their hydrogen bonds are strong. Consistent with this, the value of the electrostatic stabilization term in the MM2 calculation for the only **DDH** form of **2** is −22.3 kJ/mol, while for two of the **DDH** forms of **5** (though only 7% contributors) it is −23.1 and −23.3 kJ/mol and for two of the **DDH** forms of **6** (12% contributors) it is −22.7 and −22.8 kJ/mol. Similarly, the structural parameters of the hydrogen bonds in **5** and **6** are as good (2.75-Å interoxygen distance and 163° bond angle) as those seen in the energetically more accessible **DDH** forms of **1** and **2**. Also, the shift of 135 cm^{-1} seen in the OH stretching frequency of **5** and **6** is still quite comparable to the 130 cm^{-1} shift seen for the 8-membered ring hydrogen bond in 1,5-pentanediol.[9c]

It is clear that intramolecular hydrogen bonding is a prominent feature in these compounds. Secondly, the constraints of the [*n*.3.3] propellane skeleton significantly affect the balance among available conformers. And, finally, strong intramolecular hydrogen bonding can be manifest even in those molecules whose **DDH** conformers show significant skeletal distortion.

Acknowledgment. The assistance of Doug Hess and Wayne Duncan of the Hewlett Packard Corporation in obtaining the GC-IR results reported herein is gratefully acknowledged.

Supplementary Material Available: Tables of the conformers found in the MM2 calculations, including their energies, oxygen–oxygen distances, X–C–C–X dihedral angles, the O–H–O angles for the hydrogen bonds, and the percent probability for each conformer (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Reactions of Enamines with Dehydro Aromatic Compounds

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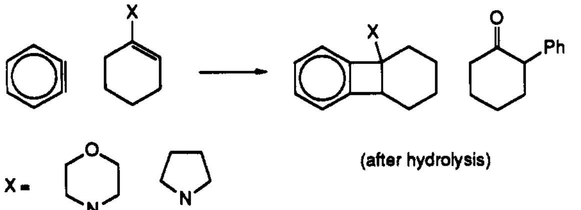
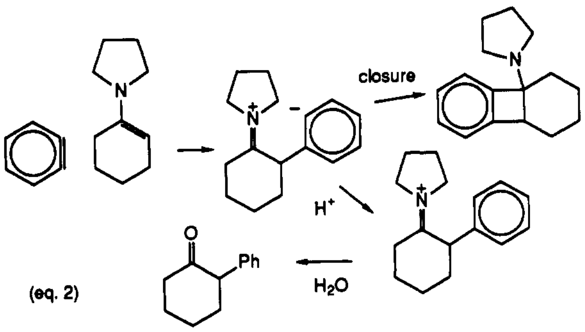
Benzyne reacts with enamines through a combination of ene and 2 + 2 cycloadditions. One of the two possible ene reactions is greatly favored. The three-dimensional intermediate, 1,2-dehydro-*o*-carborane,[1] eschews the 2 + 2 reaction in favor of the ene reaction that is less favored in the benzyne reactions. This preference is rationalized in terms of the different steric demands of the two intermediates.

Almost 30 years ago Martin Kuehne first described the reaction of benzyne with enamines. The reaction led, after hydrolysis, to 2-phenylcyclohexanone and compounds containing four-membered rings (eq 1).[2,3] Although the yields of the products depended upon reaction conditions and the method of benzyne generation, an overall mechanistic scheme was developed in which a dipolar intermediate partitioned between closure to give the aminocyclobutanes and protonation to give an iminium ion, the precursor to the ketone. This view was supported by the relative increase in cyclobutane formation when proton sources were reduced (eq 2).

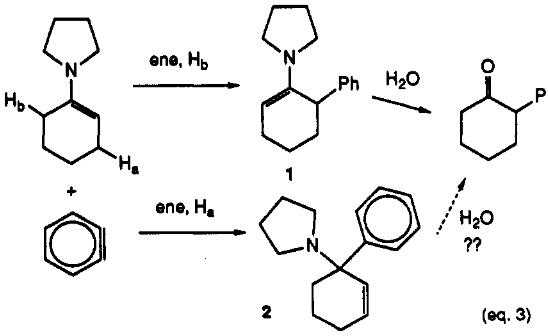


(eq. 1)



(eq. 2)

This scheme is sensible in the context of 1962, and even presages the requirements of the yet-to-be-developed theory of orbital symmetry control in its stepwise 2 + 2 reaction. However, even though at least one recent review accepts the mechanism,[4] there are other possibilities. For example, benzyne was known, even in 1962, to undergo the ene reaction with simple alkenes.[5] There are two possible ene reactions of benzyne and Kuehne's enamines. One of these, compound **1**, would surely lead to the ketone on hydrolysis, and the other, **2**, might (eq 3). Here we present evidence that the concerted[6] ene reaction and the nonconcerted 2 + 2 reaction[7] are in competition in this reaction



(eq. 3)

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[1] 1,2-Didehydro-*o*-carborane is the more correct name.

