Articles

## The Mechanism of 1,4-Addition of Dibromomethylene

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Dibromomethylene produced from the Seyferth reagent (PhHgCBr₃) may react either as a free species or while complexed with Lewis bases. Recent reports of the long-sought 1,4-addition to dienes of dibromomethylene, produced from the Seyferth reagent, to form five-membered rings therefore could be based on reactions of either free or complexed carbenes. These modes of reaction may be distinguished by product ratio dependence on the diene concentration, on the solvent basicity, and on the basicity of additives. We have found that the addition of Seyferth-generated dibromomethylene to the exo dienes 1 and 2 gives a ratio of 1,2- and 1,4-addition that is independent of all these considerations of concentration, solvent, and additive. These observations lend strong support to the assertion that 1,4-addition occurs by a concerted, symmetry-allowed pathway. When the carbene source is 11,11-dibromo-1,6-methano[10]annulene, addition to 1,2-dimethylenecyclohexane (1) gives the same proportion of 1,4-addition as for the Seyferth reagent, indicating a free carbene in both cases. Addition of dibromomethylene from the annulene to the sterically congested 2, however, gives a much augmented proportion of 1,4-addition, in fact the major pathway for the first time. This observation may indicate a complexed carbene in this case.

Dienes may react with singlet methylene either in a 1,2-sense to form a vinylcyclopropane or in a 1,4-sense to form a cyclopentene (eq 1). Both modes are allowed by

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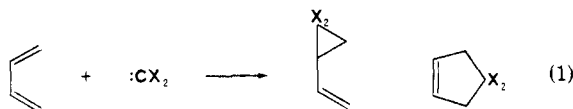
orbital symmetry.[2] 1,4-Addition of carbenes could be a very useful entry into five-membered rings, but until recently this mode was essentially unknown. In the first place, the unfavorable cisoid conformation is necessary for 1,4-addition. Secondly, as pointed out by Fujimoto and Hoffman,[2] the close approach necessary for reaction gives rise to substantial four-electron repulsion between the lone pair on methylene and the filled π orbitals on the diene.

Certain special cases notwithstanding, the first example of 1,4-addition to a simple diene was reported by Bickelhaupt and co-workers,[3] who found that dichloromethylene added to 1,2-dimethylenecycloheptane by both 1,2- and 1,4-modes, in the ratio 99/1. They later generalized the result to the five-, six-, and eight-membered rings, and to dibromomethylene and bromochloromethylene.[4] The highest yields were found with dibromomethylene. The six-membered ring (1) gave up to 10% 1,4-addition, and the seven-membered ring gave up to 19%. This significant discovery was attributed to the preexisting cisoid conformation built into the ring. The dependence of the yield of 1,4-addition on ring size suggested that steric effects influence the reaction to some degree. Electronic effects are reflected in the large dependence of the yield on the identity of the halogen substituents on methylene.

Mayr and Heigl[5] utilized the same strategy of building the cisoid conformation into the substrate, but they also reduced 1,2-reactivity by substituting all the saturated carbon atoms with methyl groups (2). Reaction of 2 with dichloromethylene gave up to 27% 1,4-addition and with dibromomethylene up to 30%, the highest proportion reported up to now.

Both research groups used a variety of methods for the generation of dibromomethylene, including the Seyferth procedure with organomercurials. The independence of the yield of 1,4-addition on the mode of carbene generation is good evidence for the intervention of free carbenes. We recently reported that the Seyferth reagent, e.g., PhHgCBr₃, produces not only the free singlet carbene, which leads to stereospecific cyclopropanation (1,2-addition), but also a complexed form of the carbene, which leads to stereomutated cyclopropane and rearrangement[6,7] (eq 2). At least for generation by the Seyferth procedure,

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it is not clear whether 1,4-addition comes from free or complexed carbene. It is possible that the mercury atom

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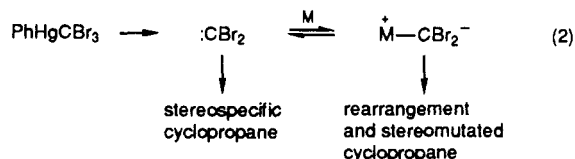(2) Fujimoto, H.; Hoffman, R. *J. Phys. Chem.* 1974, *78*, 1167-1173.

