Additions and Cycloadditions of Cyclopentadienyl Metal Compounds to Benzyne

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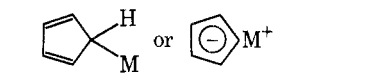
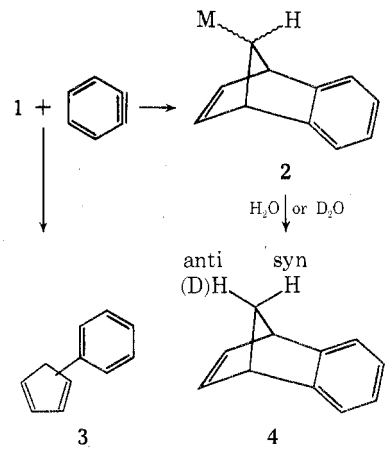
Cyclopentadienyllithium, -sodium, and -potassium add to benzyne, generated from metal amides and chlorobenzene in tetrahydrofuran (THF), to form phenylcyclopentadiene (**3**) in low yields. In contrast, cyclopentadienylmagnesium halides (CpMgX), trimethylsilylcyclopentadiene, and trimethylstannylcyclopentadiene ($CpSnMe_3$) cycloadd to benzyne, generated from *o*-bromofluorobenzene and magnesium in THF, to give 7-benzonorbornadienyl metal compounds (**2**). The major product from $CpSnMe_3$, however, is *o*-fluorotrimethylstannylbenzene. In the presence of 2 equiv of hexamethylphosphoramide, CpMgBr and benzyne produce both **2** and **3**. The results suggest a σ-bonded structure for the CpMgX which cycloadds to benzyne.

Benzyne is a highly reactive dienophile in [2 + 4] cycloadditions, undergoes [2 + 2] cycloadditions, is very susceptible to nucleophilic additions, participates in the ene reaction, and inserts into carbon–hydrogen bonds.[2] It cycloadds to both cyclopentadiene and cyclopentadienylmagnesium bromide (**1d**, CpMgBr) in refluxing tetrahydrofuran (THF) to give benzonorbornadiene (**4**) in 66 and 21% yields, respectively.[3] Deuterolysis after the CpMgBr reaction leads to **4** with 0.91 atom excess deuterium located exclusively in the anti-7 position, implying that cycloaddition produces 7-benzonorbornadienylmagnesium bromide (**2**, M = MgBr).[4] Benzyne also cycloadds to methyl-, 1,3-dimethyl-, trimethylsilyl-, and *tert*-butylcyclopentadienes and to the corresponding cyclopentadienylmagnesium chlorides to give substituted benzonorbornadienes.[5]

To determine whether the structure of CpMgBr which cycloadds to benzyne is σ- (monohapto) or π- (pentahapto) bonded, we have studied reactions of benzyne with a variety of other metallocyclopentadienes (**1**). If σ-bonded CpMgBr is the reactive species, the cycloaddition is a common Diels–Alder reaction of a 5-metallocyclopentadiene, whereas if π-bonded CpMgBr is the reactive species, the reaction is a highly unusual cycloaddition of a delocalized cyclopentadienyl anion to benzyne.



1a, M = Li(CpLi)
b, M = Na(CpNa)
c, M = K(CpK)
d, M = MgX(CpMgX)
e, M = $SiMe_3$($CpSiMe_3$)
f, M = $SnMe_3$($CpSnMe_3$)



Results

Benzyne was generated from *o*-bromofluorobenzene and magnesium turnings in THF for reactions of cyclopentadienylmagnesium, silicon, and tin compounds, and from chlorobenzene and either lithium 2,2,6,6-tetramethylpiperidide, sodium amide, or potassium amide for reactions of cyclopentadienylalkali compounds. Although many other methods of benzyne generation are known,[2] the methods chosen appeared to be the most compatible with metallocyclopentadienes.

