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Polar and Stereochemical Factors in the Carbalumination of Olefins. Addition of Triphenylaluminum to 6-Substituted Benzonorbornadienes[1]

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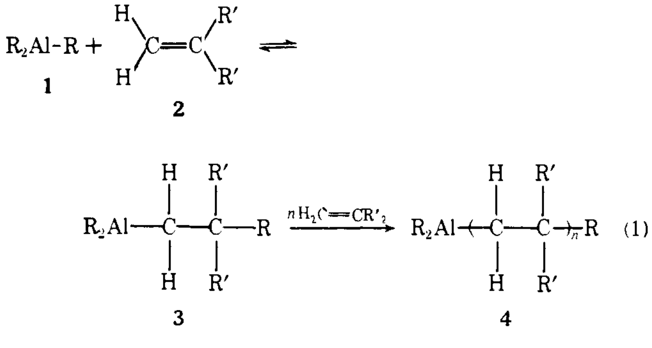
Abstract: The electronic and stereochemical factors in the carbalumination of olefins were assessed by a study of the addition of triphenylaluminum to 6-substituted benzonorbornadienes bearing protio, chloro, methyl, and fluoro groups. On the basis of the deuterium-containing 2-phenylbenzonorbornene obtained by treatment of the aluminum adduct with D_2O and the 3-phenylbenzonorbornen-2-one obtained by oxidative work-up, the carbalumination was shown to occur in an exo,syn manner without skeletal rearrangements. The regioisomeric ratios of adducts were determined to be 53:47 (7Me:6Me) for the 6-methyl case and 30:70 (7F:6F) for the 6-fluoro case by the following procedure: (a) air oxidation of the carbalumination adducts; (b) Jones oxidation of the resulting mixture of ketones and alcohol to exclusively the isomeric ketones; and (c) ^1H or ^{19}F NMR analysis of these ketones, using $Eu(fod)_3$ to separate the resonance signals and to make structural assignments. The relative reactivities of the four benzonorbornadienes in carbalumination, as determined at 80.0 ± 0.2° in benzene by the homocompetitive method, were 0.66 (Cl), 0.80 (F), 1.00 (H), and 1.30 (CH_3). The stereochemistry and substituent effects point to electrophilic attack by monomeric $(C_6H_5)_3Al$ on the olefin in the rate-determining step. Both the relative rates and the limited data on regioisomeric ratios correlate better with the modified parameter, $(\sigma_p + \sigma_m)/2$, than with σ_p^+ or σ_p. The transition state of the rate-determining step is considered to resemble a π complex, while the regioisomeric products are thought to arise in a relatively fast step whose transition state resembles a σ complex. Such a mechanism seems in best accord with the differing influences of substituents on overall rate and on product distribution.

The addition of the aluminum–carbon bond to unconjugated olefinic substrates, first reported by Ziegler and his coworkers in 1950,[2] is a reaction of great significance for organic synthesis (eq 1). First of all, the initial adduct **3**, which results from such carbalumination of **2** by **1**, is itself an aluminum alkyl and can, in principle, react with additional olefinic units to produce a long-chain aluminum alkyl **4**. With olefins like ethylene (**2**, R′ = H), the resulting straight-chain aluminum alkyls (**4**, R′ = H; R = C_2H_5) can readily be transformed into higher molecular weight α ole-



$$R_2Al{-}R + H_2C{=}CR'_2 \rightleftharpoons R_2Al{-}CH_2{-}CR'_2{-}R \xrightarrow{n\,H_2C=CR'_2} R_2Al{-}(CH_2{-}CR'_2)_n{-}R \quad (1)$$

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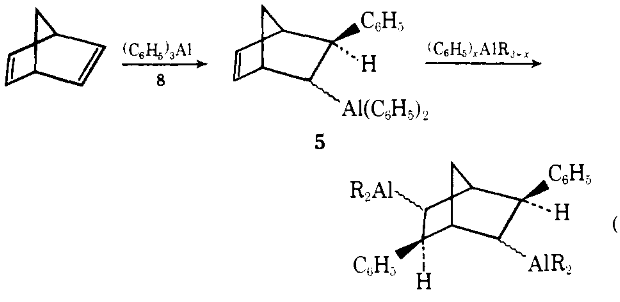
fins[3] or, alternatively, into higher straight-chain *n*-alcohols[4] (*n* ranging from 4 to ca. 20). Secondly, with olefins other than ethylene, the 1:1 reaction with the aluminum alkyl[3a,5] or aryl[6] can often be made to predominate, leading to good yields of **3** or its derivatives. In fact, under special circumstances, β,β-disubstituted olefins, such as isobutylene (**2**, R′ = CH_3), react reversibly with trimethylaluminum at 200°.[7]