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in the complexed form plays a role, and that 1,4-addition occurs in a two-step process via diradicals or dipoles. Fortunately, these mechanistic alternatives are testable by concentration studies. Moreover, the relative amounts of pathways via free and complexed carbene may be controlled by suitable choice of solvent and additives.[8] We have carried out these mechanistic tests on the substrates **1** and **2** and report the results herein. We have found not only that 1,4-addition of dibromomethylene from the Seyferth reagent is almost certainly a concerted reaction of the free carbene, but also that the yield of 1,4-addition may be increased to as high as 65% by use of an alternative source of carbene.

Results

Synthesis. 1,2-Dimethylenecyclohexane (**1**) was prepared according to the method of Wichlatz and Short[9] by elimination of two moles of water from *cis*-1,2-bis(hydroxymethyl)cyclohexane.[10] Octamethylcyclopentene was prepared according the method of Mayr et al.[5,11] 3-Methyl-1-pentyn-3-ol was converted to 3-methyl-3-penten-2-one, which was treated with methyllithium to form 2,3-dimethyl-3-penten-2-ol. Addition of hydrogen chloride to the alcohol, mixed with its diene elimination product, gave 4-chloro-3,4-dimethyl-2-pentene and its allylic isomer. Treatment of the mixed allylic chlorides with zinc chloride in the presence of 2,3-dimethyl-2-butene produced octamethylcyclopentene.[12] Addition of bromine to the cyclopentene, followed by reaction with magnesium, produced 1,2-dimethylene-3,3,4,4,5,5-hexamethylcyclopentane (**2**).[13] The amount of magnesium is critical, as an excess will result in formation of a dimer.

Addition of dibromomethylene was carried out by two methods. The Seyferth procedure required preparation of phenyl(tribromomethyl)mercury.[6] In order to have a procedure for the addition of dibromomethylene in a nonnucleophilic medium and in the absence of metals, we prepared the annulene **3**. Neutral extrusions of carbenes from annulenes and related materials have been reported,[14] but no detailed procedure for the preparation of **3** is available. Consequently, we adapted the reported procedure of Nelson and Untch[15] for the analogous dichloroannulene.

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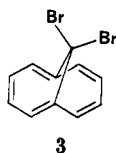
Product Studies. Addition of dibromomethylene produced from the Seyferth reagent to 1,2-dimethylene-

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Table I. Relative Amounts of Products from the Reaction of Diene 2 with Varying Amounts of the Seyferth Reagent in Benzene at 70 °C for 24 h

| $PhHgCBr_3/2$, molar ratio	4	5	6	4/5
0.1	54.7	34.7	10.6	1.58
0.2	52.7	36.2	11.1	1.46
0.3	53.5	35.1	11.4	1.52
0.4	55.0	34.0	11.0	1.62
0.5	54.3	34.5	11.2	1.57

Scheme I
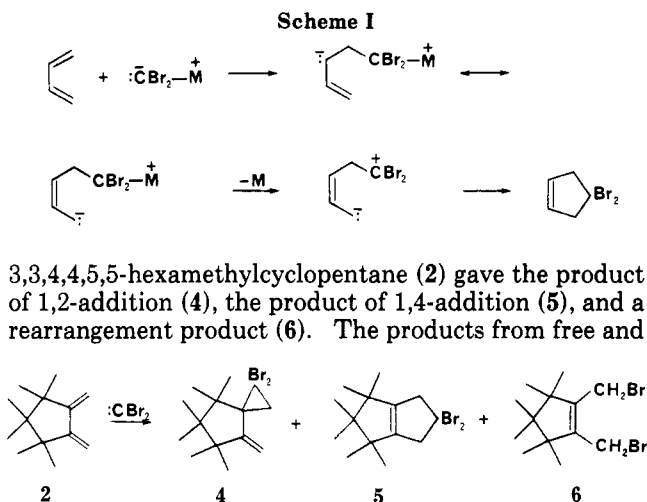
3,3,4,4,5,5-hexamethylcyclopentane (**2**) gave the product of 1,2-addition (**4**), the product of 1,4-addition (**5**), and a rearrangement product (**6**). The products from free and

complexed Seyferth-generated carbene (eq 2) have different dependencies on the concentration of the substrate.[6] Consequently, we carried out the reaction with varying ratios of Seyferth reagent and diene **2** (Table I). Compound **6** proved to be a decomposition product probably from **4**. The respective amounts of **4**, **5**, and **6** after 2 h were 64.3, 35.1, and 0.6%, after 3 h were 65.4, 33.6, and 1.0%, and after 24 h (the conditions of Table I) 54.7, 34.7, and 10.6%. All later experiments were carried out with a reaction time of 3 h in order to minimize the rearranged product.