The products from these metallocyclopentadienes and benzyne are shown in Table I. Treatment of ferrocene with benzyne generated by the organomagnesium route gave no detectable phenylcyclopentadiene (**3**) or benzonorbornadiene (**4**) and left much unreacted ferrocene. We usually tried to identify only **2–4**. The low yields are probably due to (a) other reactions of benzyne, such as formation of biphenylene and triphenylene,[6] (b) reactions of benzyne with the adducts, and (c) instability of phenylcyclopentadiene (**3**). The 1,4-diphenylcyclopentadiene and pentaphenylcyclopentadiene isolated from the CpNa reactions are examples of further reactions of 1:1 adducts with benzyne. Upon standing overnight after GLC isolation, **3** dimerized or polymerized. Since the efficiencies of its polymerization while standing in THF prior to GLC isolation, and its depolymerization in the injection port of the gas chromatograph, are not known, yields of **3** are only lower limits. On the other hand, products **2** and **4** listed in Table I were quite stable to the isolation conditions and could be detected if present in yields of ≥0.05% by GLC–mass spectrometry. The varied methods of benzyne generation must also affect the yields.

Reaction of $CpSnMe_3$ and benzyne produced benzonorbornadiene (**4**), *o*-fluorotrimethylstannylbenzene (**5**), and *anti*-7-trimethylstannylbenzonorbornadiene (**2**, M = *anti*-$SnMe_3$). Although **4** and **5** could not be separated by preparative GLC, they were identified by GLC–mass spectrometry, elemental analysis, and ^1H NMR as an 8.3:91.7 mixture. Displacement of cyclopentadienide from $CpSnMe_3$ by *o*-fluorophenylmagnesium bromide, the intermediate which leads to benzyne,[2] is analogous to the transmetalations of allyl- and vinylstannanes with lithium alkyls which produce allyl- and vinyllithium.[7] Reaction of benzyne with the displaced CpMgBr may account for the small amount of **4** produced. The configuration of **2** (M = *anti*-$SnMe_3$) was established by ^1H NMR experiments which detected long-range coupling between the syn-7 proton and vinyl protons.[8–10]

Discussion

Most of the reactivity differences in Table I may be attributed to a fundamental structural difference between al-

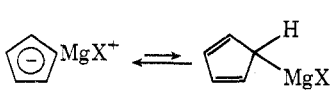
Table I. Reactions of Metallocyclopentadienes and Benzyne

Reactant	% yield[a] 2	4	3[b]
CpLi		0	3.9
CpNa[c]		0	9.9[d]
CpK		0	0.9
CpMgBr[e]		21–29	0
CpMgCl–HMPA		0.24	1.1
$CpSiMe_3$[f]	52		0
$CpSnMe_3$[g]	1.9	3.6	0

[a] Determined by GLC and based on equimolar amounts of CpM and the benzyne precursor. Of products **2** only the M = $SiMe_3$ and M = $SnMe_3$ compounds withstand hydrolysis. [b] Yields of **3** are lower limits because of its instability (see text). [c] Also isolated were 1,4-diphenylcyclopentadiene (2.1%) and pentaphenylcyclopentadiene (1.7%). [d] A tenfold excess of CpNa gave **3** in 80% yield (ref 26). [e] References 3 and 4. [f] Reference 5. [g] Also isolated was *o*-fluorotrimethylstannylbenzene (32.1%).

kali cyclopentadienides on the one hand and $CpSiMe_3$ and $CpSnMe_3$ on the other. Solid-phase ir spectra of CpLi, CpNa, and CpK[11a,b] and ir and uv spectra of CpLi and CpNa in THF solutions[11c] support pentahapto structures in which the metal is located near the C_5 axis of the cyclopentadienide. As 1 M THF solutions employed here, the alkali cyclopentadienides should consist of ion aggregates. $CpSiMe_3$ at room temperature is a mixture of 3% 1-, 7% 2-, and 90% 5-substituted[12] σ-bonded isomers,[13–15] which cycloadd to benzyne in 52% yield to produce 16% 1-, 12% 2-, 2% *syn*-7-, and 70% *anti*-7-trimethylsilylbenzonorbornadienes.[5] $CpSnMe_3$ has been shown by electron diffraction,[16] ir,[14] NMR,[17] and mass spectroscopic[13] methods to be σ bonded also. Excluding cyclopentadienylmagnesium compounds the reactivity pattern is clear: ionic pentahapto metallocyclopentadienes undergo nucleophilic addition to benzyne to produce phenylcyclopentadiene, while covalent monohapto metallocyclopentadienes cycloadd to produce metallobenzonorbornadienes. Ferrocene has a pentahapto structure[18] but is too weakly nucleophilic to add to benzyne under our conditions.