Despite extensive research on the industrial applications, little has been reported on the polar and stereochemical factors operative in the carbalumination of olefins. Indeed, what was known only served to pique one's interest. Thus, the observation that *cis*-stilbene underwent no carbalumination by triphenylaluminum after 40 h in a refluxing 0.35 M mesitylene solution[8] stands in sharp contrast to the complete reaction observed between diphenylacetylene and this aluminum aryl after 4 h in a refluxing 0.9 M mesitylene solution.[9] Since the carbalumination of acetylenes had previously been shown to be initiated by an electrophilic R_3Al monomer,[9,10] this low reactivity of an olefin vs. an acetylene toward an apparent electrophilic carbalumination was considered very unusual. In all previous studies of electrophilic additions to carbon-carbon unsaturation, olefins have generally exhibited distinctly greater reactivity than acetylenes; only in highly polar solvents are such relative reactivities inverted.[11]

As to stereochemistry and regiochemistry, the carbalumination of norbornadiene proved to be both informative and curious.[6] Both the mono- and diarylation effected by triphenylaluminum were found to yield exclusively the *exo*-phenyl derivatives, although the stereochemistry of the carbon-aluminum bonds in **5** and **6** was not determined (eq 2).



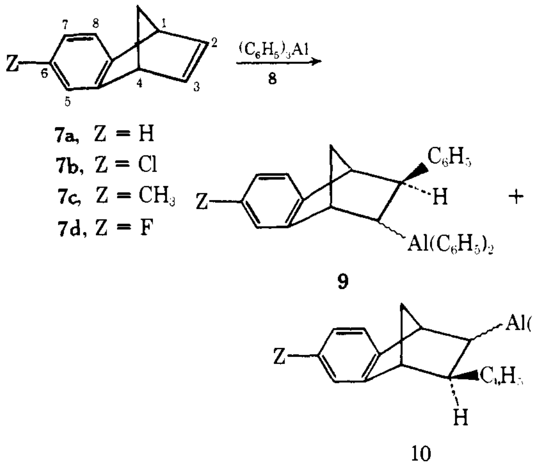
5

6

(2)

But the second arylation proved to be highly regioselective, if not regiospecific, for only the *exo,exo*-2,5-diphenyl adduct (**6**) was detectable.

Therefore, in order to assess electronic and stereochemical factors in the carbalumination of the C=C bond, the addition of triphenylaluminum (**8**) to 6-substituted benzonorbornadienes (**7**) was chosen. For a detailed study of rates and product structure (eq 3), this type of olefin has the following advantages: (a) it is more reactive in carbalumination than the sluggish acyclic olefins; (b) it possesses a cyclic structure that should permit ready determination of the syn or anti nature of carbalumination; (c) the 6-substituent could exert a polar influence on the regiochemistry of addition via homoconjugation[12] without steric interference; and (d) the resulting adducts, **9** and **10**, would have no tendency to undergo a complicating elimination of R_2AlH[6] (eq 4). The bridgehead hydrogens in **9** and **10** adjacent to either an exo or endo R_2Al group could not assume the syn-periplanar configuration seemingly necessary for a smooth dehydralumination.[13]

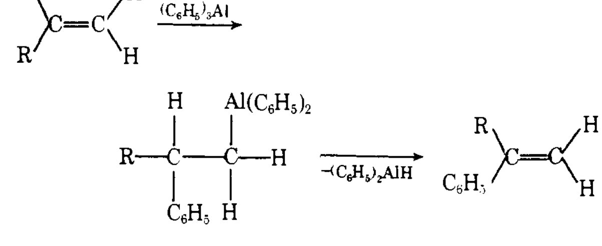


7a, Z = H
7b, Z = Cl
7c, Z = CH_3
7d, Z = F

9

10

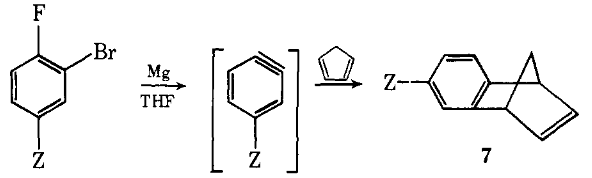
(3)



(4)

Results

Stereochemistry. The requisite 6-substituted benzonorbornadienes were obtained in 60–80% yield by general adherence to the method of Wittig and Knauss,[14] once the suitably 4-substituted 2-bromo-1-fluorobenzenes had been obtained (eq 5).

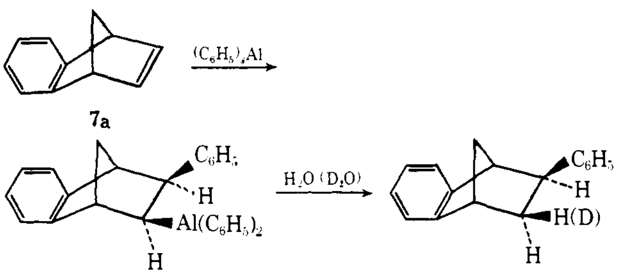


7

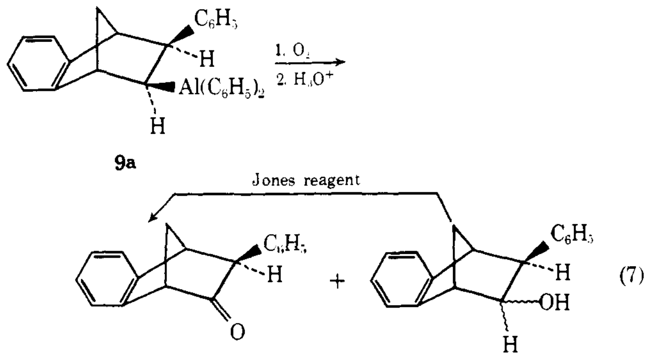
(5)