Our previous experiments[8] showed that the ratio of pathways from free and complexed carbene was strongly dependent on the solvent and the presence of certain additives. Table II shows the results of three such conditions, which previously resulted in major alteration of the ratio of pathways: CCl_4 as solvent, nitrobenzene as solvent, and zinc iodide as an additive in benzene.

Reaction of the diene **2** with dibromomethylene formed from the annulene **3** was carried out in several solvents and with varying ratios of annulene to diene (Table III).

The sterically less congested diene **1** also produces the 1,2- and 1,4-adducts (**7** and **8**, respectively) on reaction with dibromomethylene.[4] Table IV sets out the results of the
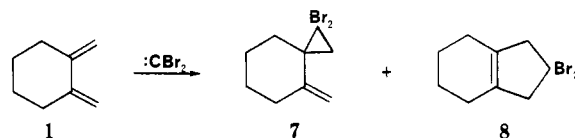
addition with either the Seyferth reagent or the annulene **3** as the source of dibromomethylene, as a function of the ratio of the carbene source and the diene, again as a test of the relative contributions from free and complexed carbene.

Discussion

The primary objective of this study was to determine whether 1,4-addition occurs by reaction of a free carbene.

Table II. Relative Amounts of Products from the Reaction of Diene 2 with Varying Amounts of Seyferth Reagent, Solvent, and Lewis Acid Additive at 70 °C for 3 h

solvent	PhHgCBr₃/diene, molar ratio	Zn₂I₂/diene, molar ratio	4	5	6	4/5
CCl₄	0.1	0.0	66.7	33.3	a	2.00
	0.2	0.0	65.5	34.5	a	1.90
	0.3	0.0	64.8	35.2	a	1.84
	0.4	0.0	65.5	34.5	a	1.90
PhNO₂	0.1	0.0	62.4	30.8	6.8	2.03
	0.2	0.0	61.5	32.0	6.5	1.92
	0.3	0.0	61.7	32.0	6.3	1.93
	0.4	0.0	60.6	30.8	8.6	1.97
C₆H₆	0.1	0.0	67.1	32.9	a	2.04
	0.1	0.5	68.5	29.3	2.2	2.34
	0.1	1.0	67.5	30.2	2.3	2.24

a Not detected.

Table III. Relative Amounts of Products from the Reaction of Diene 2 with Varying Amounts of Annulene 3 at 70 °C for 3 h

solvent	3/2	4	5	6	4/5
C₆H₆	0.1	36.4	63.6	a	0.57
	0.2	36.6	63.4	a	0.58
	0.3	35.6	64.4	a	0.55
	0.4	34.6	65.4	a	0.53
CCl₄	0.2	36.4	63.6	a	0.57
CH₃CN	0.1	35.0	57.4	7.6	0.61
	0.2	33.5	58.8	7.6	0.57
	0.3	34.9	58.4	6.7	0.60
	0.5	33.6	59.0	7.4	0.57

a Not detected.

Table IV. Relative Amounts of Products from the Reaction of Diene 1 with Varying Amounts of the Seyferth Reagent or Annulene 3 in Benzene at 70 °C for 3 h

carbene source	carbene/1	7	8	7/8
PhHgCBr₃	0.1	87.8	12.2	7.2
	0.2	89.4	10.6	8.4
	0.3	89.2	10.8	8.3
	0.4	89.0	11.0	8.1
3	0.1	89.4	10.6	8.4
	0.2	89.7	10.3	8.7
	0.3	89.3	10.7	8.3

