Quenching Studies.—A solution (each 8 ml) containing a given concentration (4.0×10^{-2} *M*) of anilides and varying concentrations of 1,3-pentadiene was placed in a 10 × 150 mm Pyrex tube, degassed by four freeze–thaw cycles on vacuum line, and sealed. The tubes were irradiated by a Halos 300-W high-pressure Hg lamp on a rotating turntable apparatus immersed in a running water bath at 15°. The products were analyzed by glc.

Sensitizing Studies.—The irradiation was carried out for 50 hr at a 2:1 molar ratio of sensitizers to anilides. A Halos 300-W high-pressure Hg lamp with Toshiba UV-35 filter, which cut off light shorter than 3300 Å, was used as a light source.

Fluorescence and Phosphorescence Emission Studies.—The fluorescence spectra were measured on a Hitachi MPF-2A fluorescence spectrophotometer and the phosphorescence spectra were measured on the same apparatus with phosphorescence attachments. All phosphorescence spectra were recorded using EPA (ethyl ether–isopentane–ethanol, 5:5:2 volume ratio) as solvent. The solvent was checked for emission at each time when a spectrum was recorded. No interference due to emission of solvent was observed. The solutions contain *ca.* 10^{-3}–10^{-1} *M* solute and they formed clear glasses without microcrystals at 77°K.

Registry No.—Ia, 2210-24-4; Ib, 1611-83-2; Id, 15796-89-1; IIa, 553-03-7; IIb, 31883-79-1; IId, 31883-80-4; benzophenone, 119-61-9; acetophenone, 98-86-2; acetone, 67-64-1; *n*-hexane, 110-54-3; ethyl ether, 60-29-7; methanol, 67-56-1.

Acknowledgments.—The authors thank Dr. Y. Izawa for his helpful advice, Professor I. Kamiya and Dr. K. Aoki for their aid in measurement of emission spectra, and Dr. Y. Takahashi for the measurement of nmr spectra.

Cycloaddition of Benzyne to Substituted Cyclopentadienes and Cyclopentadienyl Grignard Reagents

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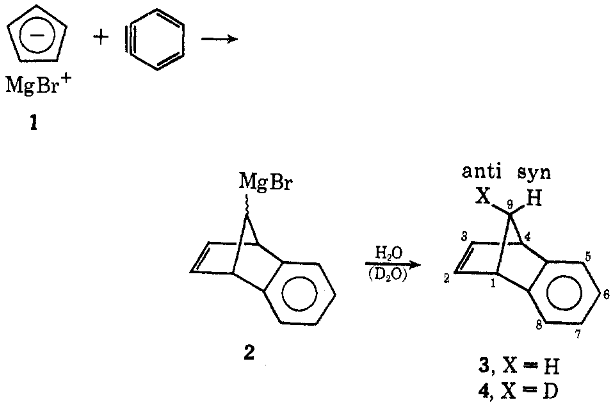
Benzyne was generated from 2-bromofluorobenzene and magnesium in tetrahydrofuran and added to isomeric mixtures of methylcyclopentadienes, 1,3-, 1,4-, and 2,5-dimethylcyclopentadienes, trimethylsilylcyclopentadienes, and *tert*-butylcyclopentadienes to give mixtures of substituted benzonorbornadienes whose isomeric distributions resembled those of the starting cyclopentadienes. Benzyne also was added to the corresponding cyclopentadienylmagnesium chlorides to give mixtures in which a 2-substituted benzonorbornadiene was always the major component. The intermediacy of 9-benzonorbornadienylmagnesium chlorides was demonstrated by stereospecific incorporation of one atom of D into the benzonorbornadienes by deuterolysis. The Grignard reactions may be described as $\pi^2s + \pi^4s$ cycloadditions, and their orientational selectivities are best explained by steric requirements in the transition state for cycloaddition.

The instability of benzyne makes it one of the most reactive dienophiles known in [2 + 4] cycloaddition and also makes it highly susceptible to nucleophilic addition, the ene reaction, insertion in carbon–hydrogen bonds, and other cycloadditions.[1] Additions of benzyne to cyclopentadiene and to cyclopentadienylmagnesium bromide (**1**) were first reported by Wittig and Knauss[2] to produce benzonorbornadiene (3,1,4-dihydro-1,4-methanonaphthalene) in 66 and 21% yields, respectively. Recently we[3] communicated that 9-benzonorbornadienylmagnesium bromide (**2**) was an intermediate in the addition of benzyne to **1** because deuterolysis of the reaction mixture produced benzonorbornadiene-*anti-9-d* (**4**). We described our results as the first well-established $\pi^2s + \pi^4s$ cycloadditions involving all-carbon anions. This paper describes additions of benzyne to cyclopentadienyl Grignards carried out to determine the influence of substitution on the course of cycloaddition. Concurrently, additions of benzyne to mixtures of isomeric substituted cyclopentadienes were investigated as control experiments for the Grignard cycloadditions.



1

2

3, X = H
4, X = D

Of the wide variety of methods available for generation of benzyne,[1] only organoalkali and organomagnesium routes appeared likely to be compatible with the cyclopentadienyl anion. The reaction of 2-bromofluorobenzene with magnesium in THF (tetrahydrofuran) was chosen because of its previous success in cycloadditions of benzyne to cyclopentadienyl-[2,3] and indenylmagnesium bromide,[3,4] because of the ease of preparation and the ionic character of cyclopentadienyl Grignard reagents, and because of failure in preliminary experiments to produce cycloadducts from cyclopentadienyllithium, *o*-dihalobenzenes, and alkyllithiums.

Results

Diene Cycloadditions.—All additions to dienes were carried out by generating benzyne from 2-bromofluorobenzene and magnesium in a refluxing THF solution about 1 *M* in the diene. The benzonornbornadienes produced in 45–65% yields were isolated by distillation and/or glpc. Several side products were

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[1] R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, N. Y., 1967.

[2] G. Wittig and E. Knauss, *Chem. Ber.*, **91**, 895 (1958).

[3] W. T. Ford, R. Radue, and J. A. Walker, *Chem. Commun.*, 966 (1970).

[4] C. F. Huebner and E. M. Donoghue, *J. Org. Chem.*, **33**, 1678 (1968).

also isolated by glpc and identified by their spectral properties and melting points as biphenylene, triphenylene, 2-fluorobiphenyl, and unreacted 2-bromofluorobenzene. Normally reaction mixtures were hydrolyzed with saturated aqueous ammonium chloride. Deuterolysis of the mixture produced from cyclopentadiene and benzyne gave **3** containing 0.05 atom excess D, demonstrating that the initially formed 2-fluorophenylmagnesium bromide produced benzyne faster than it abstracted a proton from cyclopentadiene to produce **1**.

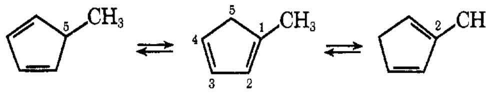
An equilibrium mixture of methyl-1,3-cyclopentadienes contained 44.5% 1-, 54.5% 2-, and <1% 5-methyl isomers by glpc at 27°.[5] Addition of a similar mixture to benzyne in refluxing THF (65–70°) produced the methylbenzonorbornadienes shown in Table I. Under these conditions the methylcyclopentadiene isomers interconverted by [1,5] sigmatropic hydrogen shifts with half-times of the same order of magnitude as the time over which benzyne was generated.[6]

Table I

Distributions of Methylbenzonorbornadienes Produced by Addition of Benzyne to Isomeric Methylcyclopentadienes and to Methylcyclopentadienylmagnesium Chloride

	% of mixture[a]		
Position of CH_3	From dienes	From Grignard	Statistical[b]
1	33	12	40
2	64	71	40
syn-9	3	17	10
anti-9	*c*	*c*	10
Yield,[d] %	45	21	

[a] Percentages measured by glpc and nmr may be considered accurate to ±2%. [b] Theoretical product distribution for nonselective addition of benzyne to Grignard and nonselective protonation at C_9 during hydrolysis. [c] Not detected by glpc or nmr; ≤1%. [d] Measured by glpc.