The benzonorbornadienes **7** reacted smoothly and completely with 1 molar equiv[15] of triphenylaluminum (**8**) in refluxing benzene solution. For the parent benzonorbornadiene (**7a**), hydrolysis led to a quantitative yield of a phenylbenzonorbornene (**11a**). Although the presence of an exo or endo substituent on the ethano bridge of a benzonorbornene is usually ascertainable by NMR analysis,[16,17] the chemical shifts of the two bridgehead protons were too close (within 2 Hz) to permit observation of the strong coupling of bridgehead-exo protons or the weak coupling of bridgehead-endo protons. But the broadened doublet of doublets centered at δ 2.75 ppm could be assigned readily to the 2-endo benzylic hydrogen; the larger coupling of 9 Hz could be ascribed to the coupling with the 3-endo proton and the smaller coupling of 5 Hz as due to the 3-exo proton. As corroboration of this assignment, it was found that treatment of aluminum adduct **9a** with deuterium oxide gave a deuterated phenylbenzonorbornene (**11a**), whose NMR spectrum now displayed only a broadened doublet centered at δ 2.75 ppm (J = 9 Hz). This result is consistent with a structure of *exo*-3-deuterio-*exo*-2-phenylbenzonorbornene. (For precedents on the hydrolysis of carbon-aluminum bonds with retention of configuration, cf. ref 1, 9, and 41.) Hence, the carbalumination is shown to have occurred in an exo,syn manner and without skeletal rearrangement (eq 6). Further assurance on the structural assignments for **9a** and **11a** was secured by the air oxidation of **9a** to yield a mixture of 3-phenylbenzonorbornen-2-one (**12a**) and the 3-phenyl-*exo*- and -*endo*-2-benzonorborneols (**13a** and **14a**). Then, by oxidation with the Jones reagent, the mixture was completely converted to the ketone (eq 7).

In the NMR spectrum of ketone **12a**, the signal due to



9a **11a** (6)



(7)

12a **13a**, OH *exo* **14a**, OH endo

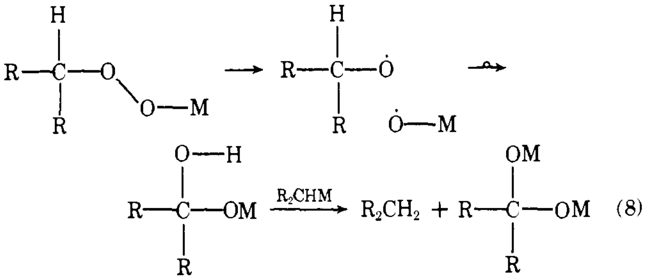
the methano bridge proton syn to the benzo ring was considerably more broadened than the signal for the anti proton. This *W* coupling could only arise from a 3-endo proton; consequently, the phenyl group must be in a 3-exo position.

Finally, it should be mentioned that phenyllithium reacts with benzonorbornadiene in tetrahydrofuran solution to yield **11a** upon hydrolysis.[18] Previous workers have added alkyllithium reagents to **7a**[19] and, based upon NMR spectral data, have also assigned the structures of the products as *exo*-2-alkylbenzonorbornenes.

Regiochemistry. Analogous phenylaluminations were achieved in high yield with the 6-chloro- (**7b**), 6-methyl- (**7c**), and 6-fluorobenzonorbornadienes (**7d**). In no case was the isolated yield less than 90%. Similar NMR spectral data for their phenyl (**11**) or ketonic (**12**) derivatives support the occurrence of only exo,syn addition without skeletal rearrangement. In these cases, however, regioisomers **9** and **10** were to be expected, and a method of determining their proportions had to be found. No applicable differences were discerned in the individual infrared spectra of **11b**, **11c**, or **11d**, nor were the regioisomers resolvable by various gas-liquid or thin-layer chromatographic analyses. Although NMR spectral measurements for ^{1}H on the 6- and 7-methyl-2-phenylbenzonorbornenes (**11c**) or for ^{19}F on the 6- and 7-fluoro mixture (**11d**) appeared to offer an analytical method, even at 100 MHz **9c** and **9d** displayed only one type of CH_3 singlet or ^{19}F octet, respectively.