Mayr[5] and Bickelhaupt[4] found similar yields for different carbene sources (Seyferth reagent, phase-transfer catalysis), in support of this conclusion. In the case of the Seyferth reagent, 1,4-addition may occur by reaction of either free or complexed carbene.[6] The free carbene should react in a concerted fashion, but the complexed carbene should react stepwise: initial reaction with one double bond, loss of the complexing agent, and finally formation of the second bond (Scheme I). The dipolar (shown), diradical, or charge complex intermediate may choose between 1,2- and 1,4-modes on purely steric grounds, and the problem of four-electron repulsion in the 1,4-mode is obviated. In system 2, the presence of the geminal methyl groups at the allylic position interferes strongly with 1,2-addition. Thus, if complexed carbene is present, 1,4-addition should be preferred more strongly. For the less sterically constrained 1, the preference for 1,4-addition from a complexed carbene should be lower.

As we showed in our earlier studies,[6,8] the primary complexing agents (M) under normal Seyferth conditions (benzene solvent) are the solvent and the phenyl ring of unreacted Seyferth reagent itself. Variation of the relative amounts of solvent, Seyferth reagent, and alkene has a significant effect on mechanistic partition between free and complexed carbene, thereby influencing the proportion of stereomutation and rearrangement. if 1,4-addition occurs wholly or in part via the complexed carbene and 1,2-ad-

dition via the free carbene, then the relative proportions of products 4 and 5 from 2 should depend on the ratio of diene to Seyferth reagent. As Table I shows, there is essentially no effect on this ratio. There is no trend in the ratio of 4 to 5 over a 5-fold change in the ratio of reactants, in contrast to the case for both rearrangement[6] and stereomutation,[7] for which a clear inverse dependence on concentration of alkene was observed.

We also found that the proportion of complexed carbene is very sensitive to the nature of the solvent and the presence of certain additives.[8] Carbon tetrachloride or nitrobenzene as solvent and zinc iodide as additive tended to raise the proportion of products from complexed carbene. The results in Table II show that these changes in conditions had no systematic effect on the ratio of 1,2- to 1,4-addition for 2.

The less sterically congested diene 1, for which we expected lower sensitivity to these tests anyway, also exhibited no systematic variation in the proportions of 1,2- and 1,4-addition on a 4-fold change in the ratio of Seyferth reagent to diene (Table IV).

These results are consistent with a 1,4-addition of the Seyferth-generated free carbene to both 1 and 2 in an essentially concerted reaction.

To date, the highest yields of 1,4-addition have been in the range 30–35% for substrate 2, both by Mayr[5] and us (Tables I and II). Consequently, it was of some surprise when we observed that dibromomethylene generated from the annulene 3 in its reaction with 2 produced 1,4-addition for the first time as the major pathway. As Table III shows, 1,4-addition comprises almost two-thirds of the product mixture. Moreover, the ratio of 1,2- to 1,4-addition is independent of the ratio of carbene source to substrate and of the use of carbon tetrachloride or acetonitrile as solvent.

Vogel and co-workers[16] have presented evidence that carbene extrusion from methanoannulenes such as 3 occurs by a stepwise process under electron impact (eq 3). If thermal decomposition takes a similar pathway,[19] we might
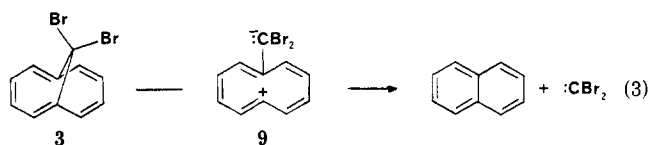
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expect that the diene **2** would react with either the complexed form **9** shown in eq 3 or the free carbene. Such a process would not be influenced by the concentration ratio of annulene to diene or by the changes in medium, provided that reaction with diene occurred primarily with the dipolar or diradical form **9**. Such a species would attack the diene **2** by a mechanism similar to that in Scheme I. The intermediate shown in Scheme I after methylene transfer (the dipole or diradical) would then choose between 1,2- and 1,4-addition on steric grounds, leading to the observed result of favored 1,4-addition.

This explanation for the very high yields of 1,4-addition from annulene **3** is offered as a hypothesis, and an alternative may be preferable. If true, however, this explanation means that the enhanced amount of 1,4-addition arises from a nonconcerted pathway, which is theoretically of less interest. The observation that the sterically less congested diene **1** does not give enhanced amounts of 1,4-addition when annulene **3** is the source of carbene (Table IV) is in agreement with a steric cause for the enhanced proportion of 1,4-addition of annulene-generated dibromomethylene to **2**.