What is the structure of the cyclopentadienylmagnesium halide which cycloadds to benzyne? Gas-phase electron diffraction[19] and solid-phase x-ray diffraction[20] studies indicate D_{5h} or D_{5d} symmetry for dicyclopentadienylmagnesium (Cp_2Mg), and an x-ray crystal structure of the tetraethylethylenediamine solvate of CpMgBr shows that the metal atom lies near the cyclopentadienide C_5 axis.[21] Although solid- and gas-phase structures are not necessarily the same as structures in solution, ir and uv spectra of Cp_2Mg, CpMgCl, and CpMgBr in THF also support pentahapto structures.[11c] It is possible that as much as 5–10% of a monohapto CpMgX could exist in equilibrium with the pentahapto species in THF solution (eq 1) and not be de-



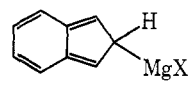
(1)

tected by ir or uv. From the reactivity pattern observed for the other metallocyclopentadienes, we propose that the CpMgX which cycloadds to benzyne is σ bonded.

In the presence of 2 equiv of hexamethylphosphoramide (HMPA) CpMgCl and benzyne produced traces of both **3** and **4**, and after deuterolysis the benzonorbornadiene contained excess deuterium according to its mass spectrum. The high affinity of HMPA for magnesium is known to increase greatly the ionic character of organomagnesium compounds.[22] HMPA could shift the equilibrium of eq 1 far to the left, which would inhibit cycloaddition of the σ-bonded form and give CpMgCl properties similar to those of alkali cyclopentadienides.

The stereospecificity of benzyne addition to CpMgX[4,5] can be explained readily by reaction of the σ-bonded isomer. Methyl, trimethylsilyl, and trimethylstannyl groups at the 5 position of cyclopentadiene all produce predominantly anti-7-substituted benzonorbornadienes, presumably because of steric hindrance between the substituents and benzyne in the transition states leading to the corresponding syn isomers. A magnesium halide group with its THF solvation shell is certainly more bulky than a methyl group and may be even larger than trimethylsilyl and trimethylstannyl groups. Therefore benzyne prefers to cycloadd to the side of the cyclopentadiene opposite the magnesium to form *anti*-7-benzonorbornadienylmagnesium halide. Deuterolysis with retention of configuration then produces exclusively benzonorbornadiene-*anti*-7-*d*.

Indenylmagnesium bromide in THF also cycloadds to benzyne to produce 9,10-dihydro-9,10-methanoanthracene.[4,23] Isoindenylmagnesium halide (**6**) is required to ex-



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plain this result with a σ-bonded intermediate. In metalloindenes the rates of [1,2] metallotropic shifts are known to increase in the order H < Si < Ge < Sn.[24] Although the highly endothermic conversion of indene to isoindene by a [1,5] sigmatropic hydrogen shift proceeds readily only at >200 °C,[25] the conversion of indenylmagnesium halide to **6** might occur readily by a [1,2] metallotropic shift. Indeed, the trimethylsilyl analogue of **6** has been trapped in a Diels–Alder reaction with tetracyanoethylene at room temperature.[24a] Also in agreement with our proposal of cycloaddition of benzyne to a σ-bonded metalloindene is the failure of indenyllithium and indenylsodium to form cycloadducts with benzyne.[26]

Experimental Section

General. Microanalyses were performed by J. Nemeth and associates. Infrared spectra were obtained either as a thin film between sodium chloride plates with a Perkin-Elmer Model 237B instrument or as a potassium bromide pellet with a Beckman IR-12 instrument. ^1H NMR spectra were obtained on Varian T-60, A-60A, A-56/60, or HA-100 spectrometers with Me_4Si as an internal standard except with compounds containing tin. The HA-100 equipped with a Hewlett-Packard Model 200ABR audio oscillator was used for decoupling experiments. Routine mass spectra were recorded on a Varian-MAT CH-5 mass spectrometer. GLC–mass spectrometry experiments were performed with a 6-ft 3% SE-30 on 100/120 Gas Chrom Q glass column on a Varian-MAT CH-7 mass spectrometer equipped with a Varian Model 2700 gas chromatograph. GLC analyses were performed on a 0.125 in. × 4 ft 20% Apiezon L on 60/80 Chromosorb W column with a helium flow of 20 ml/min on a Hewlett-Packard Model 700 instrument equipped with a thermal conductivity detector. Product yields were determined relative to an *n*-alkane internal standard without correction for thermal conductivity differences. Preparative GLC separations were performed on a Varian Model A-90-P instrument using a 0.25 in. × 10 ft 10% SE-30 on 60/80 Chromosorb W column with a helium flow of 60 ml/min. All reactions were performed with dry glassware under a dry nitrogen atmosphere.

