accompany the cycloadditions and especially in the exceptional strain of the 4 + 2 adducts of the thiophenophane. Table 4 gives the calculated strain energies of the two cyclophanes and their 4 + 2 and 2 + 2 addition products. For the furanophane, formation of either 4 + 2 or 2 + 2 adduct results in little change in strain. By contrast, for the thiophenophane, 2 + 2 cycloaddition actually relieves strain whereas 4 + 2 cycloaddition increases strain by a significant amount. This difference can be ultimately traced to geometrical differences in the products because of the longer C−S vs C−O bonds and the larger size of S vs O. These findings hold for both acetylene and dehydrocarborane cycloadditions.

Experimental Section

Reagents were used as obtained from commercial sources without further purification unless otherwise indicated. THF, cyclohexane, and diethyl ether were distilled from sodium benzophenone ketyl. Melting points were determined on a Thomas-Hoover Uni-melt capillary melting point appartus and are uncorrected. ^{1}H NMR spectra were obtained on a General Electric QE 300 spectrometer at 300 MHz, a JEOL-270 NMR spectrometer at 270 MHz, or a Bruker WM 250 spectrometer at 250 MHz. ^{13}C NMR spectra were obtained on a General Electric QE 300 spectrometer at 75.0 MHz. Gas chromatographic/mass spectrometric analyses were performed on a Hewlett Packard 5890/5971 Series II gas chromatograph/mass spectrometer with either a 25 m, 0.2 mm i.d., 0.33 μm film thickness HP-1 capillary column or a 50 m, 0.2 mm i.d., 0.33 μm film thickness HP-1 capillary column. Preparative gas chromatography was performed on a Gow-Mac 580 gas chromatograph with an aluminum column (6 ft × 1/4 in.) packed with 10% OV-101 on Chromosorb WHP. Precise masses were measured on a KRATOS MS50 RFA high-resolution mass spectrometer.

Computational Details. Calculations using the AM1 semiempirical molecular orbital and density functional methods available in the SPARTAN 3.0 program were run on a Silicon Graphics Indigo2. All geometries were fully optimized with no symmetry constraints. For the cyclophanes and derivatives in which several chain conformations were possible, molecular mechanics conformation searches, augmented by intuition-driven manual manipulations, were carried out, and the few lowest energy conformations so obtained were then used as starting

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geometries for the quantum chemical calculations. "Cyclophane strain" energies were calculated relative to a strainless [8]cyclophane standard obtained by computing the energies of 2,5-dipentylthiophene and 2,5-dipentylfuran and then subtracting the calculated energy of ethane. This procedure effectively removes the terminal methyl groups. The energy changes relative to the dimethyl systems were identical at −35.4 kcal/mol, so further "strainless [8]cyclophane" energies were simply obtained by subtracting this quantity from the energies of compounds in the dimethyl series.

Reaction of 1,2-Dehydro-*o*-carborane (1) with Thiophene. Isolation of Benzo-*o*-carborane (2). A solution of *o*-carborane (1.97 g, 13.7 mmol) in cyclohexane (45 mL) was added dropwise to a solution of butyllithium (2.0 M in cyclohexane, 14.0 mL, 28.0 mmol) and cyclohexane (20 mL) at 0 °C under an argon atmosphere. The resulting white precipitate was stirred in solution for 1 h at room temperature. The system was then cooled to 0 °C, bromine (2.24 g, 0.72 mL, 14.0 mmol) was added dropwise, and stirring was continued at 0 °C for another 1 h. Freshly distilled thiophene (11.8 g, 11.2 mL, 140 mmol) in cyclohexane (10.0 mL) was then added dropwise to the reaction mixture. The suspension was maintained at 0 °C during the addition, after which the mixture was stirred at room temperature for 1 h and then heated to reflux. The progress of the reaction was monitored by periodically analyzing aliquots by GC/MS. After completion of the reaction (≈20 h), the mixture was cooled to room temperature, water (20 mL) was added, and the layers were separated. The aqueous layer was extracted with ether (5 × 10 mL), and the ether extracts were combined with the organic layer. The combined extracts, after being washed with water (10 mL) and then saturated brine solution (10 mL), were dried over $MgSO_4$. Removal of the solvent at the rotary evaporator gave a yellow semisolid, which was then chromatographed (SiO_2/hexanes) to yield a white solid. After recrystallization from aqueous ethanol, colorless needles of benzo-*o*-carborane (**2**) were obtained (0.51 g, 19%): mp 111−112 °C (lit.[14] 110 °C); ^1H NMR ($CDCl_3$, 300 MHz) δ 1.10−3.40 (br m, 10 H, BH), 6.27 (m, 2 H), 6.48 (m, 2 H).

Reaction of 1,2-Dehydro-o-carborane (1) with 2,5-Dimethylthiophene. Isolation of 2,5-Dimethylbenzo-*o*-carborane (5). To the suspension of the bromo anion in cyclohexane was added a solution of 2,5-dimethylthiophene (15.71 g, 15.95 mL, 140 mmol) in cyclohexane (10.0 mL). The suspension was maintained at 0 °C during the addition, after which the mixture was stirred at room temperature for 1 h and then heated to reflux. The progress of the reaction was monitored by periodically analyzing aliquots by GC/MS. After completion of the reaction (≈20 h), the mixture was cooled to room temperature, water (20 mL) was added, and the layers were separated. The aqueous layer was extracted with ether (5 × 10 mL), and the ether extracts were combined with the organic layer. The combined extracts, after being washed with water (10 mL) and then saturated brine solution (10 mL), were dried over $MgSO_4$. Removal of the solvent at the rotary evaporator gave a yellow semisolid, which was then chromatographed (SiO_2/hexanes). First to elute was **5**, which was recrystallized from aqueous ethanol to afford 2,5-dimethylbenzo-*o*-carborane as colorless needles (461 mg, 15%). The subsequent column fractions containing a mixture of **5** and another adduct were freed of solvent at the rotary evaporator and subjected to preparative GC. A fraction was obtained that contained a mixture of **5** and another compound (**12**) in a 3:1 ratio as determined by ^1H NMR spectroscopy.