[2] Kuehne, M. E. *J. Am. Chem. Soc.* **1962**, *84*, 837.

[3] Keyton, D. J.; Griffin, G. W.; Kuehne, M. E.; Bayha, C. E. *Tetrahedron Lett.* **1969**, 4163.

[4] Alt, G. H.; Cook, A. G. In *Enamines: Synthesis, Structure, and Reactions*, 2nd Ed.; Cook, A. G., Ed.; Dekker: New York, 1988; pp 197–198.

[5] Hoffmann, R. W. *Dehydrobenzene and Cycloalkynes*; Academic: New York, 1967; p 197.

[6] Hill, R. K.; Morgan, J. W.; Shetty, R. V.; Synerholm, M. E. *J. Am. Chem. Soc.* **1974**, *96*, 4207.

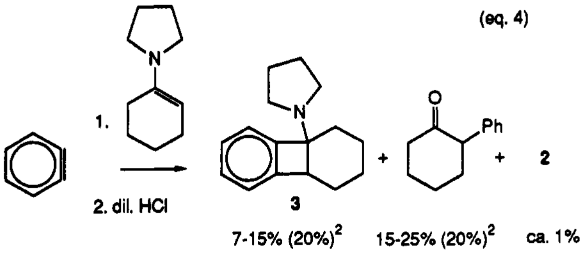
[7] Jones, M., Jr.; Levin, R. H. *J. Am. Chem. Soc.* **1969**, *91*, 6411.

0022-3263/92/1957-3803$03.00/0

and make comparisons between these ene reactions of benzyne and those of its three-dimensional cousin, 1,2-dehydro-*o*-carborane.[1,8]

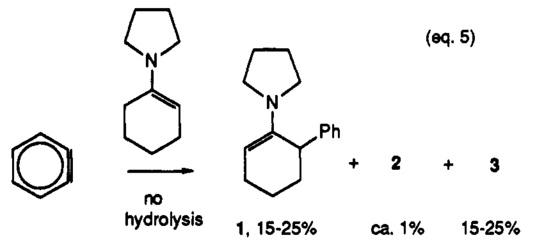
Our plan was a simple one: run the reactions of benzyne with an enamine without a hydrolysis step and take advantage of 30 years of advances in analytical technology to search for the products of ene reaction. Presumably, they should appear in place of the ketone.

When benzyne generated from 1-bromo-2-fluorobenzene and magnesium in tetrahydrofuran (THF) was allowed to react with 1-pyrrolidinocyclohexene followed by Kuehne's hydrolytic workup, we obtained the two reported products, 2-phenylcyclohexanone and **3**, as well as traces of **2**, one of the two possible products of an ene reaction. Identification was by comparison with data in the literature[2] as well as analysis by ^1H and ^{13}C NMR spectroscopy, IR spectroscopy, and high-resolution mass spectrometry. Crucial to the identification of **2** was the presence of two signals for "olefinic" hydrogens in the ^1H NMR spectrum at δ 6.36 (d, 1 H, J = 13 Hz) and 5.85 (m, 1 H). The presence of doublet and multiplet signals argues strongly for the structure assigned in which the double bond occupies the position proximate to the spiro carbon (eq 4).



(eq. 4)

When the reaction was repeated without hydrolysis and the products worked up by distillation, no ketone could be found and a new product, **1**, appeared in its place in approximately the same amount (eq 5).