Materials. The *o*-bromofluorobenzene (Aldrich), chlorotrimethylstannane (Aldrich), magnesium turnings (Baker), sodium amide (Fisher), *n*-BuLi in hexane (titrated as 2.31 M, Alfa), and 3.1 M ethylmagnesium chloride in ether (Alfa) were used as obtained. The chlorobenzene (Fisher), 2,2,6,6-tetramethylpiperidine (Aldrich), and hexamethylphosphoramide (Aldrich) were distilled from calcium hydride under nitrogen. Cyclopentadiene was prepared by cracking its dimer immediately before use. Tetrahydrofu-

ran was distilled under nitrogen from sodium benzophenone ketyl just before use.

Cyclopentadienyllithium (1a) and Benzyne. A solution of 3.3 g (50 mmol) of cyclopentadiene and 7.77 g (55 mmol) of 2,2,6,6-tetramethylpiperidine in 30 ml of THF was added dropwise over a period of 30 min to 104 mmol of *n*-butyllithium in hexane at −78 °C. A white precipitate formed during the addition. After the mixture had warmed to room temperature, the solvent was removed under vacuum and replaced with 30 ml of THF. The white solid dissolved. The solution was heated to reflux, and 5.63 g (50.0 mmol) of chlorobenzene in 20 ml of THF was added dropwise over a period of 40 min. Reflux was continued for 1 h. Solid NH_4Cl (10 g) was added to the cooled solution, 15 min later 200 ml of water was added cautiously, and the solution was acidified with concentrated HCl. The phases were separated, and the aqueous phase was extracted with three portions of ether. The combined organic phases were extracted with two 200-ml portions of 1 N HCl, two 200-ml portions of 5% $NaHCO_3$, and 200 ml of saturated NaCl, dried ($MgSO_4$), and concentrated on a rotary evaporator. GLC analysis at 200 °C using *n*-$C_{17}H_{36}$ as an internal standard showed a 3.9% yield of phenylcyclopentadiene (**3**) identified as described in the CpNa reaction which follows. Several small peaks of retention time similar to that of benzonorbornadiene (**4**) were observed, but were proven not to be **4** by GLC–mass spectrometry.

Cyclopentadienylsodium (1b) and Benzyne. A solution of 6.6 g (0.10 mol) of cyclopentadiene in 25 ml of THF was added dropwise with stirring to 8.19 g (0.21 mol) of sodium amide in 35 ml of THF at 25°. After stirring for 1 h the mixture was heated to reflux, and 11.25 g (0.10 mol) of chlorobenzene in 30 ml of THF was added dropwise over a period of 45 min. Reflux was maintained for 1 h more, the mixture was neutralized with 12 g of solid NH_4Cl, and 2 h later water was added cautiously. The mixture stood overnight. After acidification with HCl the phases were separated and the aqueous phase was extracted with three portions of ether. The combined organic phases were extracted with two 200-ml portions of 1 N HCl, two 200-ml portions of 5% $NaHCO_3$, and 200 ml of saturated NaCl and dried ($MgSO_4$). The ether was removed on a rotary evaporator. Addition of CCl_4 to the residual oil gave 0.27 g of red-brown precipitate which was recrystallized from ethanol to yield 0.23 g (1.06 mmol, 2.1%) of 1,4-diphenylcyclopentadiene: mp 155–159 °C (lit. mp 156,[27a] 158–158.5,[27b] 155.5–157 °C[27c]); ir (KBr) 3070 (m), 1500 (m), 1452 (m), 920 (m), 754 (s), and 695 cm^{-1} (s); mass spectrum (70 eV) *m/e* (rel intensity) 220 (2), 219 (19), 218 (100), 217 (27), 216 (7), 215 (19), 203 (16), 202 (26), 115 (14); calcd for $C_{17}H_{14}$, (P + 1)/P = 18.7%, (P + 2)/P = 1.75%. The ^1H NMR spectrum agreed with that in the literature.[27c]