The regioisomeric ratios for the methyl- and fluorobenzonorbornadiene cases were finally determined by means of the oxidation sequence exemplified in eq 7. The isomeric ratio of the final ketonic products, **12c** and **12d**, could be estimated by means of NMR analysis with the lanthanide shift reagent Eu(fod)$_3$. In the methyl case, the observed regioisomeric ratio was 53:47 (7Me:6Me); with the fluoro ketones, the ratio of isomers was 30:70 (7F:6F).

Before structural assignments are made to the components of these ratios, some comment is in order on whether the oxidation sequence reflects accurately the ratio of the original regioisomers **9** and **10**. First of all, the oxidation of carbon-metal bonds by O_2 seems to be of a free-radical nature and to proceed via metal hydroperoxide intermediates.[4,5,20-23] Consequently, it appears reasonable that there should be little difference in the reactivity of the C_2–Al bonds in **9** and **10** toward oxygen. Secondly, although only 80% of **9** and **10** could be converted to oxidized products, **12**, **13**, and **14**, it is again reasonable that the processes leading directly to ketone **12** and hydrocarbon **11** are of a free-radical, and hence nonselective, character[24] (eq 8).

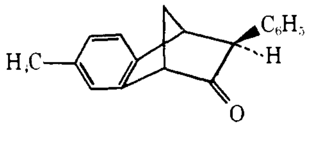


$$\mathrm{R{-}\underset{R}{\overset{H}{C}}{-}O{-}O{-}M} \longrightarrow \mathrm{R{-}\underset{R}{\overset{H}{C}}{-}\dot{O}} \quad \mathrm{\dot{O}{-}M} \longrightarrow$$

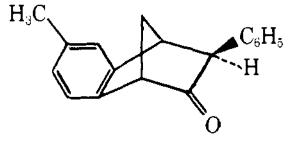
$$\mathrm{R{-}\underset{R}{\overset{O-H}{C}}{-}OM} \xrightarrow{\mathrm{R_2CHM}} \mathrm{R_2CH_2} + \mathrm{R{-}\underset{R}{\overset{OM}{C}}{-}OM} \quad (8)$$

Thirdly, from the material balance obtained for the oxidation of the mixture of **12**, **13**, and **14** by the Jones reagent, it appears that the alcohols **13** and **14** are oxidized essentially quantitatively to the ketone **12**. Thus, it is concluded that NMR analysis of the regioisomeric ketonic mixtures, **12c** and **12d**, does constitute a reliable method for determining the original regioisomeric ratio of **9** and **10**.

The NMR spectrum of the 6- and 7-methyl isomeric ketones displayed a single methyl resonance at δ 2.32 ppm. Addition of the Eu(fod)$_3$ reagent to the sample in $CDCl_3$ caused the appearance downfield of two methyl signals in a ratio of 53:47. Furthermore, the major component's signal was shifted farther downfield. With $1/R^3$ dependence on the lanthanide-induced downfield shift for protons,[25,26] even for protons of the bicyclo[2.2.1]heptane,[27] the major isomer must be the 7-methyl-*exo*-3-phenylbornen-2-one (**12c**, 7-Me). As estimated from Dreiding models, the vector distance *R* from the carbonyl group, which coordinates with Eu^{3+}, to the 7-methyl is ca. 0.5 Å shorter than to the 6-methyl. This method of structure assignment is in accord with that applied to benzonorbornadiene *exo*-oxide[28] and does not ignore possible dependence of this induced shift on angular factors.[29] The relative angles between the assumed axis of the oxygen-europium bond (a linear extension of the carbon-oxygen bond) and 6- and 7-methyl carbon-carbon bonds are ca. 42 and 47°, respectively. The experimentally observed downfield shifts of both methyl signals confirm that such angles are less than 54°, above which angle upfield shifts begin to occur.[29]



12c (7-Me), 53%



12c (6-Me), 47%

A similar analysis using ^{19}F NMR spectroscopy was applied to the 6- and 7-fluoro isomeric ketones. In this case, the individual fluoro signals of the isomers were directly observable without resort to a lanthanide shift reagent. The observed signals in a ratio of 30:70 were both shifted downfield upon adding Eu(fod)$_3$, but the signal of the minor isomer was shifted 18 Hz, compared with a shift of 6 Hz for the major isomer. For reasons analogous to those presented for the methyl isomers, these results show that the major isomer is the 6-fluoro-*exo*-phenylbenzonorbornen-2-one (**12d**).