Conclusions

The ratio of products from 1,2- and 1,4-addition of Seyferth-generated dibromomethylene to dienes **1** and **2** is independent of the concentration of the diene, of the nucleophilicity of the solvent, and of the presence of zinc iodide as an additive. The ratio of products from free and complexed carbene normally is sensitive to these factors. These results are consistent with a 1,4-addition that occurs entirely from the free carbene, by a concerted, symmetry-allowed process. The proportion of 1,4-addition is significantly enhanced when dibromomethylene generated from annulene **3** adds to the sterically congested diene **2**. This unique result is consistent with a stepwise addition in this case.

Experimental Section

Proton NMR spectra were obtained on a Varian XLR-400 spectrometer. Chemical shifts are reported in parts per million downfield from Me$_4$Si. Mass spectra were obtained on a Hewlett-Parkard Model 5985B GC-MS system. Gas chromatography was performed on a Hewlett-Packard 5890A gas chromatograph with a capillary column packed with HP-1 Methyl Silicon Gum at 120 °C with the flame ionization detector at 180 °C. Peak areas were measured by electronic integration on a Hewlett-Packard 3393A reporting integrator. Values shown in the tables were obtained by averaging the results from three or four injections.

cis-**1,2-Bis(hydroxymethyl)cyclohexane** was prepared according to the method of Bartlett et al.[10] in 67% yield: bp 104 °C (0.7 mmHg); ^{1}H NMR (CDCl$_3$) δ 1.4–1.9 (m, 10 H), 3.53 (q, 2 H, J_{vic} = 4.0 Hz, J_{gem} = –11.2 Hz), 3.71 (q, 2 H, J_{vic} = 7.9 Hz, J_{gem} = –11.2 Hz), 4.36 (s, 1 H), 4.38 (s, 1 H).

1,2-Dimethylenecyclohexane (1) was synthesized according to a U.S. Patent[7] in 74% yield: bp 56 °C (88 mmHg) (lit.[7] bp 48.8–49.4 °C (55 mmHg)), refractive index n^{20}_D = 1.4750; ^{1}H NMR (CDCl$_3$) δ 1.62 (m, 4 H, aliphatic β), 2.23 (m, 4 H, aliphatic α), 4.61 (s, 2 H), 4.90 (s, 2 H).

3-Methyl-3-penten-2-one.[11,13] Into a 1-L, two-necked flask equipped with a dropping funnel and a condenser were placed 200 mL of CHCl$_3$, 120 mL of glacial HOAc, and 10 mL of concentrated H$_2$SO$_4$, and the mixture was heated to 80 °C. Over 15 min, 98.2 g (1.0 mol) of 3-methyl-1-pentyn-3-ol was added. The reaction mixture was heated under reflux for an additional 1 h and was cooled to room temperature. Ice water (300 mL) was added, and the mixture was extracted with 300 mL of ethyl ether. The red water phase was additionally washed with 150 mL of ether, and the combined ether layers were neutralized in a 5-L beaker with NaHCO$_3$. The layers were separated, the ether layer was washed with saturated NaHCO$_3$, the organics were dried (MgSO$_4$), and the solvent was removed. Distillation at 66 °C (58

mmHg) (lit.[13] bp 35–37 °C (30 mmHg)) gave the product: 70 g (70%); ^{1}H NMR (CDCl$_3$) δ 1.77 (s, 3 H), 1.86 (d, 3 H), 2.30 (s, 3 H), 6.75 (d, 1 H, J = 6.8 Hz).