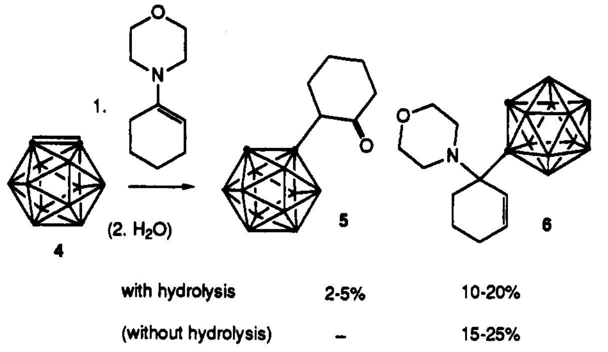


(eq. 5)

In **1** a single "olefinic" hydrogen appeared in the ^1H NMR spectrum as a singlet at δ 4.5. Treatment of the reaction mixture containing **1** with dilute HCl led to 2-phenylcyclohexanone in good yield after extraction with ether. Remaining in the aqueous layer were **3**, **2**, and traces of **1**.

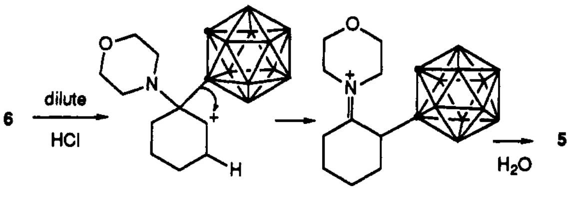
Accordingly, it seems reasonable to replace the previous mechanism in which a dipolar intermediate partitions between protonation and closure with a new, related process in which a concerted[6] 4 + 2 ene reaction and a presumably nonconcerted 2 + 2 cycloaddition[7,8] both lead to products. Although we cannot exclude the possibility that some or all of the observed ene product **1** comes from a dipolar intermediate in this case (as originally proposed[2,4]), there is strong evidence for the concerted ene reaction of benzyne in other systems.[6]

We have recently described a number of ene reactions of 1,2-dehydro-*o*-carborane (**4**), a three-dimensional relative of 1,2-dehydrobenzene, benzyne.[8,9] We have now examined reactions of **4** with 1-morpholinocyclohexene and 1-morpholinocyclopentene. In the first case, reaction with the enamine, followed by mild hydrolysis, yielded a ketone **5** and one product of ene reaction, **6**. When the reaction was examined before hydrolysis the ketone was replaced by a higher yield of **6**. Two other products of the same molecular weight as **6** were formed, but in less than 1% yield (eq 6; in this equation and all equations containing carboranes, the dots represent carbons and the other vertices borons; there is a hydrogen at every unsubstituted vertex).



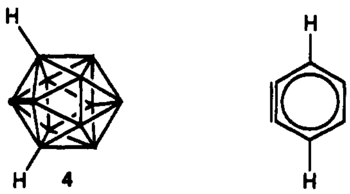
(eq. 6)

The hydrolysis of **6** to **5** presents more problems than the straightforward conversion of enamine **1** to 2-phenylcyclohexanone. Nonetheless, it clearly occurs on hydrolysis and is nearly quantitative when **6** is treated with dilute HCl. We suggest the following protonation–migration–hydrolysis mechanism for the reaction (eq 7).



(eq. 7)

The outstanding differences between the reactions of **4** and those of benzyne are the absence of products of 2 + 2 addition of **4** and the predominant formation of different ene products in reactions of **4** and benzyne. We can speculate on the reason for the change in preference for **1** in the benzyne reaction and **6** in the dehydro-*o*-carborane reaction. Although there are great differences in steric demands imposed by benzyne and **4**, they are not dictated so much by the "fatness" of **4**, as by the direction in which the hydrogens adjacent to the "extra" or "dehydro" bond point. In **4**, the dehydro bond is guarded by two carbon–hydrogen bonds which extend in quite a different direction than do the pair of flanking carbon–hydrogen bonds in benzyne.



4

In the reaction of **4** with the enamine, interaction of the dehydro bond with hydrogen H_b requires one of the

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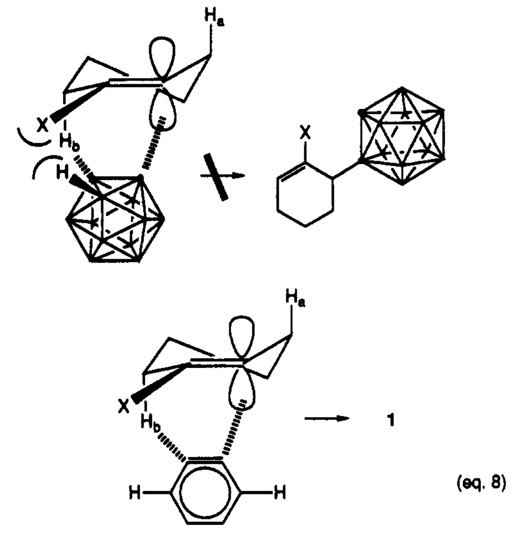
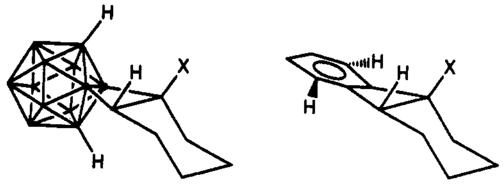
(8) Ghosh, T.; Gingrich, H. L.; Kam, C. K.; Mobraaten, E. C.; Jones, M., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 1313.