Relative Reactivities. The relative rates of addition of triphenylaluminum (**8**) to the 6-substituted benzonorbornadienes (**7a–d**, Z = H, Cl, CH_3, and F) were determined in benzene solution at 80.0 ± 0.2° by the homocompetitive

Table I. Typical Homocompetitive Kinetic Run between Triphenylaluminum and the 6-Chloro, 6-Methyl-, and 6-Protiobenzonorbornadienes[a]

Time, min	Olefin (H)[b], Peak area	Olefin (H) Adduct	Olefin (Me)[b]	Olefin (Me) Adduct	Olefin (Cl)[b]	Olefin (Cl) Adduct
5.3	228	18	250	26	250	13
10.3	196	34	221	47	236	26
22.7	172	76	179	102	212	54
40.2	127	118	128	154	117	94
80.1	70	170	61	214	119	149
166	22	225	14	268	56	224

[a] Conditions: in benzene solution at 80.0 ± 0.2° with initial concentrations of 7.45×10^{-2} M in benzonorbornadiene, 7.78×10^{-2} M in the 6-methyl derivative, and 7.54×10^{-2} M in the 6-chloro derivative, and 0.254 M in triphenylaluminum. [b] The olefin and adduct peak areas were converted into molar ratios by means of experimentally determined response factors, R = (moles of olefin)/(moles of adduct) × (area of adduct)/(area of olefin), either by use of known mixtures or successive GC injections.

Table II. Typical Homocompetitive Kinetic Run between Triphenylaluminum and the 6-Chloro- and 6-Fluorobenzonorbornadienes[a]

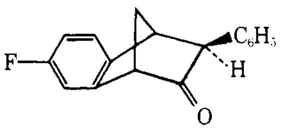
Time, min	Olefin (Cl)[b] Peak area	Olefin (Cl) Adduct	Olefin (F)[b]	Olefin (F) Adduct
10.8	267	31	246	32
20.7	243	56	226	61
40.0	221	106	184	113
80.1	147	171	125	183
160	79	253	59	256
327	20	285	15	283

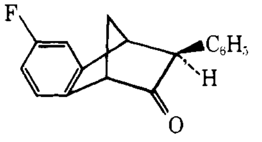
[a] Conditions: in benzene solution at 80.0 ± 0.2° with initial concentrations of 9.51×10^{-2} M in the 6-chloro-, 9.63×10^{-2} M in the 6-fluorobenzonorbornadiene, and 0.195 M in triphenylaluminum. [b] Cf. footnote *b* in Table I.

Table III. Observed Relative Rate Ratios as a Function of Time

Time, min	k_K/k_{Me}	k_H/k_{Cl}	k_{Cl}/k_F
10	0.60 ± 0.17[a]	1.41 ± 0.11[a]	0.82 ± 0.00
22	0.71 ± 0.06	1.56 ± 0.04	0.82 ± 0.00
40	0.78 ± 0.01	1.51 ± 0.01	0.80 ± 0.02
80	0.79 ± 0.02	1.50 ± 0.02	0.82 ± 0.00
166	0.79 ± 0.02	1.50 ± 0.02	0.85 ± 0.03
Av	0.77 ± 0.03	1.52 ± 0.02	0.82 ± 0.01

[a] This point was outside of two standard deviations and was discarded.


12d (7-F), 30%


12d (6-F), 70%

method[30] (Tables I and II). The relative rates remained constant throughout the competitive runs (Table III), thereby giving assurance that all the olefinic substrates followed the same kinetic law for their reaction with **8**, regardless of the extent of reaction. The observed relative rates, k_Z/k_H, of 0.66 for Cl, 0.80 for F, and 1.30 for CH_3, were reproducible to within ±0.02.

Discussion

Kinetics. From previous detailed kinetic studies of the carbalumination of olefins[31-32] and acetylenes,[10] it is known that the reaction is first order in unsaturated hydrocarbon and one-half order in the organoaluminum reagent. For these hydrocarbons and for the benzonorbornadienes considered here, the most reasonable scheme would be the rate-determining attack of monomeric R_3Al on the hydrocarbon substrate:

$$[(C_6H_5)_3Al]_2 \rightleftharpoons 2(C_6H_5)_3Al \tag{9}$$

$$(C_6H_5)_3Al + \mathbf{7} \xrightarrow[\text{slow}]{k} \mathbf{9} + \mathbf{10} \tag{10}$$

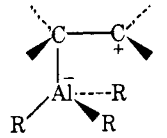
The small but real increase in the reactivity of the 6-substituted benzonorbornadienes (**7**), as Z is, in turn, Cl, F, H, and CH_3, is generally parallel with the electron-donating properties of the Z group. This trend in reactivity is consistent with the electrophilic attack of monomeric $(C_6H_5)_3Al$ on the olefin in the rate-determining step (eq 10).

Linear Free Energy Correlations. In order to quantify this relationship between relative reactivity and electron donation by Z, linear free energy correlations were sought between k_{rel} and electronic parameters for Z, such as σ_p, σ_p^+, and $(\sigma_p + \sigma_m)/2$. These σ parameters stand for the Hammett homo-para (C_6) value, the Hammett-Brown homo-para (C_6) value, and the average value of the Hammett homo-para (C_6) and homo-meta (C_7) parameters, respectively. An attempted linear plot of the logarithms of k_{rel} vs. σ^+ gave a straight line with much scatter in the points (correlation coefficient r = 0.89). On the other hand, log k_{rel} correlated quite well with either σ_p of Z (r = 0.98, slope ρ of −0.74) or $(\sigma_p + \sigma_m)/2$ (r = 0.99, ρ = −0.66, Figure 1). Although there is no decisive difference in the fit of the correlations for these two parameters, the known character of electronic influences in benzonorbornadienes[33,34] would suggest that $(\sigma_p + \sigma_m)/2$ is the more realistic parameter for polar reactions. Any 6-substituent is homo-para to C_2 but also homo-meta to C_3; thus, any polar interaction at the double bond involving delocalization of charge should have both meta and para contributions.[33,34] Sizable homobenzylic contributions have been observed, for example, in the rates of solvolysis of 6- and 7-substituted benzonorbornen-2-(*exo*)-yl *p*-brosylates.[12]