An equilibrium mixture of the dimethylcyclopentadienes has been estimated to contain >90% 1,3, <5% 1,4, and <5% 2,5 isomers by uv and Raman spectroscopy at ambient temperature.[10] The pmr spectrum of the mixture used here showed no signal at higher field than δ 1.7. Therefore it contained ≤1% of the 2,5 isomer, but the relative amounts of 1,3 and 1,4 isomers were unknown. The distribution of dimethylbenzonorbornadienes formed by cycloaddition of this mixture[6] to benzyne is shown in Table II. Presumably the relative amounts of 1,3 and 1,4 isomers formed were not greatly different from the relative amounts of starting 1,3- and 1,4-dimethylcyclopentadiene. The product mixture contained much more of the 2,*syn*-9-dimethyl isomer than the reactant mixture contained of 2,5-dimethylcyclopentadiene, indicating that benzyne reacted faster with 2,5- than with 1,3- and 1,4-dimethylcyclopentadienes.

Table II

Distributions of Dimethylbenzonorbornadienes Produced by Addition of Benzyne to Isomeric Dimethylcyclopentadienes and to 1,3-Dimethylcyclopentadienylmagnesium Chloride[a]

	% of mixture		
Positions of CH_3	From dienes	From Grignard	Statistical
1,3	82	26	40
1,4	13	3	20
2, *syn*-9	5	71	20
2, *anti*-9	*c*	*c*	20
Yield, %	59	32	

[a] See footnotes of Table I.

An equilibrium mixture of trimethylsilylcyclopentadienes contained 3% 1-, 7% 2-, and 90% 5-substituted isomers by the integrated areas of the trimethylsilyl peaks in their pmr spectrum at 30°.[9] The mixture used in this work contained 4% 1-, 11% 2-, and 85% 5-trimethylsilylcyclopentadiene at 42° by the same method. Cycloaddition of the mixture[6] to benzyne at 65–70° produced the trimethylsilylbenzonorbornadienes shown in Table III.

Table III

Distributions of Trimethylsilylbenzonorbornadienes Produced by Addition of Benzyne to Isomeric Trimethylsilylcyclopentadienes and to Trimethylsilylcyclopentadienylmagnesium Chloride[a]

	% of mixture		
Position of $(CH_3)_3Si$	From dienes	From Grignard	Statistical
1	16	16	40
2	12	61	40
syn-9	2	21	10
anti-9	70	2	10
Yield, %	52	14	

[a] See footnotes of Table I.

An equilibrium mixture of *tert*-butylcyclopentadienes contained only the 1 and 2 isomers in 53:47 relative amounts according to their 220-MHz pmr spectrum at 22°, but it is not known which was the major isomer. Cycloaddition of the mixture[6] to benzyne at 65–70° produced the *tert*-butylbenzonorbornadienes shown in Table IV.

Table IV

Distributions of *tert*-Butylbenzonorbornadienes Produced by Addition of Benzyne to Isomeric *tert*-Butylcyclopentadienes and to *tert*-Butylcyclopentadienylmagnesium Chloride[a]

	% of mixture		
Position of $(CH_3)_3C$	From dienes	From Grignard	Statistical
1	33	10	40
2	67	90	40
syn-9	*c*	*c*	10
anti-9	*c*	*c*	10
Yield, %	57	29	

[a] See footnotes of Table I.

Grignard Cycloadditions.—Substituted cyclopentadienylmagnesium chlorides were prepared from ethylmagnesium chloride and the previously described diene mixtures. One additional side product, 2-ethylbi-

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(5) S. McLean and P. Haynes, *Tetrahedron*, **21**, 2313 (1965).

(6) Half-times at 65° for conversions of 5- to 1-methylcyclopentadiene in CCl_4,[7] 1,5- to 1,2-dimethylcyclopentadiene neat,[8] and 5- to 1-trimethylsilylcyclopentadiene in benzene[9] were 1.15, 5.0, and 32 min, respectively. Benzyne generation times were 15–60 min.

(7) S. McLean, C. J. Webster, and R. J. D. Rutherford, *Can. J. Chem.*, **47**, 1555 (1969).

(8) S. McLean and P. Haynes, *Tetrahedron*, **21**, 2329 (1965).

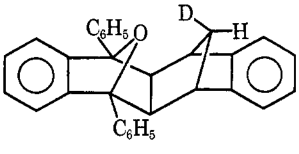
(9) A. J. Ashe, *J. Amer. Chem. Soc.*, **92**, 1233 (1970).

(10) V. A. Mironov, E. V. Sobolev, and A. N. Elizarova, *Tetrahedron*, **19**, 1939 (1963).

phenyl, formally derived from one molecule of excess ethylmagnesium chloride and two molecules of benzyne, was found in Grignard cycloadditions. No 2-fluorophenylcyclopentadiene (reported by Wittig and Knauss[2]) or other compound formed from any cyclopentadiene was found.

Incorporation of 0.90–0.98 atom of deuterium into product mixtures by deuterolysis proves that cycloadditions proceeded *via* the Grignard reagents **2** and **6a–c**. The product distributions obtained from methyl-, 1,3-dimethyl, trimethylsilyl-, and *tert*-butylcyclopentadienylmagnesium chlorides are shown in Tables I–IV and are compared to statistical distributions that would be obtained by nonselective cycloaddition of benzyne to cyclopentadienyl anions. The distributions of Grignard cycloadducts in Tables I–IV represent only deuterated products. All nondeuterated products were assumed to be formed by cycloaddition of benzyne to a trace of residual dienes. Two observations based on the product distributions for Grignard cycloadditions are clear. (1) Benzyne added selectively to substituted cyclopentadienylmagnesium chlorides, favoring placement of substituents at the 2 position of the benzonorbornadienes. (2) Most or all of the 9-substituents in the benzonorbornadienes were syn as a result of stereospecific protonation anti to the benzene ring during hydrolysis.

Structure Proof.—Stereospecific formation of **4** was proven by two pmr methods. (1) In **3** H_{9s} and H_{9a} gave an AB quartet, but in **4** only a single broad peak appeared at δ 2.12, the chemical shift of H_{9s} in **3**.[11] (2) By the method of Cristol and Noreen[13] the diphenylisobenzofuran adduct (**5**) of **4** had no detectable H_{9a}, and its H_{9s} signal appeared as a broad multiplet with no splitting >2 Hz. These results indicated $\leq 5\%$ D in position 9s and $\geq 95\%$ D in position 9a. The extent and position of deuteration were independent of the method of deuterolysis. Addition of D_2O to the reaction mixture, addition of the reaction mixture to D_2O, and addition of the reaction mixture to D_2O containing excess acetic acid-*O-d* dropwise with rapid stirring all incorporated 0.91–0.97 atom excess D. Therefore no hydrogen exchange took place after deuterolyses.