5: mp 112−112.5 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.1−3.4 (br m 10 H, BH), 2.20 (s 6 H), 6.00 (s, 2 H); ^{13}C NMR ($CDCl_3$, 75.0 MHz) δ 22.0, 120.0, 134.5; precise mass calculated for $C_8{}^{11}B_8{}^{10}B_2H_{18}$ 222.2412, found 222.2419.

12: ^1H NMR ($CDCl_3$, 300 MHz, by subtracting peaks for **5**) δ 4.20 (m), 5.16 (m).

Reaction of 1,2-Dehydro-*o*-carborane (1) with [8](2,5)Thiophenophane.[17] A solution of *o*-carborane (2.00 g, 14.0 mmol) in ether (20 mL) was added dropwise to a solution of butyllithium (2.0 M in cyclohexane, 14.0 mL, 28.0 mmol) and ether (20 mL) at 0 °C under an argon atmosphere. The resulting white precipitate was stirred in solution for 1 h at room temperature. The system was then cooled to 0 °C, bromine (2.24 g, 0.72 mL, 14.0 mmol) was added dropwise, and stirring was continued at 0 °C for another 1 h. After this period, the resulting solution was added dropwise to a solution of [8](2,5)-thiophenophane (1.36 g, 7.00 mmol) in ether (10 mL). The reaction mixture was maintained at 0 °C during the addition, after which it was stirred at room temperature for 1 h and then heated to reflux. The progress of the reaction was monitored by periodically analyzing aliquots by GC/MS. After completion of the reaction (≈72h), the mixture was cooled to room temperature, water (20 mL) was added, and the layers were separated. The aqueous layer was extracted with ether (5 × 10 mL), and the ether extracts were combined with the organic layer. The combined extracts, after being washed with water (10 mL) and then saturated brine solution (10 mL), were dried over $MgSO_4$. Removal of the solvent at the rotary evaporator gave a brown semisolid, which was chromatographed (SiO_2/ hexanes) to yield **10** (320 mg, 14%). A small portion of this compound was subjected to preparative GC. A fraction was obtained which contained only new compound **11**.

10: ^1H NMR ($CDCl_3$, 250 MHz) δ 0.80−3.30 (br m, 10 H, B*H*), 1.30 (m, 4 H), 1.45 (m, 4 H), 1.65 (m, 2 H), 1.80 (m, 2 H), 2.45 (m, 2 H), 2.80 (m, 2 H), 4.25 (d, J = 6 Hz, 1H), 5.20 (d, J = 6 Hz, 1H) Crystals of **10** suitable for X-ray analysis were obtained by the slow evaporation of a solution of **10** in 2-propanol.

11: ^1H NMR ($CDCl_3$, 300 MHz) δ 0.80−3.30 (br m, 10 H, B*H*), 1.30 (m, 4 H), 1.45 (m, 4 H), 1.65 (m, 2 H), 1.80 (m, 2 H), 2.45 (m, 2 H), 2.80 (m, 2 H), 6.10 (d, J = 15 Hz, 1 H), 6.35 (d, J = 15 Hz, 1 H); precise mass for calculated $C_{14}{}^{11}B_8{}^{10}B_2H_{28}$ 304.3194, found 304.3158. Crystals of **11** suitable for X-ray analysis were obtained by slow evaporation of a solution of **11** in 2-propanol.

Reaction of 1,2-Dehydro-*o*-carborane (1) with [8](2,5)Furanophane.[24] The bromo anion was prepared as above, and the solution was then added dropwise to a solution of [8](2,5)furanophane (1.35g, 7.57 mmol) in ether (10 mL). The reaction mixture was maintained at 0 °C during the addition, after which it was stirred at room temperature for 1 h and then heated to reflux. The progress of the reaction was monitored by periodically analyzing aliquots by GC/MS. After completion of the reaction (≈72 h), the mixture was cooled, water (20 mL) was added, and the layers were separated. The aqueous layer was extracted with ether (5 × 10 mL), and the ether extracts were combined with the organic layer. The combined extracts, after being washed with water (10 mL) and then saturated brine solution (10 mL), were dried over $MgSO_4$. Removal of the solvent at the rotary evaporator gave a brown semisolid. This crude product was analyzed by ^1H NMR spectroscopy and then was chromatographed (SiO_2/ hexanes) to yield a mixture (803 mg, 33%) of **13** and **14** in a 2:1 ratio. Further attempts to purify these two compounds by preparative GC and HPLC were unsuccessful.

13: ^1H NMR ($CDCl_3$, 270 MHz) δ 0.80−3.40 (br m), 1.15 (m), 1.50 (m), 1.85 (m), 2.00 (m), 6.40 (s).

14: ^1H NMR (by subtracting the peaks for **7**) δ 0.80−3.40 (br m), 1.15 (m), 1.50 (m), 1.85 (m), 4.20 (m), 4.70 (m).

Supporting Information Available: Text presenting X-ray experimental details and tables giving structure solution and refinement parameters, bond lengths, bond angles, and anisotropic thermal parameters for **11** (9 pages). Ordering information is given on any current masthead page.

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