Other evidence supporting the choice of the modified parameter, $(\sigma_p = \sigma_m)/2$, to describe electronic influences in **7** can be adduced from the observed regioisomeric ratios. Albeit analytical difficulties permitted only two such ratios to be determined, and these in an indirect way, the logarithm of ratio, [% 6 isomer]/[% 7 isomer], did give a linear correlation with $(\sigma_p + \sigma_m)/2$ for the 6-methyl-, 6-protio-, and 6-fluorobenzonorbornadienes (r = 0.97 and ρ = −1.4). It is appreciated that three-point plots do not represent a strenuous test of a correlation but, on the other hand, the log [% 6]/[% 7] does not correlate at all well with σ_p.

Nature of the Transition State. The carbalumination of the C=C bond demands an electrophilic, exo,syn attack of monomeric triphenylaluminum on the benzonorbornadiene substrate. The observed ρ of −0.66 for k_{rel} (Figure 1) and the influence of the 6-substituent on the regioisomeric ratio speak for the accelerating influence of π electron availability in the olefin. Both nucleophilic and free-radical pathways can be dismissed as incompatible with the facts: (a) instead of the observed rate *decrease*, the changing of the electron-donating methyl group in **7** to an electron-withdrawing fluoro or chloro group should have *increased* the relative rates, if nucleophilic carbalumination were operative; and (b) free-radical additions to the norbornenyl or benzonorbornenyl strained C=C bond are known to yield anti adducts or a mixture of syn and anti adducts,[16] rather than the observed exclusively exo,syn adducts.

For the transition-state configuration in such electrophilic attack, three limiting models deserve consideration: (1) a σ-bonded complex (**15**); (2) a π-complexlike adduct (**16**); and (3) a trapezoidal array, in which the new C–Al bond is more established than the new C–C bond (**17**). A fourth possibility (**18**), a so-called "four-centered" rectangular variant of **17**, suffers from the "forbiddenness" of thermal suprafacial $[2_s + 2_s]$ processes.[35,36]



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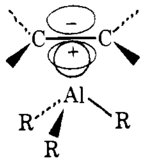

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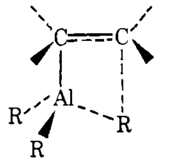

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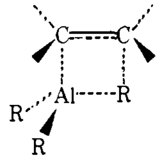


18

The absence of skeletal rearranged products in these carbaluminations and the small absolute ρ value of -0.66 in the correlation of log k_{rel} vs. $(\sigma_p + \sigma_m)/2$ (Figure 1) argue against a σ-like complex (**15**). The development of much positive character on an olefinic carbon of **7** would be expected to provoke the kind of skeletal rearrangements well known in bicyclo[2.2.1]heptyl systems.[37] Also, in well-authenticated carbonium ion processes, such as the solvolysis of benzonorbornen-2-(*exo*)-yl *p*-brosylates,[12] the relative rates correlated with σ_p^+ with a ρ of a large absolute value (-3.3).

With the data available from this and previous studies,[32,38] a rational, but not compelling, choice between transition states **16** and **17** can be made. For electrophilic aromatic attack, Olah has recently summarized evidence indicating that attack of stronger electrophiles on aromatic rings involves the rate-determining formation of π complexes. Weaker electrophiles, on the other hand, tend to involve the rate-determining formation of the generally accepted σ complex or Wheland configuration.[39] This distinction permits a rationale of why strong electrophiles can show a low-substrate selectivity (e.g., $k_{\mathrm{toluene}}/k_{\mathrm{benzene}}$), yet show a high-site selectivity (e.g., ortho + para/meta). Substrate selectivity would be controlled by rate-determining π-complex formation, while site selectivity would be determined by the relative rates of σ-complex formation in a kinetically fast step.

Applied to carbalumination, this viewpoint would lead one to look for a varying electronic sensitivity in overall rates vs. regioisomeric ratios, if a π-complex transition state (**16**) were rate determining. On the other hand, transition state **17** implies that overall rates of addition and the resulting regioisomeric ratio should be determined in the same step; therefore, electronic influences would be identical for both.