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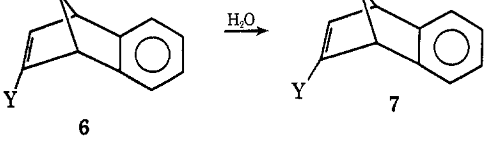
All of the gross structures of cycloadducts were determined by elemental analysis, mass spectra, and ir spectra. Some spectra were obtained with mixtures of two isomers because of inability to separate them by glpc. The mass spectra all had intense molecular ions, peaks due to loss of CH_3 and CH_2 groups, and peaks at m/e 141 ($C_{11}H_9^+$) and 115 ($C_9H_7^+$). Base peaks for the methyl- and dimethylbenzonorbornadienes arose from loss of CH_3. Base peaks for the trimethylsilyl compounds were m/e 73 [$(CH_3)_3Si^+$] and for the *tert*-butylbenzonorbornadienes were the molecular ion or m/e 141. The fragmentation patterns were very similar to those reported for other benzonorbornadiene derivatives.[12c] The ir spectra all had peaks at approximately 3060, 2960, 2925, 1450, and 1010 cm^{-1} and in the 890–690-cm^{-1} region in agreement with observations of other substituted benzonorbornadienes.[12d]

The substituted benzonorbornadienes were identified by their pmr spectra listed in Table V. Chemical shifts and coupling constants generally agreed with literature data for other benzonorbornadienes,[12] and integrated areas of spectral peaks also supported the assignments.

In all compounds unsubstituted at C_9 in which chemical shifts for H_{9a} and H_{9s} could be assigned, H_{9s} appeared at higher field as previously observed.[12] Long-range couplings between H_2, H_3, and H_{9s} were used to make the assignments. Coupling constants were determined by first-order analyses when possible. For compounds in which H_2 and H_3 were chemically equivalent, the vinyl region of the spectrum appeared as approximately a triplet, the AA′ portion of an AA′XX′ spectrum. In such cases just the sum $J_{1,2} + J_{1,3}$ could be determined.[12d] All couplings were verified by double irradiation experiments.

Configurations of compounds bearing the substituents listed in Table V or deuterium at C_9 were assigned by long-range coupling and by chemical analogy. The long-range coupling between H_2 and H_{9s} is well known in norbornenes and norbornadienes[12,14,15] as well as in benzonorbornadienes.[12] In this investigation the $J_{1,2}$ and $J_{1,3}$ values observed were ≤ 0.5 Hz but clearly discernible by decoupling experiments. No such couplings could be detected in compounds assigned as *syn*-9-substituted benzonorbornadienes.

In Grignard cycloadditions hydrolyses of all of the intermediate 9-substituted 9-benzonorbornadienylmagnesium chlorides (**6a–c**) produced *syn*-9-substituted benzonorbornadienes (**7a–c**). Moreover, deuterolyses of all 9-benzonorbornadienylmagnesium halides incorporated deuterium in the *anti*-9 position of the benzonorbornadiene, as evidenced by the lack of H_{9a} signals and the disappearance of $J_{9s,9a}$ in the H_{9s} signals in their pmr spectra. *anti*-9-Methylbenzonorbornadiene (**8**) was not produced by either diene or



6 **7**

a, X = CH_3; Y = H
b, X = CH_3; Y = CH_3
c, X = $Si(CH_3)_3$; Y = H

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[11] The relative chemical shifts of H_{9s} and H_{9a} in **3** have been established by specific deuteration and by consistent long-range coupling between $H_{2,3}$ and H_{9s} in benzonorbornadiene derivatives.[12]

[12] (a) N. Inamoto, S. Masuda, K. Tori, K. Aono, and H. Tanida, *Can. J. Chem.*, **45**, 1185 (1967); (b) K. Tori, K. Aono, Y. Hata, R. Muneyuki, T. Tsuji, and H. Tanida, *Tetrahedron Lett.*, 9 (1966); (c) S. J. Cristol and G. W. Nachtigall, *J. Org. Chem.* **32**, 3738 (1967); (d) M. E. Brennan and M. A. Battiste, *ibid.*, **33**, 324 (1968).

[13] S. J. Cristol and A. L. Noreen, *J. Amer. Chem. Soc.*, **91**, 3969 (1969). I thank Dr. Cristol for supplying copies of their nmr spectra of **5**.

[14] (a) B. Franzus, W. C. Baird, Jr., N. F. Chamberlain, T. Hines, and E. I. Snyder, *ibid.*, **90**, 3721 (1968); (b) A. P. Marchand and J. E. Rose, *ibid.*, **90**, 3724 (1968); and references in these papers.

[15] (a) E. I. Snyder and B. Franzus, *ibid.*, **86**, 1166 (1964); (b) P. Laszlo and P. v. R. Schleyer, *ibid.*, **86**, 1171 (1964); (c) J. C. Davis, Jr., and T. V. Van Auken, *ibid.*, **87**, 3900 (1965); (d) N. H. Werstiuk, *Can. J. Chem.*, **48**, 2310 (1970).

TABLE V

PROTON MAGNETIC RESONANCE SPECTRA OF SUBSTITUTED BENZONORBORNADIENES

A. Chemical Shifts ($\delta_{CCl_4}^{TMS}$)[a]

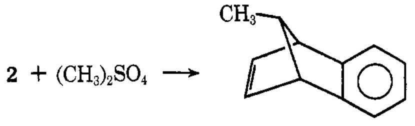
Substituents	Registry no.	H_1	H_4	H_2	H_3	H_{5-8}	H_{9s}[b]	H_{9a}[b]	CH_3
None[c]		3.76		6.66		6.7–7.2	2.15	2.18_5	
1-CH_3	31893-12-6		3.74	~6.7	6.38	6.7–7.2	AB 2.15		1.65
2-CH_3	31893-13-7	3.67	3.41		6.09	6.65–7.2	2.14_0	2.24_8	1.77
syn-9-CH_3	31893-14-8	3.45			6.6–7.4			~2.8	0.67
anti-9-CH_3	31893-15-9	3.50		6.49		6.7–7.3	2.74		1.03
1,3-$(CH_3)_2$	31893-16-0		3.38	5.82		6.75–7.2	2.09_2	2.22_8	1.59, 1.78
1,4-$(CH_3)_2$	31893-17-1			6.33		6.7–7.2	AB 2.12		1.58
2, *syn*-9-$(CH_3)_2$	31893-18-2	3.34	3.08		6.11	6.7–7.2		2.78	0.63, 1.77
1-$Si(CH_3)_3$	31862-26-7		3.82		6.7–7.5		AB 2.14		0.22
2-$Si(CH_3)_3$	31893-19-3	3.84_5, 3.90		6.93		6.7–7.1	2.14	2.14	0.03
syn-9-$Si(CH_3)_3$	31893-20-6	3.81		6.85		6.7–7.1		2.12	−0.38
anti-9-$Si(CH_3)_3$	31893-21-7	3.85		6.67		6.68–7.10	2.23		0.01
1-$C(CH_3)_3$	31893-22-8		3.71	6.63	6.71	6.7–7.3	2.16	2.22	1.24
2-$C(CH_3)_3$	31893-23-9	3.73			6.08	6.7–7.2	2.14	2.18	1.01

B. Coupling Constants (|J|, Hz)[d]

Substituents	1,2; 3,4	1,3; 2,4	1,9s; 1,9a; 4,9s; 4,9a[e]	2,9s; 3,9s	9s,9a	2,CH_3; 3,CH_3	9s,CH_3; 9a,CH_3
None[c]	$\Sigma^f = 3.9$		1.6	0.4	6.9		
2-CH_3	$\Sigma^f = 3.4$		1.6	0.4	6.7	1.8	
anti-9-CH_3	$\Sigma^f = 3.8$		1.8	0.5			6.5
1,3-$(CH_3)_2$	*g*	*g*	1.65	0.3	6.8	1.5	
2, *syn*-9-$(CH_3)_2$	*g*	*g*	1.5			1.7	6.7
1-$Si(CH_3)_3$	*g*	*g*	1.6	*g*	*g*		
2-$Si(CH_3)_3$	2.8	0.85	1.55	<0.3	*g*		
syn-9-$Si(CH_3)_3$	$\Sigma^f = 3.7$		1.25				
anti-9-$Si(CH_3)_3$	$\Sigma^f = 3.9$		1.5	0.4			
1-$C(CH_3)_3$	2.7	1.2	1.7	0.5, <0.3	6.8		
2-$C(CH_3)_3$	3.0	1.1	1.65	<0.3	*g*		