2,3-Dimethyl-3-penten-2-ol.[11,13] Into a 1-L, three-necked flask with a N$_2$ inlet, dropping funnel, reflux condenser, and stirrer was placed 10.7 g (1.54 mol) of Li in 120 mL of ether ether. Methyl iodide (99.3 g, 0.7 mol) in 120 mL of ethyl ether was added over 3 h at a rate to allow ether to reflux slowly. The reaction mixture was stirred for an additional 2 h under reflux and was cooled with an ice water bath. To this cooled solution (0 °C) was added 55.7 g (0.57 mol) of 3-methyl-3-penten-2-one over a period of 2 h, and the reaction mixture was left at 0 °C overnight. The unreacted Li pieces were removed, and the organic phase was washed with saturated NaCl (with caution) and dried (MgSO$_4$). The ether was removed, and the residue was distilled to give 25 g of 2,3-dimethyl-3-penten-2-ol and 7 g of 2,3-dimethyl-1,3-pentadiene. For the alcohol: ^{1}H NMR (CDCl$_3$) δ 1.32 (s, 6 H), 1.60 (d, 3 H, J = 6.8 Hz), 1.67 (s, 3 H), 5.57 (q, 1 H, J = 6.8 Hz). For the diene: ^{1}H NMR (CDCl$_3$) δ 1.73 (d, 3 H, J = 7.2 Hz), 1.80 (s, 3 H), 1.90 (s, 3 H), 4.86 (s, 1 H), 4.97 (s, 1 H), 5.69 (q, 1 H, J = 7.2 Hz).

4-Chloro-3,4-dimethyl-2-pentene and 4-Chloro-2,3-dimethyl-2-pentene.[11,13] A stream of HCl was passed through 25 g of the above mixture of alcohol and diene in 150 mL of pentane for 1 h. After separation from water, the organic phase was dried (MgSO$_4$) and distilled at 63 °C (47 mmHg) to give 16.2 g of the two chloroalkenes in a ratio of 1/1.17: ^{1}H NMR for 4-chloro-3,4-dimethyl-2-pentene (CDCl$_3$) δ 1.63 (d, 3 H), 1.73 (s, 6 H), 1.81 (s, 3 H), 5.63 (q, 1 H, J = 6.6 Hz); ^{1}H NMR for 4-chloro-2,3-dimethyl-2-pentene (CDCl$_3$) δ 1.54 (d, 3 H, J = 6.4 Hz), 1.69, 1.71 (2 s, 6 H), 1.76 (s, 3 H), 5.26 (q, 1 H, J = 6.4 Hz).

1,2,3,3,4,4,5,5-Octamethyl-1-cyclopentene was prepared according to the literature[11,13] in 46% yield: bp 37–42 °C (0.3 mmHg); ^{1}H NMR (CDCl$_3$) δ 0.77 (s, 6 H), 0.87 (s, 12 H), 1.5 (s, 6 H).

1,2-Bis(bromomethyl)-3,3,4,4,5,5-hexamethyl-1-cyclopentene was prepared according to Klein and Mayr.[12,13] Further purification on a silica gel column gave pure product in 50% yield: ^{1}H NMR (CDCl$_3$) δ 0.81 (s, 6 H), 1.06 (s, 12 H), 4.07 (s, 4 H).

1,2-Dimethylene-3,3,4,4,5,5-hexamethylcyclopentane (2).[11] To a solution of 1.3 g (3.8 mmol) of 1,2-bis(bromomethyl)-3,3,4,4,5,5-hexamethyl-1-cyclopentene in 15 mL of tetrahydrofuran were added 0.19 g (7.7 mmol) of Mg and a crystal of iodine. After heating for 2 h under reflux, H$_2$O was added, and the mixture was extracted with petroleum ether. The organic layers were dried, and the solvent was removed. Purification on a silica gel column with hexane as an eluent gave the product (0.5 g, 73%), which requires storage under N$_2$ at temperatures below 0 °C: ^{1}H NMR (CDCl$_3$) δ 0.76 (s, 6 H), 1.07 (s, 12 H), 4.77 (s, 2 H), 5.38 (s, 2 H).

11,11-Dibromotricyclo[4.4.1.0^{1,6}]undeca-3,8-diene was prepared according to procedure by Vogel[17] in 40% yield: mp 119–122 °C from methanol; ^{1}H NMR (CDCl$_3$) δ 2.36–2.52 (m, 8, AB portion of ABX), 5.53 (s, 4 H); TLC showed one spot at R_f = 0.50 (isotrelin R_f = 0.56).