If the rate- and product-determining transition state were to resemble **17**, then both the relative rates and the regioisomeric ratios would be expressible in terms of partial rate factors for the attack of the $(C_6H_5)_3Al$ electrophile on C_2 or C_3 of the hydrocarbon substrate (**7**): namely

$$k_{\mathrm{rel}} = \frac{k_Z}{k_0'} = \frac{k_2 + k_3}{2k_0} \text{ and product ratio } = \frac{[6]}{[7]} = \frac{k_3}{k_2}$$

The k_Z and k_0' represent the overall rates for the 6-substituted and unsubstituted benzonorbornadienes, respectively; and k_0, k_2, and k_3 are the partial rate factors for attack at one position of the unsubstituted benzonorbornadiene or for attack at each dissimilar position of the 6-substituted benzonorbornadiene. Now, if one solves these equations simultaneously, one can obtain the ratios of k_2/k_0 and k_3/k_0.

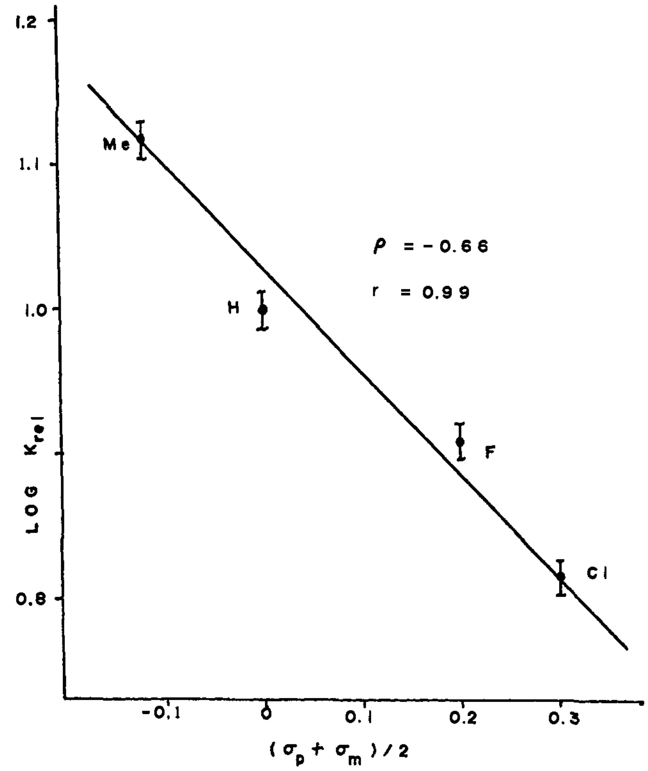


Figure 1. Plot of the logarithm of the relative rate, k_Z/k_H, vs. the modified Hammett parameter, $(\sigma_p + \sigma_m)/2$, for the addition of triphenylaluminum to 6-substituted benzonorbornadienes in benzene at 80.0°.

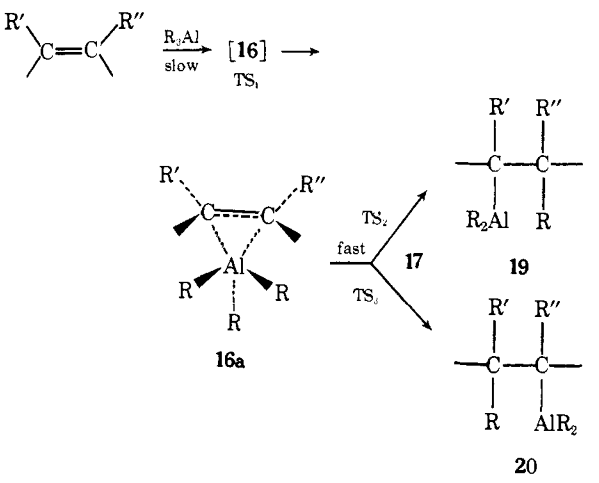
With reference to the numbering in eq 3, k_3 should be enhanced with respect to k_2 and k_0 for $Z = CH_3$; conversely, it follows that $k_2 > k_3 < k_0$ for Z = F. By use of the observed relative rates and product ratios, one obtains values:

$$Z = CH_3\text{: } k_3/k_0 = 1.38;\ k_2/k_0 = 1.22$$

$$Z = F\text{: } k_3/k_0 = 0.48;\ k_2/k_0 = 1.12$$

that is, the rate of attack of $(C_6H_5)_3Al$ at C_3 is increased or decreased relative to k_0, as would be expected from the σ values of the substituent homo-para to C_2. However, the k_2/k_0 ratios would lead one to conclude that attack at C_2 is also enhanced for $Z = CH_3$ or F. Since C_2 is homo-meta to Z, it is unreasonable that both a CH_3 ($\sigma_m = -0.069$) and F substituent ($\sigma_m = +0.336$) would enhance attack at C_2. Thus, the assumption that both relative reactivity and product ratios are determined in the same step (**17**) leads to incompatible partial rate ratios. We therefore conclude that relative rates and product ratios are subject to differing electronic influences and hence are determined at different stages along the reaction coordinate. Although this demonstrated inconsistency between partial rate factors is based only upon few data, other arguments can be marshaled against **17** and in favor of **16** as the configuration of highest energy.