[a] Values are believed accurate to ±0.04 ppm unless otherwise indicated to be approximations. [b] Chemical shift differences between H_{9s} and H_{9a} are believed accurate to ±0.005 ppm. Values listed as AB denote the average chemical shift. [c] The chemical shifts reported are from this investigation. They are different from but agree favorably with previous reports.[12b,c] [d] J values were determined by first-order analysis to ±0.3 Hz, except for $J_{2,9s}$ ±0.1 Hz. [e] Average value of all such couplings. [f] $\Sigma = J_{1,2} + J_{1,3}$. NOTE ADDED IN PROOF.—The coupling patterns observed may be equally compatible with $J_{1,2} = 3.1$, $J_{1,3} = 0.9$, $J_{1,4} = 1.9$ Hz or similar values according to the analysis of W. B. Smith, S. Biesemeier, and D. L. Davenport, *J. Org. Chem.*, **36**, 2853 (1971), but the spectra available do not permit distinction between the $J_{1,4} = 0.0$ and $J_{1,4} = 1.9$ assignments. [g] Could not be determined from spectra available.

Grignard cycloaddition, but it was obtained by methylation of **2**. Both hydrolysis and methylation of the intermediates from Grignard cycloaddition gave stereospecific *anti*-9 capture of the incoming electrophile. The structural assignments in Table V have been based both on observations of $J_{2,9s}$ and on stereospecific capture of Grignard cycloadducts.



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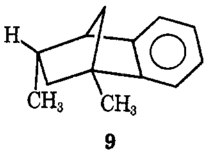
None of the structural assignments depend on relative chemical shifts of syn- and anti-9 substituents of isomeric benzonorbornadienes. However, in both methyl and trimethylsilyl compounds the syn-9 substituent appeared 0.36–0.39 ppm further upfield than the anti-9 substituent, as expected from location of the methyl groups in the shielding region of the aromatic ring current.

Hydrogenation of a mixture of dimethylbenzonorbornadienes and isolation by glpc gave samples of 1,-*endo*-3- and *endo*-2,*syn*-9-dimethylbenzonorbornenes (**9** and **10**). The easily identifiable aliphatic hydrogen peaks in the pmr spectrum of **9** were $\delta_{CCl_4}^{TMS}$ 0.52 (d, J = 6.8 Hz, 3 H, *endo*-3-CH_3), 1.50 (s, 3 H, 1-CH_3), 1.62 (AB q, 2 H, $H_{9a,9s}$), 2.8–3.0 (br d, J = 4.5–5.0 Hz, 1 H, H_4). The easily identifiable aliphatic hydrogen peaks in the pmr spectrum of **10** were $\delta_{CCl_4}^{TMS}$ 0.52 (d, J = 6.6 Hz, 3 H, *endo*-2-CH_3), 0.68 (d, J = 6.8 Hz, 3 H, *syn*-9-CH_3), 2.65–2.95 (m, 2 H, $H_{1,4}$). The peaks at 0.52 in **9** and **10** were assigned to *endo*-methyls because of their identical chemical shifts. The peak at δ 0.68 in **10** was assigned to syn-9-methyl because of its preparation by sterospecific exo hydrogenation, not because its position was unaffected by removal of the shielding anistropy of the C_2–C_3 double bond. (Hydrogenation of an *anti*-9-methyl compound presumably would proceed more slowly or with different stereoselectivity.) Similar chemical shift arguments 3 in the past have led to errors in assignments of the syn- and anti-9 hydrogens of **3**[12a] and the syn- and anti-7 hydrogens of norbornene.[14] Moreover, the chemical shifts of the methyl groups in *syn*- and *anti*-7-methyl-



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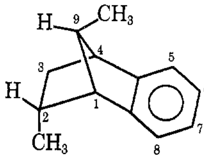

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norbornene are δ 0.70 and 0.79, respectively,[16] and both methyl groups in the *N*-phenylmaleimide adduct of 5,5-dimethylcyclopentadiene appear at δ 1.05.[5] All of these data indicate that chemical shifts must not be used to assign configuration at the bridge position in norbornenes, benzonorbornadienes, and related compounds.

Discussion

Diene Cycloadditions.—At 65–70° isomerizations of substituted cyclopentadienes by [1,5] sigmatropic hydrogen shifts competed with their cycloadditions to benzyne.[6] The detailed rate data for isomerization and cycloadditions needed to determine accurately relative rates of addition of the various methyl-, dimethyl-, *tert*-butyl-, and trimethylsilylcyclopentadienes to benzyne are not available, but, since the starting diene mixtures were either at or close to equilibrium during cycloaddition, the product distributions in Tables I, II, and IV indicate qualitatively the relative reactivities of the cyclopentadienes by position of alkyl substitution to be $2 > 1$. No estimation of relative reactivity of 5-methyl- or 2,5-dimethyl-1,3-cyclopentadiene is warranted because of uncertainties in the relative yields of minor cycloadducts. A similar analysis of the equilibrium mixture of trimethylsilyl-1,3-cyclopentadienes and the distribution of their cycloadducts with benzyne indicates their relative reactivities by position of substitution to be $1 > 2 > 5$. The lesser reactivity of 5-trimethylsilyl-1,3-cyclopentadiene can be explained by steric hindrance to addition of benzyne to its *syn*-trimethylsilyl face. The greater reactivity of 1- than of 2-trimethylsilyl-1,3-cyclopentadiene may be due to the greater polarity of the former, expected from the slightly electron-withdrawing resonance effect ($\sigma_m = -0.121$, $\sigma_p = -0.072$)[17] of the trimethylsilyl group.

The preferred mode of addition of benzyne to 5-methyl- and 2,5-dimethyl-1,3-cyclopentadiene placed the 9-methyl groups in the benzonorbornadienes syn to the benzene ring. In other Diels–Alder reactions of 5-methyl-1,3-cyclopentadiene, *N*-phenylmaleimide added endo to form syn and anti bridge methyl compounds in about equal amounts,[5] and maleic anhydride formed a 12:1 mixture of isolated endo adducts in which the major product was presumed to have the bridge methyl group syn to the norbornene double bond (anti to the incoming dienophile)[18] because of the abnormally slow addition of 5,5-dimethyl-1,3-cyclopentadiene to maleic anhydride.[19] However, the latter and other[20] stereochemical assignments based on chemical shifts of bridge protons or bridge methyl groups in Diels–Alder adducts of 5-methylcyclopentadienes must be considered questionable because of the more recently demonstrated unreliability of such chemical shift arguments.[5,15] Cycloadditions of common dienophiles to other 5-substituted 1,3-cyclopentadienes have given both syn and anti adducts.[21]

The preferred *syn*-9-methyl orientation in benzyne adducts of 5-methyl-1,3-cyclopentadienes can be explained by attractive van der Waals forces between the methyl group and benzyne. The optimum overlap of the reactive orbitals of benzyne and the π bonds of a cyclopentadiene places the planes of the reactants nearly perpendicular to each other in the transition state for cycloaddition, minimizing steric hindrance with a 5 substituent on cyclopentadiene. Attractive interaction between the bridge methyl group and the incipient dienophile has been offered to explain the slow rate of retro Diels–Alder fragmentation of 1,7,7-trimethylbicyclo[2.2.1]heptene compared to that of bicyclo[2.2.1]heptene.[22] Preferred endo orientations of methyl groups in the Diels–Alder adducts of cyclopentadiene and methyl-substituted acrylic acids, esters, and nitriles have been explained both by attraction of the methyl groups of the dienophiles to the C_3–C_4 bond of cyclopentadiene and by steric hindrance between methyl groups and the 5 hydrogen of cyclopentadiene in the transition state for cycloaddition.[23] Similar explanations have been offered for the prevailing endo orientation of addition of cyclopentene,[24] norbornene,[25] cyclopropene,[26] and propene[27] to cyclopentadiene.[28] In contrast, analogs of cyclopentadiene which have lone pair or π-bonded electrons at the 5 position gave nearly equal mixtures of exo and endo adducts with cycloalkene dienophiles, as in the additions of cyclopropene to furan[29] and cyclopentene to tetraphenylcyclopentadienone.[30]