(9) Huang, Q.; Gingrich, H. L.; Jones, M., Jr. *Inorg. Chem.* **1991**, *30*, 3254.

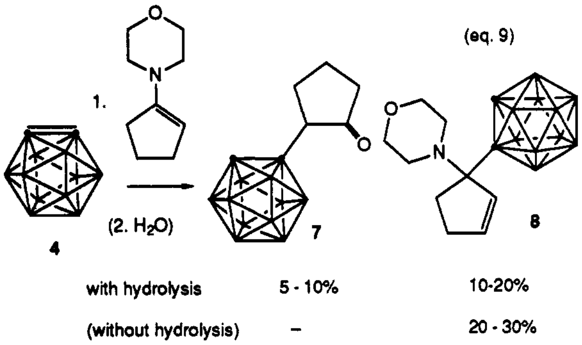
flanking hydrogens to approach ring "X" very closely. By contrast, reaction of benzyne with H_b requires no such energetically unhappy event (eq 8).



The difference in the direction in which the flanking hydrogens point may also help to explain why benzyne forms cyclobutanes and 4 does not. The figure shows the products, but the transition states for their formations must share some of the evident destabilizing interactions.



Reaction of 4 with 1-morpholinocyclopentene is similar. Reaction followed by mild hydrolysis led to 7 and 8 in 5–10% and 10–20% yield, respectively. When the hydrolysis step was omitted, 8 could be isolated in 20–30% yield and 7 could not be found (eq 9). When treated with dilute HCl compound 8 could be hydrolyzed to 7.



In summary, benzyne reacts with enamines through a combination of ene and 2 + 2 cycloadditions. One of the two possible ene reactions is greatly favored. The three-dimensional intermediate, 1,2-dehydro-*o*-carborane, eschews the 2 + 2 reaction in favor of the ene reaction that is less favored in the benzyne reactions. This preference is rationalized in terms of the different steric demands of the two intermediates.

Experimental Section

Reactions were run under Ar. All solvents were purified and dried by standard procedures. Separations and purifications of the crude products were carried out by preparative GC on a 6-ft × 1/4-in. aluminum column packed with 20% OV-17 on Chromosorb WHP 80/100 (carrier gas, helium). Melting points were determined in a capillary melting point tubes. Analytical GC was performed on a 6-m SPB-1 glass capillary column (carrier gas, helium). GC/MS was performed on a 20-ft OV-111 glass capillary column (carrier gas helium). ^1H NMR and ^{13}C NMR spectra were measured at 300 and 75 MHz, respectively.

Yields were determined in the following way. All reactions of 1,2-dehydro-*o*-carborane lead to substantial amounts of polymeric boron-containing materials. Passage through a short silica gel column removes the high molecular weight materials but can lead to hydrolysis of enamines. In sensitive cases (enamines) we assumed that the crude products contained the same percentage of polymeric material and analyzed the crude products without passage through the silica gel column. Compounds collected by preparative GC were weighted and compared to the weight of material injected to determine the yields. The ranges reported reflect the uncertainties noted above and in collection efficiency. They are conservative measures. Literature yields[2] were reproduced quite closely. Analytical GC revealed no substantial unknown volatile products.

Reaction of Benzyne with 1-Pyrrolidinocyclohexene. A. With Hydrolysis. A suspension of magnesium (0.83 g, 34 mmol) in anhydrous THF (100 mL) and 1-bromo-2-fluorobenzene (5.95 g, 34.0 mmol) was stirred vigorously under an Ar flow and warmed gently until the reaction started. Then, 1-pyrrolidinocyclohexene (Aldrich, 5.14 g, 34.0 mmol) was added dropwise. After the reaction mixture was stirred for 6 h at reflux and 24 h at rt, an excess of dilute HCl was added until pH = 2, and the mixture was stirred for another 8 h. The aqueous layer was extracted with ether (4 × 25 mL). The extracts were washed with water until pH = 7, dried ($MgSO_4$) overnight, and concentrated using a rotary evaporator to give the crude product, a brown liquid which contained 2-phenylcyclohexanone (ca. 20% yield). Further purification by preparative GC (20% OV-17 column, 100–220 °C) provided a sample, mp 56–58 °C (lit.[2] mp 54–56 °C).