11,11-Dibromotricyclo[4.4.1.0^{1,6}]undeca-2,4,8-triene was prepared according to the modified procedure of Nelson and Untch.[14] In a 500-mL flask equipped with a reflux condenser and a N$_2$ inlet were stirred 12.3 g (0.04 mol) of undecadiene and 27.2 g (0.12 mol) of DDQ in 200 mL of purified and dried dioxane[18] at room temperature for 24 h and then at 80 °C for 12 h. The dark orange-brown mixture was cooled to room temperature, dioxane was removed under vacuum, and 1400 mL of hexane was added and stirred for 1 h. The mixture was filtered to remove the reducd DDQ, and the filtrate was washed with H$_2$O (5 × 100 mL). The aqueous layers initially were dark red and became successively lighter. The hexane solution was dried (MgSO$_4$) and filtered, and the solvent was removed under reduced pressure to yield a dark powder. The powder was placed as a solid at the top of the column and eluted with hexane until evaporation yielded no more of the fluffy, white crystals: 9.5 g (79%); mp 129–132 °C; ^{1}H NMR (CDCl$_3$) δ 2.30, 2.36, 2.77, 2.83 (m, 4 H, J = 16.5 Hz), 5.53 (broad s, 2 H), 5.75–5.79, 6.18–6.22 (AA'BB', 4 H); TLC showed one spot at R_f = 0.46.

8,9,10,11-Tetrabromotricyclo[4.4.1.0^{1,6}]undeca-2,4,8-triene.[14] In a 500-mL, round-bottomed flask fitted with a mechanical stirrer, an alcohol thermometer, an additional funnel, and an inlet tube for N$_2$ was dissolved 3.02 g (0.01 mol) of the triene in 200

mL of dry CH_2Cl_2 (distilled from CaH_2). Bromine (1.6 g, 0.01 mol) in 30 mL of CH_2Cl_2 was added dropwise at -78 °C over 45 min. The resulting orange solution was stirred for an additional 10 min and was warmed to room temperature. The solvent was removed to give a yellow powder. The crude product (4.5 g) was applied as a solid to the top of a silica gel column and eluted with cyclohexane. The product appeared as a white band in the translucent column while the colored impurities remained near the origin. The yield was 2.3 g (50%): mp 124-125 °C; ^{1}H NMR ($CDCl_3$), δ 2.46-2.52, 2.70-2.75, 3.21-3.26 (m, 4 H), 3.91-3.98, 4.28-4.35 (m, 2 H), 5.63-5.68, 6.17-6.26 (AA'BB', 4 H); TLC showed one spot at R_f = 0.32.

1,6-Dibromomethano[10]annulene (3).[14] In a 500-mL, two-necked, round-bottomed flask with an air condenser were dissolved 4.0 g (0.0087 mol) of the tetrabromo triene and 10.6 g (0.085 mol) of 1,5-diazobicyclo[4.3.0]non-5-ene in 170 mL of dry dimethylformamide (distilled over CaH_2 and stored under molecular sieves, 4 Å). The light yellow solution was magnetically stirred under N_2 at room temperature for 3 days. The resulting orange solution was poured into 100 mL of H_2O, and 100 mL of 3 N HCl was added. The mixture was extracted (5×) with ether, and the green-yellow ether layer was separated from the lower orange, cloudy aqueous layer. The combined ether layers were washed with H_2O and dried ($MgSO_4$), and the solvent was removed under vacuum. The crude product was purified on a silica gel column by elution with hexane. Crystallization from ether gave fluffy yellow crystals: 0.5 g (20%); mp 98 °C; ^{1}H NMR ($CDCl_3$) δ 6.76-6.94 (m, unresolved pattern); UV (cyclohexane) 387 (vw), 285 (w), 257 (s), 222 (m) nm; IR (KBr) 1559, 1311, 1238, 1181, 823, 757, 569, 564, 462, 417 cm^{-1}.

Phenyl(tribromomethyl)mercury[19] was prepared in 60-75% yield, mp 119-120 °C (lit.[19] mp 118-120 °C), as white needles from hexane/$CHCl_3$ solvent.