Grignard Cycloadditions.—Cyclopentadienyl Grignard reagents in THF consist of planar, aromatic cyclopentadienide ions associated with magnesium and halide ions according to their ir and uv spectra.[31] The extent of aggregation at high concentrations in THF is not known, but analogy to a wide variety of ionic organoalkali compounds suggests that they are ion pairs or higher aggregates.[32] The low conductivities of alkali cyclopentadienides and magnesium cyclopentadienide in THF also support aggregation.[33]

The high reactivity of benzyne has resulted in its capture by [2 + 2], [3 + 2], and [4 + 2] cycloaddi-

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[30] K. N. Houk, *Tetrahedron Lett.*, 2621 (1970).

[31] W. T. Ford, *J. Organometal. Chem.*, **32**, 27 (1971).

[32] For extensive reviews see (a) M. Szwarc, "Carbanions, Living Polymers, and Electron-Transfer Processes," Interscience, New York, N. Y., 1968, Chapters V and VI; (b) J. F. Garst in "Solute–Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969, pp 539–605.

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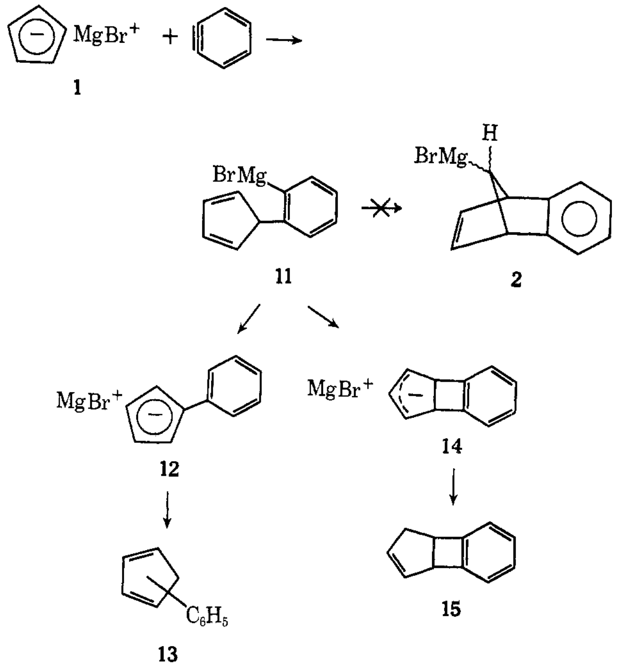
tions,[34] ene reactions, and nucleophilic additions.[1] An [8 + 2] cycloaddition of benzyne to a heptafulvene was reported recently.[36] In many instances nucleophilic addition and cycloaddition to benzyne proceeded at similar rates, particularly when an organometallic route to benzyne was used. The triphenylene, biphenylene, 2-fluorobiphenyl, and 2-ethylbiphenyl found as side products in the present investigation indicate that nucleophilic additions of 2-fluorophenylmagnesium bromide, 2′-fluoro-2-biphenylylmagnesium bromide, and ethylmagnesium bromide to benzyne and cycloadditions of cylopentadienes and cyclopentadienylmagnesium bromides to benzyne all proceeded at similar rates. No product explicable by stepwise nucleophilic addition of cyclopentadienylmagnesium bromide (or chloride) to benzyne was isolated. The products expected from such an addition would be either phenylcyclopentadiene (**13**) or 6,7-benzobicyclo[3.2.0]hepta-2,6-diene (**15**) as shown in Scheme I.

SCHEME I

EXPECTED COURSES OF STEPWISE ADDITION OF CYCLOPENTADIENYLMAGNESIUM BROMIDE TO BENZYNE



Conversion of the intermediate 2-(5-cyclopenta-1,3-dienyl)phenylmagnesium bromide (**11**) to the known intermediate **2** is highly unlikely because it would require Grignard addition to the 2 position of a 1,3 diene and convert a more stable aryl Grignard reagent to a less stable secondary alkyl Grignard reagent. For similar reasons there is no likely path for rearrangement of **12** or **14** to **2**.

The simplest mechanism which accounts for intermediate Grignards **2**, **6a–c**, and isomers of **6a–c** is [3 + 2] cycloaddition[34] of benzyne to cyclopentadienyl anions, which may also be called $\pi^4s + \pi^2s$ cycloaddition.[37] This mode of cycloaddition is predicted theoretically to be concerted.[37] Benzyne is thought to be a ground-state singlet on the basis of theory[38] and experiments which have demonstrated that it adds stereospecifically [4 + 2] to isomeric 2,4-hexadienes[39,40] and *trans,trans*-dimethyl muconate[39] and nonspecifically [2 + 2] to the isomeric 1,2-dichloroethylenes,[39] isomeric propenyl ethers,[41] and *trans*-cyclooctene.[42] It is well known that benzyne[43] and tetrahalobenzynes[44] are reactive enough to destroy the aromaticity of a benzene ring by cycloaddition. Reaction of tetrafluorobenzyne and nickelocene gave two 1:1 adducts, one of which was postulated to be formed *via* [3 + 2] cycloaddition.[45]

Methyl-, 1,3-dimethyl-, *tert*-butyl-, and trimethylsilylcyclopentadienylmagnesium chloride were added to benzyne in order to characterize better the transition states of these anionic cycloadditions. Benzyne's instability makes its reactions exothermic and accounts for its ability to convert relatively stable aromatic cyclopentadienyl Grignards to much less stable secondary alkyl Grignards. It follows that the transition state should more nearly resemble starting materials than products.[46] If product stability were important, the ease of formation of 9-substituted benzonorbornadienyl Grignard reagents would be $Si(CH_3)_3 > H > CH_3 > C(CH_3)_3$ because of the relative abilities of these groups to stabilize adjacent carbanions.[47] The product distributions for addition of benzyne to each cyclopentadienyl Grignard reagent (Tables I–IV) show no correlation with the expected relative stabilities of substituted 9-benzonorbornadienyl Grignard reagents.

If substituents were to perturb the charge density within a cyclopentadienide ion, the positions of highest charge density would be expected to react most readily with electrophilic benzyne. Methylation of the methylcyclopentadienyl anion was found by McLean and Haynes[5] to produce a 3.5:1.0:0.2 distribution of 1,5-:2,-5-:5,5-dimethylcyclopentadienes. Their product distribution was rationalized with a Hückel molecular orbital calculation which gave the π-electron densities at the 1, 2, and 3 positions of the anion as 1.01, 1.28, and 1.22, respectively. In contrast, ^{13}C nmr chemical

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(34) This nomenclature refers to the number of atoms in each addend which become part of the new ring of the adduct.[35]

(35) (a) R. Huisgen, R. Grashey, and J. Sauer in "The Chemistry of Alkenes," S. Patai, Ed., Interscience, New York, N. Y., 1964, p 739; (b) R. Huisgen, *J. Org. Chem.*, **33**, 2291 (1968).

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(41) (a) I. Tabushi, R. Oda, and K. Okazaki, *Tetrahedron Lett.*, 3743 (1968); (b) H. H. Wasserman, A. J. Solodar, and L. S. Keller, *ibid.*, 5597 (1968).