The aqueous portion was neutralized with dilute NaOH until pH = 8 and then extracted with ether (4 × 25 mL). The extracts were washed with water until pH = 7, dried ($MgSO_4$) overnight, and concentrated using a rotary evaporator to give the crude product, a brown liquid which contained 3 (7–15% yield) and 2 (ca. 1% yield). Further purification by preparative GC (20% OV-17 column, 100–250 °C) provided samples. Compound 3: FT-IR (film) 2937, 749 cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm) 7.09–7.23 (m, 4 H), 3.66 (s, 1 H), 2.78–2.82 (m, 2 H), 2.66–2.69 (m, 2 H), 1.90–2.18 (m, 6 H), 1.76–1.80 (m, 4 H), 1.44–1.48 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ (ppm) 149.3, 146.5, 128.5, 127.6, 123.1, 69.7, 48.5, 45.4, 31.0, 24.5, 24.3, 19.0, 18.5; HRMS calcd for $C_{16}H_{21}N$ 227.1674, found 227.1660. Compound 2: FT-IR (film) 2848, 776, 755 cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm) 7.08–7.67 (m, 5 H), 6.36 (d, 1 H, J = 13 Hz), 5.85 (m, 1 H), 3.73 (m, 1 H), 3.09 (m, 1 H), 2.56 (s, 4 H), 2.00–2.38 (m 4 H), 1.79–1.95 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ (ppm) 134.6, 129.0, 128.0, 127.0, 126.8, 126.2, 66.5, 54.0, 36.9, 33.1, 24.0, 21.8; HRMS calcd for $C_{16}H_{21}N$ 227.1674, found 227.1669.

B. Without Hydrolysis. The reaction was conducted as described above. Ater 6 h at reflux and 24 h at rt, the solution was distilled at 10 mm (bp 80–100 °C) to remove the solvent and unreacted starting materials. The residue was extracted with anhydrous ether (4 × 25 mL), and the extracts were concentrated using a rotary evaporator to give the crude product, a dark brown liquid which contained almost no ketone, but 3 (15–25% yield), 2 (ca. 1% yield), and 1 (15–25% yield). Further purification by preparative GC (20% OV-17 column, 100–250 °C) provided a sample of 1. Compound 1: FT-IR (film) 2935, 758, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm) 7.14–7.37 (m, 5 H), 4.49 (s, 1 H), 3.65 (s, 1 H), 2.94 (m, 2 H), 2.81 (m, 2 H), 1.55–2.35 (m, 8 H), 1.40 (br s, 2 H); ^{13}C NMR ($CDCl_3$) δ (ppm) 145.9, 143.5, 129.1, 128.5, 126.3, 95.4, 58.0, 47.8, 43.2, 33.3, 25.3, 18.1; HRMS calcd for $C_{16}H_{21}N$ 227.1674, found 227.1682.

Hydrolysis of 1. To the reaction mixture containing 1 (ca. 1.3 g) made by procedure B was added an excess of dilute HCl (10%, 4.1 mL) and water (20 mL). The reaction mixture was stirred for 8 h at rt under an Ar flow and then extracted with ether (4 × 25 mL). The extracts were washed with water until pH = 7, dried ($MgSO_4$) overnight, and concentrated using a rotary evaporator to give the crude product, a brown liquid which contained 2-phenylcyclohexanone. Analytical GC revealed only a single peak (>95%) that was shown by preparative GC (20%

OV-17, 100–220 °C) to be 2-phenylcyclohexanone. The yield of hydrolysis was estimated by injecting a portion of a solution of the crude 2-phenylcyclohexanone in ether, measuring the percentage of the injected material corresponding to the product, and using this percentage to calculate the amount of 2-phenylcyclohexanone in the crude material (1.0 g, ca. 96% yield). Response factors were not measured. Further purification by column chromatography (silica gel) and preparative GC provided a sample of 2-phenylcyclohexanone. The acidic aqueous layer was neutralized with dilute NaOH and extracted with ether (4 × 25 mL). The extracts were washed with water until pH = 7, dried ($MgSO_4$) overnight, and concentrated on a rotary evaporator to give a brown liquid which was shown by GC to contain **3**, **2**, and traces of **1**.