Reaction of Annulene 3 with the Dienes. The reaction at 10 mol % of diene **2** with 1 mol % of annulene **3** is given as an example. A stock solution of 0.07 g (3.93 × 10^{-4} mol) of diene **2** and 4.30 g (5.51 × 10^{-2} mol) of benzene was placed in a 5-mL volumetric flask. Into a tube containing 2.4 mg of annulene **3** (7.85 × 10^{-6} mol) was quickly added 1 mL of stock solution and 1 mL of benzene. The tube was stoppered and placed in dry ice. The reaction mixture was degassed by four repetitions of pumping, thawing, and refreezing on a vacuum line at 0.05 mmHg. After the final degassing cycle, the tube was carefully sealed. Individual reaction tubes were marked and stored at dry ice temperature until an entire set had been prepared and sealed. The tubes were then immersed in a bath at 70 °C for 3 h. At that time the tubes were removed from the bath and stored in a dry ice bath for processing, which consisted of thawing the solution, opening the tube, and analyzing the raw material by GC gas chromatography. From each sample, the solvent was removed under vacuum, $CDCl_3$ was added, and the NMR integration was performed. The ratio was established from integration of characteristic protons on the three- and five-membered rings of the product. The overall yield ranged from 50 to 65% based on a GC analysis of volatile materials. The products from **2** were **4** [^{1}H NMR ($CDCl_3$) δ 0.90, 0.93, 1.09, 1.19 (four s, 12 H), 1.12 (s, 6 H), 1.75 (s, 2 H), 4.65, 5.13 (m, 2 H]] and **5** [^{1}H NMR ($CDCl_3$) δ 0.86 (s, 6 H), 0.95 (s, 12 H), 3.36 (s, 4 H)]. The products from **1** were **7** [^{1}H NMR ($CDCl_3$) δ 1.7-2.0 (m, 8 H), 2.24 (td, 1 H), 2.45 (dt, 1 H), 4.64, 4.94 (d, 2 H)] and **8** [^{1}H NMR ($CDCl_3$) δ1.7-2.0 (m, 8 H) 3.45 (s, 4 H)].[21]

(21) Since the completion of this paper, stereochemical evidence in favor of a concerted, one-step mechanism has been reported for 1,4-addition. Kraakman, P. A.; de Wolf, W. H.; Bickelhaupt, W. *J. Am. Chem. Soc.* **1989**, *111*, 8534-8535. Also see: Le, A. N.; Jones, M., Jr.; Bickelhaupt, F.; de Wolf, W. H. *Ibid.* **1989**, *111*, 8491-8493.

Diastereoselectivity of Organometallic Additions to Nitrones Bearing Stereogenic N-Substituents[1]

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The diastereoselectivity of organometallic additions to nitrones bearing stereogenic α-arylethyl, β-methoxyalkyl, and β-(silyloxy)alkyl substituents on nitrogen has been investigated. High and complementary diastereoselectivity (90-94%) was observed in the additions of Grignard reagents to nitrones (e.g. **22** and **23**) bearing the potentially chelating β-methoxyalkyl group. However, the opposite selectivity resulted from the reaction of methylmagnesium bromide with the corresponding silyl ether (**27**). The relative stereochemistry of selected hydroxylamine adducts was established by reduction of their phosphate and carbonate derivatives to known amines (**37a,b** and **39**), by periodate cleavage of a β-hydroxy hydroxylamine (**41b**), and by various correlations (Scheme II). The high facial diastereoselectivity observed with the *N*-(β-methoxyalkyl)nitrones is explained by a simple chelation model (Scheme III).

Diastereoselective addition of organometallic reagents to the C=N bond of imines and their derivatives offers an attractive approach for asymmetric synthesis of amines.[3] High asymmetric induction has been observed

in organometallic additions to imines,[4,5] oximes,[6] and hydrazones[7-9] bearing hydroxy, alkoxy, or carbonyl substit-

(1) (a) Portions of this work were presented at the joint American Chemical Society-Canadian Institute of Chemistry meeting in Toronto, Ontario, June 7, 1988. (b) Taken in part from the Ph.D. Thesis of Z.-Y. Chang, University of Illinois, Urbana–Champaign, 1988.

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(3) For reviews on organometallic additions to imines and their derivatives, see: (a) Volkmann, R. A. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I. Eds.; Pergamon Press: Oxford, 1990; Vol. 1, Schreiber, S. L., Ed. (b) Kleinman, E.; Volkmann, R. A. In *Ibid.* Vol. 2, Heathcock, C. H., Ed. We wish to thank Dr. Volkmann for preliminary copies of these reviews.

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