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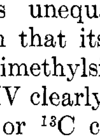
(45) D. M. Roe and A. G. Massey, *J. Organometal. Chem.*, **20**, P1 (1969).

(46) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).

(47) (a) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, Chapter II; (b) D. J. Peterson, *J. Organometal. Chem.*, **9**, 373 (1967); (c) G. A. Gornowicz and R. West, *J. Amer. Chem. Soc.*, **90**, 4478 (1968); (d) A. E. Bey and D. R. Weyenberg, *J. Org. Chem.*, **31**, 2036 (1966); (e) F. Jaffe, *J. Organometal. Chem.*, **23**, 53 (1970).

shifts of the ring carbon atoms in methyl- and 1,3-dimethylcyclopentadienylmagnesium chloride in THF indicate nearly equal π-electron densities at all ring positions,[48] in disagreement with the HMO results. The HMO calculation predicts the major cycloadduct of methylcyclopentadienylmagnesium chloride and benzyne to be a 9-methyl isomer, while the ^{13}C chemical shifts predict nearly statistical distribution of cycloadducts. The anion-stabilizing ability of silicon should increase electron density at the α carbon in trimethylsilylcyclopentadienylmagnesium chloride, an hypothesis supported by the ^{13}C chemical shifts of its ring carbon atoms.[48] This unequal charge distribution leads to the prediction that its major cycloadduct to benzyne would be 1-trimethylsilylbenzonorbornadiene. The data in Tables I–IV clearly indicate no correlation between either HMO or ^{13}C chemical shift estimates of charge distribution in substituted cyclopentadienyl Grignard reagents and the substituent orientations in their benzyne adducts.

Nevertheless, methylation of and benzyne addition to the methylcyclopentadienyl anion (**16a**) both preferred formation of a new carbon–carbon bond at the 2 position. Although it is unlikely that the benzyne addition proceeded stepwise, one new bond could be more nearly formed in the transition state than the second. The substituent orientations of benzyne adducts of the methyl-, 1,3-dimethyl-, and trimethylsilylcyclopentadienylmagnesium chloride additions are compatible with control of orientation of the earlier formed bond by the same factors which orient methylation of methylcyclopentadienyl anion at positions 2 > 3 > 1, and control of orientation of the later formed bond at positions 3(4) > 2(5) > 1 by steric effects. Thus formation of the first bond at C_2 would make C_4 and C_5 available for the second bond, with C_4 favored for steric reasons. The lack of a 9-*tert*-butylbenzonorbornadiene product from benzyne addition to *tert*-butylcyclopentadienylmagnesium chloride may be explained by steric hindrance to formation of the first new bond at C_2 in **16b**. Formation of the first bond at C_3 would make C_1 and C_5 available for the second bond with C_5 favored. Generally greater steric influence should be expected on formation of the second bond because at that time the addends are held together more tightly.



16a, R = CH_3
b, R = $C(CH_3)_3$

This discussion points out the similarities between alkylation of and benzyne addition to methylcyclopentadienide but unfortunately does not explain the preferred orientation of reactions at the 2 position. Mechanisms involving cationic or radical intermediates can also be devised for these cycloadditions, but they seem intuitively less likely in view of the carbanionic nature of cyclopentadienyl Grignard reagents. However, the intermediacy of benzonorbornadienyl Grignards **2** and **6a–c** and of isomers of **6a–c** is firmly established by deuteration.

Experimental Section

General.—Microanalyses were performed by J. Nemeth and associates. Infrared spectra were obtained as thin films between sodium chloride plates on a Perkin-Elmer 521 instrument. Mass spectra were obtained on a Varian-MAT CH-5 instrument by J. Wrona. Deuterium analyses of the molecular ions were performed at low ionizing voltage to minimize fragmentation. Nmr spectra were obtained at ambient temperature in carbon tetrachloride on Varian T-60, A-60-A, HA-100, and HR-220 instruments. The HA-100 equipped with a Varian V-4315 frequency counter and a Hewlett-Packard Model 200ABR audio oscillator was used for chemical shift measurements and decoupling experiments.

Materials.—Tetrahydrofuran was distilled from calcium hydride just before use. 2-Bromofluorobenzene (Aldrich), deuterium oxide, 99.5% (Columbia), acetic acid-*O-d*, 99.5% (Aldrich), magnesium turnings (Baker), diphenylisobenzofuran (Aldrich), and ethylmagnesium chloride, 3.0 *M* in THF (Alpha) were used as obtained. Cyclopentadiene and methylcyclopentadiene were obtained from their dimers (Aldrich) by distillation and stored at −78° until use. The mixture of trimethylsilylcyclopentadienes was prepared from cyclopentadienyl sodium and freshly distilled chlorotrimethylsilane in THF.[49] The mixture of *tert*-butylcyclopentadienes was prepared from cyclopentadienylmagnesium bromide and freshly distilled 2-chloro-2-methylpropane in diethyl ether.[50]

1,3- and 1,4-dimethylcyclopentadienes were obtained as a mixture from 3-methyl-2-cyclopentenone (Aldrich) and methylmagnesium bromide by the method of McLean and Haynes.[5] In my hands dehydration of the intermediate 1,3-dimethyl-2-cyclopentanol occurred spontaneously during work-up. The dimethylcyclopentadienes were collected in a Dry Ice trap during removal of ether with a rotary evaporator and were redistilled, bp 85–97° (760 mm) (lit.[5] for pure 1,3-dimethylcyclopentadiene, 93–95°).

Analytical and Preparative Glpc.—Some analyses were performed with 0.125-in. columns on a Hewlett-Packard Model 700 instrument with thermal conductivity detector, and other analyses and all preparative separations were performed wih 0.25-in. columns on a Varian Model A-90-P instrument. The following columns were used: (A) 6 ft × 0.125 in. 10% UCW-98 on 80/100 Diataport S; (B) 20 ft × 0.125 in. 10% diethylene glycol succinate on 60/80 Chromosorb G; (C) 6 ft × 0.25 in. 20% Apiezon L on 60/80 Chromosorb W; (D) 10 ft × 0.25 in. 20% Apiezon L on 60/80 Chromosorb W; (E) 6 ft × 0.25 in. 20% SE-30 on 60/80 Chromosorb W. Isomeric compounds were assumed to have equal thermal conductivities. Compounds were proven stable under the glpc isolation conditions by lack of isomerization upon reinjection of pure isomers.

Diene Cycloadditions.—By the general method of Wittig and Knauss[2] an equimolar amount of 2-bromofluorobenzene in twice its volume of THF was added dropwise with stirring under nitrogen over 15–60 min to a 1 *M* solution of diene(s) in THF refluxing over 1 equiv of magnesium. After cooling to 25° the mixture was hydrolyzed with stirring by dropwise addition of saturated aqueous ammonium chloride or of deuterium oxide followed by ammonium chloride. The THF solution was separated. The aqueous residue was washed twice with diethyl ether, and the combined organic solution was dried and evaporated. Cycloadducts were isolated by distillation and/or glpc of the remaining yellow liquid.

Grignard Cycloadditions. General Procedure.—A 1 *M* solution of the cyclopentadienylmagnesium chloride was prepared by refluxing a THF solution of the diene and a 5–10% excess of ethylmagnesium chloride under nitrogen until the vinyl hydrogen nmr signals of the diene were completely replaced by ring hydrogen signals of the cyclopentadienyl Grignard. Generation of benzyne from an equimolar amount of 2-bromofluorobenzene,

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[50] (a) R. Riemschneider and R. Nehring, *Monatsh. Chem.*, **90**, 568 (1959); (b) R. Riemschneider, A. Reisch, and H. Horak, *ibid.*, **91**, 805 (1960).

hydrolysis, and isolation of products were carried out by the method used in diene cycloadditions.