Generation of 1,2-Dehydro-*o*-carborane. To a solution of butyllithium (10 mL, 2 M solution in pentane; 20 mmol) in ether (10 mL) at 0 °C under an Ar flow was added dropwise with stirring a solution of *o*-carborane (1.44 g, 10 mmol) in ether (10 mL). After the reaction mixture was stirred at rt for 1 h and cooled to 0 °C, bromine (1.6 g, 10 mmol) was added very slowly. The resulting clear solution was stirred at 0 °C for an additional 0.5 h. The reaction mixture was expected to generate 1,2-didehydro-*o*-carborane[8,9] (~10 mmol) and was used immediately to run the following reactions.

Reaction of 1,2-Dehydro-*o*-carborane with 1-Morpholinocyclohexene. A. With Hydrolysis. To the reaction mixture used for generating 1,2-didehydro-*o*-carborane (10 mmol) was added a solution of 1-morpholinocyclohexene (Aldrich, 3.35 g, 20 mmol) in ether (5 mL). The reaction mixture was warmed to rt, stirred for 1 h, and then heated at reflux for 24 h. Upon cooling, the reaction mixture was treated with water (15 mL). The ethereal layer was separated, washed with water until pH = 7, dried ($MgSO_4$) overnight, and concentrated by using a rotary evaporator to give the crude brown liquid product, which contained two products, **5** (2–5% yield) and **6** (10–20% yield). A further purification by preparative GC (20% OV-17 column, 100–270 °C) provided samples of **5** and **6**. Compound **5** was a white solid; mp 118–120 °C; FT-IR (film): 2590, 2572, 1711 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ (ppm) 5.15 (s, 1 H), 3.28 (m, 1 H), 1.6–2.6 (m, 8 H), 1.2–3.2 (m, 10 H, BH); ^{13}C NMR (C_6D_6) δ (ppm) 206.4, 74.5, 60.8, 53.3, 42.9, 36.7, 27.6, 25.2. Anal. Calcd for $C_8H_{20}B_{10}O$: C, 39.99; H, 8.39. Found: C, 40.22; H, 8.47. Compound **6** was a yellow liquid: ^{1}H NMR ($CDCl_3$) δ (ppm) 5.13 (br s, 1 H), 4.87 (br s, 1 H), 3.6–3.8 (m, 4 H), 3.28 (br s, 1 H), 2.93–3.05 (m, 4 H), 1.61–2.47 (m, 6 H), 0.8–3.5 (br m, 10 H, BH); ^{13}C NMR (C_6D_6) δ (ppm) 144.9,[10] 112.8, 79.6, 67.0, 59.7, 50.8, 36.8, 28.5, 23.9, 16.2; HRMS calcd for $C_{12}H_{27}{}^{11}B_8{}^{10}B_2NO$ 309.3096, found 309.3066.

B. Without Hydrolysis. The reaction was carried out as described above. After cooling, the reaction mixture was distilled at 10 mm (bp 100–120 °C) to remove the solvent and the unreacted starting materials. The residue was extracted with ether (4 × 25 mL), and the extracts were concentrated by using a rotary evaporator to give the crude product, a dark brown liquid which contained a major product **6** (15–25% yield). Further purification by and preparative GC (20% OV-17 column, 100–270 °C) provided a sample of **6**.

Hydrolysis of 6. To the crude reaction mixture made by procedure B containing **6** (0.60 g) was added an excess of dilute HCl (10%, 4.1 mL) and water (20 mL). The reaction mixture was stirred for 8 h at rt under an Ar flow and then extracted with ether (4 × 25 mL). The extracts were washed with water until pH = 7, dried ($MgSO_4$) overnight, and concentrated by using a rotary evaporator to give the crude **5**. Analysis as before (under Hydrolysis of **1**) led to an estimate of 0.42 g of **5** (ca. 96% yield). Further purification by column chromatography (silica gel) and preparative GC (20% OV-17 column, 100–240 °C) provided a sample of **5**.