The CCl_4 filtrate was distilled and 1.41 g (9.92 mmol, 9.9%) of phenylcyclopentadiene (**3**) was collected at 115–120 °C (0.2 Torr) [lit. bp 73 °C (5 Torr),[26] 180–220 °C (760 Torr)[28]]. Neat liquid **3** dimerized or polymerized upon standing overnight. A pure sample was obtained by preparative GLC at 230°: ^1H NMR ($CDCl_3$) δ 3.05 (m), 3.23 (d, J = 1.2 Hz), 6.08 (m), 6.33 (m), 6.48 (m), 6.75 (m), 7.0–7.5 (broad m). The relative peak areas at 3.05–3.23, 6.08–6.75, and 7.0–7.5 were 2:3:5. The relative peak areas at 3.05 and 3.23 were 4:3, tentatively assigned to the methylene protons of 2-phenylcyclopentadiene and 1-phenylcyclopentadiene, respectively. This ^1H NMR spectrum agrees with a previous report.[26] Mass spectrum (70 eV) *m/e* (rel intensity) 143 (53), 142 (94), 141 (100), 116 (20), 115 (98), 89 (25), 69.5 (33), 57.6 (26), 51 (23), 38 (35).

Anal. Calcd for $C_{11}H_{10}$: C, 92.91; H, 7.09. Found: C, 92.76; H, 6.99. The distillation residue was dissolved in dichloromethane and filtered through a short silica gel column. Distillation of solvent left an oil which was crystallized from methylene chloride–hexane to give 0.16 g (0.348 mmol, 1.7%) of 1,2,3,4,5-pentaphenylcyclopentadiene: mp 243–254 °C (lit. mp 244–246,[29a] 258–259 °C[29b]); ^1H NMR ($CDCl_3$) δ 4.90 (s, 1 H), 6.9–7.4 (broad m, 25 H); mass spectrum (70 eV) *m/e* (rel intensity) 448 (7), 447 (40), 446 (100), 420 (35), 291 (18); calcd for $C_{35}H_{26}$, (P + 1)/P = 38.5%, (P + 2)/P = 7.41%. Its ir spectrum agreed with that in the literature.[29c]

Cyclopentadienylpotassium (1c) and Benzyne. Potassium amide was prepared from 4.3 g (110 mg-atoms) of potassium, a trace of ferric chloride hexahydrate, and ca. 150 ml of liquid ammonia in the usual manner.[30] The ammonia was evaporated and replaced with 40 ml of THF. A solution of 3.3 g (50 mmol) of cyclopentadiene in 10 ml of THF was added dropwise, producing a white precipitate, and the mixture was allowed to stand for 1 h. Upon heating to reflux, most of the precipitate dissolved, and a solution of 5.63 g (50.0 mmol) of chlorobenzene in 15 ml of THF was added dropwise over a period of 45 min. The remainder of the procedure was identical with that described for **1a**. GLC analysis at 185 °C showed no trace of benzonorbornadiene, and at 200 °C using *n*-$C_{16}H_{34}$ as an internal standard, the yield of phenylcyclopentadienes was determined to be 0.9%.