Benzonorbornadiene-*anti*-9-*d* (4). A.—On a 36-mmol scale, cyclopentadiene was converted to cyclopentadienylmagnesium bromide (pmr δ 5.96, s) in 2.5 hr. Deuterolysis was carried out by dropwise addition of D_2O to the Grignard mixture. Distillation through a 15-cm Vigreaux column gave crude **4**, bp 83–89° (13 mm) [lit.[2] bp 82.5–83° (12 mm)], 1.5 g (29%). By pmr **4** was contaminated with 15% of dicyclopentadiene and 2-ethylbiphenyl. Comparison of the areas of its proton signals at δ 3.76 and 2.12 indicated 0.90 atom excess D at the 9 position. Glpc on column E at 200° gave **4** >99.5% pure by analysis on column A at 185°. It contained 0.915 atom excess D by mass spectrometry.

B.—On a 19-mmol scale the final Grignard mixture was added by syringe to 2.5 ml of D_2O. A white gel formed during addition. Glpc on column C at 150° gave **4** which contained 0.97 atom excess D by pmr.

C.—On a 10-mmol scale the Grignard mixture was added dropwise by syringe to a rapidly stirred solution of 2.0 ml acetic acid-*O-d* and 5.0 ml D_2O. Glpc on column D at 165° gave **4** which contained 0.97 atom excess D by pmr.

The **diphenylisobenzofuran adduct of 4 (5)** was prepared according to Cristol and Noreen[13] in 54–61% yield after one crystallization from chloroform–ethanol, mp 252–254° (uncorrected). The adduct from A contained 0.907 atom excess D by mass spectrometry and adducts from A and C contained no trace of *anti*-9 hydrogen by 100-MHz pmr.

Addition of benzyne to methylcyclopentadienes on a 20-mmol scale gave methylbenzonorbornadienes in 45% yield (by glpc comparison to biphenyl standard on column C). Glpc on column C at 150° separated three isomers with retention times of 13.0, 15.5, and 18.0 min and relative areas (column A, 130°) of 3:35:62. A pmr spectrum of the mixture had methyl signals with relative areas 3:31:66 corresponding to the *syn*-9-, 1-, and 2-methyl compounds.

Anal. (of the isomeric mixture). Calcd for $C_{12}H_{12}$: C, 92.26; H, 7.74. Found: C, 92.15; H, 7.77.

1-Methylbenzonorbornadiene and 2-methylbenzonorbornadiene as isolated were each >95% pure by glpc on column C and identified by their ir, mass, and pmr spectra.

***syn*-9-Methylbenzonorbornadiene (7a)** as isolated contained 25% of its 1-methyl isomer. It was identified in the mixture by its pmr spectrum.

***anti*-9-Methylbenzonorbornadiene (8)** was prepared on a 20-mmol scale by adding dropwise at 25° the final Grignard mixture from cycloaddition of benzyne and cyclopentadienylmagnesium chloride to 7 ml of freshly distilled dimethyl sulfate. After stirring for 30 min the mixture was extracted with water and diethyl ether. The ether solution was washed three times with *M* sodium hydroxide and once with saturated sodium chloride, dried, and evaporated to a black oil. Chromatography over silica gel with petroleum ether (bp 30–60°) as eluent gave a brown oil which contained a 90:10 mixture of **3**:**8** by glpc on column A. The mixture was separated with column C at 155° and the components were identified by their pmr spectra. The yield of **8** was ≤3% by comparison to **3**.

Addition of benzyne to methylcyclopentadienylmagnesium chloride was followed by deuterolysis on a 20-mmol scale. Generation of methylcyclopentadienylmagnesium chloride (pmr δ 5.73, AA′BB′) required 12 hr. The product mixture was analyzed by methyl peak areas in its pmr spectrum and by glpc on column C at 150° to contain 18% by glpc (16% by pmr) *syn*-9-methyl-, 13% (11%) 1-methyl-, and 69% (73%) 2-methylbenzonorbornadiene. Overall yield by glpc was 21%.

2-Methylbenzonorbornadiene-*anti*-9-*d* was isolated >95% pure by glpc on column C and identified by pmr, ir, and mass spectra. Its pmr spectrum was identical with that in Table V except that H_{9s} appeared as a single broad band at δ 2.14, H_{9a} was absent, and H_1 and H_4 were narrower. It contained 0.949 atom excess D by mass spectrometry.

Addition of Benzyne to 1,3- and 1,4-Dimethylcyclopentadiene. A.—On a 1.0-mmol scale the product mixture contained 81% 1,3-, 14% 1,4-, and 5% 2, *syn*-9-dimethylbenzonorbornadiene by pmr comparison of methyl peaks. By glpc on column C at 175° the yield was 59% of two components with retention times and relative areas of 10.0 (18%) and 12.2 min (82%). Collection from column C and identification by pmr showed that the first was a mixture of 1,4- and 2,*syn*-9 isomers and the second was the 1,3 isomer.

B.—On a 45-mmol scale benzyne was added to a mixture of ~70% 1,3-dimethylcyclopentadienylmagnesium chloride and ~30% dimethylcyclopentadienes (composition determined by pmr). Cycloadducts were isolated by distillation, bp 90–103° (9 mm), in 48% yield. The distillate was purified and analyzed by glpc on column C to contain 59% 1,4- and 2,*syn*-9- and 41% 1,3-dimethylbenzonorbornadiene.

Anal. (of the isomeric mixture). Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.52; H, 8.34.

1,3-Dimethylbenzonorbornadiene was isolated from B >95% pure by glpc on column C and identified by its pmr, ir, and mass spectra.

2,*syn*-9-Dimethylbenzonorbornadiene (7b) was isolated from B contaminated with 8% 1,3 and 9% 1,4 isomer by pmr. It was identified by its pmr, ir, and mass spectra.

1,4-Dimethylbenzonorbornadiene was obtained from B as 23% of a mixture which contained 77% 2,*syn*-9 isomer and identified by its pmr spectrum.

Addition of benzyne to 1,3-dimethylcyclopentadienylmagnesium chloride on a 20-mmol scale gave a 32% yield (glpc on column C at 160°) of dimethylbenzonorbornadienes after deuterolysis. Generation of the Grignard (pmr δ 5.46, s; 2.02, s) required 60 hr for 97.5% conversion. The product mixture was purified with column C and analyzed with column B to contain 69% 2,*syn*-9- and 1,4- and 31% 1,3-dimethylbenzonorbornadiene. The product distribution from Grignard in Table II includes deuterated products only.

1,3-Dimethylbenzonorbornadiene-*anti*-9-*d* as isolated was >95% pure by column C and identified by pmr, ir, and mass spectra. Its pmr spectrum was identical with that in Table V except that H_{9s} was broad, H_{9a} was missing, and H_4 was narrowed. It contained 0.812 atom excess D by mass spectrometry, indicating that part of its was formed from 1,3-dimethyl-1,3-cyclopentadiene instead of 1,3-dimethylcyclopentadienylmagnesium chloride.

2,*syn*-9-Dimethylbenzonorbornadiene-*anti*-9-*d* was isolated with column C and identified by ir, mass, and pmr spectra. It contained 10% of its 1,4 isomer by pmr, which showed 9-CH_3 as a singlet, no trace of H_{9a}, and H_1 and H_4 narrower than reported in Table V. By mass spectrometry it contained 0.987 atom excess D, indicating that virtually all of it was formed from 1,3-dimethylcyclopentadienylmagnesium chloride.