Reaction of 1,2-Dehydro-*o*-carborane with 1-Morpholinocyclopentene. A. With Hydrolysis. To the reaction mixture used for generating 1,2-didehydro-*o*-carborane (10 mmol) was added a solution of 1-morpholinocyclopentene (Aldrich, 3.06 g, 20 mmol) in ether (5 mL). The reaction mixture was warmed to rt, stirred for 1 h, and then heated at reflux for 24 h. After cooling, the reaction mixture was treated with water (15 mL). The ethereal layer was separated, washed with water until pH = 7, dried ($MgSO_4$) overnight, and concentrated by using a rotary evaporator to give the crude product, a brown liquid, containing **7** (5–10% yield) and **8** (10–20% yield). Further purification by preparative GC (20% OV-17 column, 100–270 °C) provided samples of **7** and **8**. Compound **7** was a white solid: mp 100.5–102.5 °C; FT-IR (film) 3079, 2585, 1739, 725 cm^{1-}; ^{1}H NMR ($CDCl_3$) δ (ppm), 5.05 (s, 1 H), 2.83 (m, 1 H), 1.7–2.5 (m, 6 H), 1.2–3.2 (br m, 10 H, BH); ^{13}C NMR (C_6D_6) δ (ppm) 212.1 73.3, 58.7, 51.5, 38.4, 32.4, 19.4; HRMS calcd for $C_7H_{18}{}^{11}B_8{}^{10}B_2O$ 226.2361, found 226.2318. Compound **8** was a yellow liquid: ^{1}H NMR ($CDCl_3$) δ (ppm) 4.90 (s, 1 H0, 4.48 (s, 1 H), 3.72 (br s, 4 H), 3.49 (d, *J* = 7.5 Hz, 1 H), 2.88 (m, 2 H), 2.65 (m, 2 H), 2.05–2.6 (m, 4 H), 1.2–3.2 (br m, 10 H, BH); ^{13}C NMR (C_6D_6) δ (ppm) 151.8,[10] 109.3, 79.3, 66.3, 59.6, 50.4, 47.1, 32.2, 28.8; HRMS calcd for $C_{11}H_{25}{}^{11}B_8{}^{10}B_2$ NO 295.2940, found 295.2926.

B. Without Hydrolysis. The reaction was carried out as described above. After cooling, the reaction mixture was distilled at 10 mm (bp 100–120 °C) to remove the solvent and the unreacted starting materials. The residue was extracted with ether (4 × 25 mL), and the extracts were concentrated by using a rotary evaporator to give the crude product, a dark brown liquid which contained **8** (20–30% yield). Further purification by preparative GC (20% OV-17 column, 100–270 °C) provided a sample of **8**.

Hydrolysis of 8. To the crude reaction mixture containing **8** (0.50 g) made by procedure B was added an excess of dilute HCl (10%, 4.1 mL) and water (20 mL). The reaction mixture was stirred for 8 h at rt under an Ar flow and then extracted with ether (4 × 25 mL). The extracts were washed with water until pH = 7, dried ($MgSO_4$) overnight, and concentrated on a rotary evaporator to give **7**. Analysis as before (under Hydrolysis of **1**) led to an estimate of the yield of **7** as ca. 97%. Further purification by column chromatography (silica gel) and preparative GC (20%, OV-17 column, 100–240 °C) provided a sample of **7**.

Acknowledgment. Support for this work from the National Science Foundation through Grants CHE-8800448 and CHE-90-24996 is gratefully acknowledged. A.L.M. thanks the MARC program of the NIH for a Fellowship.

Registry No. **1**, 26974-24-3; **2**, 141346-32-9; **4**, 127065-16-1; **5**, 141346-33-0; **6**, 141346-34-1; **7**, 141346-35-2; **8**, 141346-36-3; benzyne, 462-80-6; 1-pyrrolidinocyclohexene, 1125-99-1; 1-bromo-2-fluorobenzene, 1072-85-1; 1-morpholinocyclohexene, 670-80-4; 1-morpholinocyclopentene, 936-52-7; *o*-carborane, 16872-09-6.

Supplementary Material Available: ^{1}H NMR spectra of compounds **1**–**3** and **5**–**8** (7 pages). Ordering information is given on any current masthead page.

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(10) In neither **6** nor **8** can we be certain of the position of both olefinic carbons. The signals at 112.8 (**6**) and 109.3 (**8**) ppm are strong and in the "normal" range. Weaker signals appear at 144.9 (**6**) and 151.8 (**8**) and are tentatively assigned to the other olefinic carbons. Note that the ^{1}H NMR spectra leave no doubt as to the presence of two different olefinic hydrogens.