Cyclopentadienylmagnesium Chloride (1d) and Benzyne with HMPA. A mixture of 0.97 g (40.0 mg-atoms) of magnesium turnings, 6.5 ml of 3.1 M ethylmagnesium chloride in ether (20.2 mmol), 1.32 g (20.0 mmol) of cyclopentadiene, and 10 ml of THF was stirred at 25 °C for 30 min until ethane evolution subsided, and refluxed for 2.5 h. An aliquot was examined by ^1H NMR to confirm the absence of unreacted cyclopentadiene. The mixture was cooled, 7.35 g (41.0 mmol) of HMPA was added, the mixture was brought to reflux, and a solution of 3.5 g (20.0 mmol) of *o*-bromofluorobenzene in 7.35 g (41.0 mmol) of HMPA was added dropwise over a period of 45 min. The mixture was refluxed for 1 more h and cooled to 25 °C and 20 ml of 99.8% D_2O was added. After standing overnight the solution was acidified with concentrated HCl, and an ether solution was prepared for GLC analysis by the procedure used for the reaction of **1a**. A 1.1% yield of phenylcyclopentadiene was determined by GLC at 200° using *n*-$C_{17}H_{36}$ as an internal standard. The yield of benzonorbornadiene (**4**) was determined similarly at 185 °C to be 0.24%. Although several peaks (<1%) of similar retention time to benzonorbornadiene (**4**) were observed, the correct identification of **4** was confirmed by a programmed GLC–mass spectrometry run from 90 to 260 °C at 4 °C/min. The mass spectrum assigned to benzonorbornadiene (**4**) showed 100% monodeuteration by analogy to the spectrum of an all-protio sample reported[31] assuming the P − 1 peak arises from loss of a hydrogen or deuterium atom from the 7 position with no deuterium isotope effect. Mass spectrum (70 eV) *m/e* (rel intensity) 144 (11), 143 (89), 142 (100), 141 (42), 140 (10), 117 (19), 116 (42).

5-Trimethylstannylcyclopentadiene (1f)[32] was prepared from cyclopentadiene and diethylaminotrimethylstannane:[33] bp 64.5–68.0 °C (9–10 Torr) [lit. bp 38 (3 Torr),[32] 85 °C (10 Torr)[34]]. Because **1f** formed a white powder upon exposure to air, it was stored and used under dry nitrogen.

5-Trimethylstannylcyclopentadiene (1f) and Benzyne. To 0.49 g (20.0 mg-atoms) of magnesium turnings, 2.24 g (9.8 mmol) of **1f**, and 5 ml of THF at reflux a solution of 1.75 g (10.0 mmol) of *o*-bromofluorobenzene in 5 ml of THF was added dropwise over a period of 15 min. Reflux was continued for 1 h. A tarry precipitate formed upon the addition of ether. The ether solution was decanted, and a portion of it was used to determine the yields of benzonorbornadiene (**4**, 3.6%) and *o*-fluorotrimethylstannylbenzene (**5**, 32.1%) by GLC relative to *n*-$C_{14}H_{30}$ at 180 °C. The yield of *anti*-7-trimethylstannylbenzonorbornadiene (**2**, M = *anti*-$SnMe_3$, 1.9%) was determined relative to *n*-$C_{15}H_{32}$ at 200 °C. Another portion of the ether solution was separated into two components by preparative GLC at 250 °C. The shorter retention time component was a mixture of **4** (4.55% by weight, 8.3 mol %) and **5** (the remainder) by GLC analysis at 160 °C. This mixture could not be separated conveniently by preparative GLC. ^1H NMR (CCl_4) showed the expected multiplets for **4**[35] and δ 0.48 (s, 9 H, J = 55 Hz for ^{117}Sn and ^{119}Sn satellites[36]) and 6.9–7.6 (m, 4 H) for **5**. Ir (film) 3060 (w), 2975 (m), 2915 (w), 1595 (m), 1465 (s), 1460 (s), 1435 (s), 1258 (m), 1200 (s), 1190 (s), 1105 (m), 1055 (m), 824 (m), 814 (m), 755 (s), and 727 cm^{-1} (m). GLC–mass spectra (70 eV) showed the expected spectra for **4**[31] and for **5**: *m/e* (rel intensity) 260 (0.96), 258 (0.67), 245 (100), 243 (74), 241 (45), 239 (2), 237 (3), 227 (18), 225 (13), 223 (8), 215 (13), 213 (10), 211 (7), 210 (13), 208 (9), 206 (5), 197 (7), 195 (5), 193 (3), 169 (8), 167 (6), 165 (4), 139 (35), 137 (26), 135 (23), 96 (5), and 95 (2).

Anal. Calcd for $C_9H_{13}FSn$ with 8.3 mol % $C_{11}H_{10}$: C, 45.67; H, 5.22. Found: C, 45.73, H, 5.21.