Hydrogenation of dimethylbenzonorbornadienes by the sodium borohydride–chloroplatinic acid method of Brown and Brown[51] was performed with 0.6 mmol of mixture B. Products with retention times of 11.2 and 12.8 min were separated with column C at 140° and identified as *endo*-2,*syn*-9- and 1,*endo*-3-dimethylbenzonorbornene (**9** and **10**, respectively) by their pmr spectra (see Results). Relative yields were 56 and 44% and the overall yield was 21% by glpc on column B.

Addition of benzyne to trimethylsilylcyclopentadienes on a 20-mmol scale gave a 52% yield by glpc of trimethylsilylbenzonorbornadienes. Separation and analysis with column D at 220° gave 17% 1- (retention time 13.1 min), 15% 2- and *syn*-9- (17.2 min), and 68% *anti*-9-trimethylsilyl (19.6 min) isomers. Analysis of the mixture by areas of trimethylsilyl peaks in its pmr spectrum indicated 16% 1, 11% 2, 2% *syn*-9, and 71% *anti*-9 isomers.

Addition of Benzyne to Trimethylsilylcyclopentadienylmagnesium Chloride. A.—On a 20-mmol scale a 14% yield of trimethylsilylbenzonorbornadiene was found by glpc on column D. Generation of the Grignard reagent (pmr δ 0.12, s, 9 H; 6.13, AA′BB′, 4 H) required 10 hr. The mixture was purified with column D and analyzed by pmr to contain 14% 1-, 58% 2-, 18% *syn*-9, and 10% *anti*-9-trimethylsilyl isomers. The deuterolysis of run B indicated that part of these products must have come from trimethylsilylcyclopentadiene, not from the Grignard reagent.

Anal. (of the mixture). Calcd for $C_{14}H_{18}Si$: C, 78.44; H, 8.46. Found: C, 78.59; H, 8.36.

B.—A mixture of 71% trimethylsilylcyclopentadienylmagnesium chloride and 29% trimethylsilylcyclopentadiene isomers (determined by pmr) was prepared from 19.6 mmol of trimethylsilylcyclopentadiene and 14 mmol of ethylmagnesium chloride. Addition of benzyne and deuterolysis gave a 27% yield of trimethylsilylbenzonorbornadienes by glpc on column D. Analysis and separation on column D gave 16% 1, 57% 2 and *syn*-9, and

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(51) H. C. Brown and C. A. Brown, *J. Amer. Chem. Soc.*, **84**, 1493, 1494, 1495 (1962).

27% *anti*-9 isomers. By mass spectrometry these fractions contained 0.649, 0.947, and 0.046 atom excess D, respectively. By pmr the two compound mixture contained 73% 2 and 27% *syn*-9 isomers. The product distribution in Table III was calculated by assuming that only deuterated material was formed from the Grignard reagent.

1-Trimethylsilylbenzonorbornadiene was isolated from the preceding mixture (A) >95% pure and identified by its pmr, ir, and mass spectra.

2- and *syn*-9-trimethylsilylbenzonorbornadiene were isolated from mixture A as a 77:23 mixture (by pmr) and identified by their pmr, ir, and mass spectra.

***anti*-9-Trimethylsilylbenzonorbornadiene** was isolated from the diene cycloaddition >95% pure and identified by its pmr, ir, and mass spectra.

1-trimethylsilylbenzonorbornadiene-*anti*-9-*d* was isolated from mixture B and identified by its pmr spectrum, which showed a reduction in area and broadening of the $H_{9a,9s}$ signal but no other change from the data given in Table V. It contained 0.649 atom excess D by mass spectrometry. The *anti*-9-*d* configuration was assumed by analogy to other examples in this paper.

2- and *syn*-9-trimethylsilylbenzonorbornadiene-*anti*-9-*d* were isolated as a 73:27 mixture from run B and were identified by their combined pmr spectra, which were identical with those presented in Table V except for a slightly narrower H_1, H_4, multiplet and an H_{9a}, H_{9s} singlet equivalent to 0.75 H. The mixture contained 0.947 atom excess D by mass spectrometry. The *anti*-9-*d* configuration in the 2 isomer was assumed by analogy to previous examples.

Addition of benzyne to *tert*-butylcyclopentadienes on a 4.7-mmol scale gave a 57% yield by glpc of *tert*-butylbenzonorbornadienes. Separation and analysis with column D at 225° gave 33% 1 (retention time 21 min) and 67% 2 (15 min) isomers. Analysis of the mixture prior to glpc by areas of *tert*-butyl peaks in its pmr spectrum indicated 34% 1 and 66% 2 isomers.

Anal. (of the isomeric mixture). Calcd for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.74; H, 8.89.

1- and 2-*tert*-butylbenzonorbornadiene as isolated by glpc were each >95% pure and were identified by their pmr, ir, and mass spectra.

Addition of Benzyne to *tert*-Butylcyclopentadienylmagnesium Chloride.—On a 19-mmol scale the Grignard reagent (pmr δ 1.20, s, 9 H; 5.79, AA′BB′, 4 H) was generated in 12 hr. After deuterolysis a yield of 29% *tert*-butylbenzonorbornadiene was found by glpc. Analysis and separation on column D gave 12% 1 and 88% 2 isomers which contained 0.724 and 0.898 atom excess D, respectively. The product distribution in Table IV was calculated by assuming that the distribution of deuterated material was identical with that formed *via* Grignard.

1-*tert*-Butylbenzonorbornadiene-*anti*-9-*d* was isolated >95% pure and identified by its pmr, ir, and mass spectra.

2-*tert*-Butylbenzonorbornadiene-*anti*-9-*d* was isolated >95% pure and identified by its pmr, ir, and mass spectra. Its pmr spectrum showed a broad peak at δ 2.14 for H_{9s} and a much weaker half of an AB spectrum for residual H_{9a} compared to its undeuterated analog.

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Pseudo π Bonding in Saturated Hydrocarbons

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INDO MO calculations on a number of geometries of ethane lead us to conclude that the fraction of s character in the C–C "single" bond is directly proportional to the pseudo π bond order between the two atoms. This and previous results suggest that the length of the C–C "single" bond may be determined primarily by the π bond order.

The question as to the extent to which the carbon–carbon bond length depends upon π bond order or upon the hybridization in the σ bond has been the subject of considerable debate for several years.[2–6] Many studies have involved attempts to define appropriate models for single bonds resulting from the overlap of different types of hybrid atomic orbitals (sp^n, different n) in unsaturated and strained saturated hydrocarbons.

Maksić and Randić[6] recently examined a number of saturated hydrocarbons, for which the structures are accurately known, and used the method of maximum overlap[7] to calculate the hybridization of the atomic orbitals involved in the various bonds. These authors found a close correlation between the experimental bond lengths and the amount of s character calculated for the hybrid orbitals forming the single bonds. Miyazaki,[5] however, pointed out one of the dangers in using the localized bond approximation particularly for hybrid orbitals with little s character and came to the surprising conclusions that by neglecting the π overlap in ethylene and acetylene the calculated equilibrium bond lengths were essentially identical with those calculated for ethane. This would imply that π overlap is entirely responsible for the shortening of the carbon–carbon bond in the former two molecules. The question therefore arises: *If* bond lengths *are* essentially independent of the hybridization in the σ bond, how does one explain the correlations of Maksić and Randić[6] which were obtained for a large number of *saturated* hydrocarbons?

Because of the many difficulties inherent in experimental approaches to this question, we considered it highly desirable to examine the problem from a theoretical point of view. The INDO[8] approximate SCF MO method which has now been adequately tested and has been shown to give reliable results appeared to us to be most appropriate for this purpose. In this communi-

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[2] For a recent, concise review of the status of this controversy, see R. A. Alden, J. Kraut, and T. G. Traylor, *J. Amer. Chem. Soc.*, **90**, 74 (1968), and references cited therein.

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