The longer retention time component isolated by preparative GLC was *anti*-7-trimethylstannylbenzonorbornadiene: ^1H NMR (CCl_4) δ 0.13 (s, 9 H, J = 51 Hz for ^{117}Sn and ^{119}Sn satellites[36]), 2.58 (m, 1 H), 4.01 (m, 2 H) 6.78–7.20 (m, 6 H). Irradiation at δ 2.58 sharpened the upfield portion of the δ 6.78–7.20 multiplet, and irradiation at δ 6.80 simplified δ 2.58 to a triplet (J = 2.4 Hz), establishing δ 2.58 as a syn-7 proton.[8-10] Ir (film) 3060 (m), 2965 (m), 2900 (m), 1453 (m), 1440 (m), 1190 (m), 843 (m), 758 (s), and 695 cm^{-1} (s). GLC–mass spectrum (70 eV) *m/e* (rel intensity) 306 (5), 304 (4), 302 (2), 291 (72), 289 (74), 287 (59), 265 (32), 263 (24), 261 (21), 165 (31), 163 (34), 161 (15), 141 (95), and 115 (100).

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Registry No.—**1a**, 16733-97-4; **1b**, 4984-82-1; **1c**, 30994-24-2; **1d** (X = Cl), 34766-85-3; **1f**, 2726-34-3; *anti*-**2f**, 57496-94-3; **3** 1-phenyl isomer, 1961-98-4; **3** 2-phenyl isomer, 2327-56-2; **4**, 4453-90-1; **5**, 2542-07-6; benzyne, 462-80-6; sodium amide, 7782-92-5; 1,4-diphenylcyclopentadiene, 57496-95-4; 1,2,3,4,5-pentaphenylcyclopentadiene, 2519-10-0; potassium amide, 17242-52-3; ethylmagnesium chloride, 2386-64-3; diethylaminotrimethylstannane, 1068-74-2; cyclopentadiene, 542-92-7.

References and Notes

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Highly Stereoselective Preparations of *anti*-7-Benzonorbornadienyl Grignard Reagents

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Grignard reagents have been prepared in tetrahydrofuran from *anti*- and *syn*-7-chlorobenzonorbornadiene (*anti*-Cl and *syn*-Cl) and *anti*- and *syn*-7-bromobenzonorbornadiene (*anti*-Br and *syn*-Br) by three methods: reaction with magnesium turnings, reaction with activated magnesium prepared by reduction of magnesium halide with potassium metal, and reaction with sodium naphthalenide (NaNaph) in the presence of magnesium halide. Deuterolyses of the Grignard solutions give deuterated benzonorbornadiene (**2**) with >85% overall retention of configuration from *anti*-Cl and *anti*-Br by the magnesium metal methods. Carbonation of the Grignard reagent from *anti*-Br and magnesium turnings also proceeds with high overall retention of configuration. The stereoselectivity does not depend on particle size or purity of the magnesium. In contrast, *syn*-Cl and *syn*-Br give deuterated **2** by the same methods with little or no stereoselectivity. The NaNaph method gives little stereoselectivity with any of the substrates but produces the Grignard reagents in higher yields. Sizable amounts of undeuterated benzonorbornadiene are formed in all of the preparations using magnesium turnings or activated magnesium. Grignard reagent formation and deuterolysis with *anti*-7-bromobenzonorbornene (**5**) also proceed with high retention of configuration. The Grignard reactions at saturated carbon with *anti*-Br, *anti*-Cl, and **5** are far more stereoselective than any previously reported. The results are discussed in terms of a mechanism of Grignard formation which proceeds by rate-limiting electron transfer to give a radical intermediate bound to the magnesium surface.

Both reaction of *anti*-7-chlorobenzonobornadiene (**1a**) with magnesium turnings in tetrahydrofuran (THF)[2] and cycloaddition of benzyne to the cyclopentadienyl Grignard reagent in THF[3] followed by deuterolysis give benzonorbornadiene-7-*d* (**2**) with the D incorporated >90% stereoselectively anti. Assuming that deuterolysis proceeds with retention of configuration,[4] both preparations must lead to the *anti*-7-benzonorbornadienyl Grignard reagent (**3**).

Three possible reasons for the stereoselectivity of these reactions are: (1) Both proceed stereoselectively to form **3**, and **3** is configurationally stable under the preparation and trapping conditions. (2) Both **3** and its syn isomer are formed but