A reaction energy profile in better accord with the relative rates, the regioisomeric ratios, the correlations with $(\sigma_p + \sigma_m)/2$ values and the foregoing failure to obtain compatible partial rate factors would be that shown in eq 11. This scheme involves a rate-determining transition state resembling a π complex (**16**), followed by transition states of lower energy (possibly resembling **17**), which then lead to the regioisomers **19** and **20** in relatively rapid steps (eq 11). Since the formation of π complexes between unsaturated hydrocarbons and silver ion, or other Lewis acids, is generally rapid and readily reversible, it may rightly be asked why the formation of **16a** should be rate determining in car-

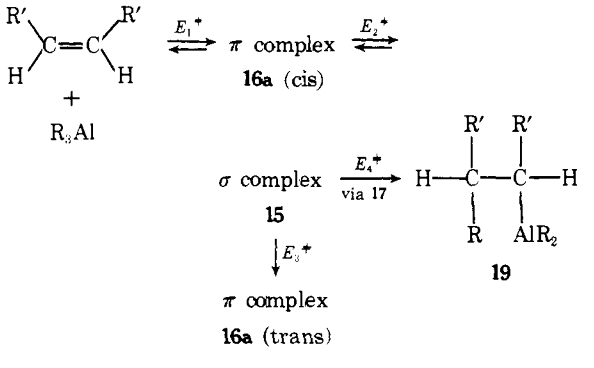


(11)

balumination. The endoergic processes contributing to the activation energy for **16** would be the following: (1) formation of monomeric $(C_6H_5)_3Al$ from the dimer present in benzene solution;[15] (2) the steric repulsions between the phenyl groups and the hydrocarbon substituents (R′, R″, and C_6H_5 in **16**); (3) change of hybridization in the Al center of monomeric $(C_6H_5)_3Al$ from sp^2 toward sp^3 in **16**; and (4) partial disruption of the carbon–carbon π bond.

The scheme given in eq 11 and the foregoing energy contributions to transition state **16** can also be invoked to explain the unusual relative reactivity of acetylenes vs. olefins toward carbalumination (cf. supra). For example, diphenylacetylenes and benzonorbornadienes, which have relative reactivities of ca. 1:100, are both $>10^3$ more reactive than *cis*- or *trans*-diphenylethylenes.[8,10] Clearly, the second and fourth factors would lead to a higher reactivity of the acetylenes and norbornadienes, which would offer less steric hindrance to the approach of $(C_6H_5)_3Al$ and whose π bonds are more readily disrupted. That olefins are pronouncedly less reactive in carbalumination reveals the great importance of steric factors and, consequently, of the close approach of the aluminum reagent to the unsaturated bond (i.e., in **16** and **16a**). Such intimate π complexation with acetylenes and norbornadienes is probably much stronger than the labile complexes formed with silver ion.

On the other hand, there is evidence that both π and σ complexation with acyclic olefins may not be rate determining in the carbalumination reaction, but that possibly a transition state like **17** may be the configuration of highest energy. Thus, for example, *cis*-diarylethylenes undergo $(C_6H_5)_3Al$-catalyzed isomerization to *trans*-diarylethylenes at temperatures (<200°) where no carbalumination can be detected.[8] Because of steric factors, it would appear that the olefin-$(C_6H_5)_3Al$ π complex (**16a**) would be looser and hence of lower energy than analogous acetylene complexes. Such a π complex could pass over a higher energy barrier to the σ complex (**15**), which would seem responsible for the cis,trans isomerization, but still a higher barrier (**17**) would have to be surmounted to achieve carbalumination (eq 12), where $E_4^‡ \gg E_2^‡ > E_3^‡ > E_1^‡$.



(12)

Finally, it should be noted that a rate-determining formation of a π complex also seems to best explain the steric and electronic effects observed in the hydralumination of alkynes.[40,41] Moreover, the existence of the high-energy intermediate **16a** postulated in these kinetic studies is supported by the detection of unusually stable π complexes in equilibrated systems, both in the liquid[42-45] and the solid phase.[46]

Experimental Section

General Techniques. Techniques for the preparation, handling, and storage of organoaluminum reagents have been described previously.[9,10] The preparation of glassware, the scrupulous drying and deoxygenating of apparatus and solvents, and the removal of representative organoaluminum aliquots for analysis, which must be undertaken for reliable kinetic results, are described in detail in a previous report.[41] The purity of the nitrogen atmosphere employed here, the types of spectral and gas chromatographic instrumentation used, and any specialized technique for kinetic or spectral measurements can also be found in the same article. All reactions involving the use of organomagnesium or organoaluminum compounds were performed under an atmosphere of highly purified nitrogen.

Melting points were determined in capillary tubes with a Thomas-Hoover Unimelt (oilbath) apparatus and are corrected. The infrared spectra were measured either on neat liquids or on solid samples dissolved at 10% (w/w) solutions in CCl_4 and the spectra recorded with a Perkin-Elmer Infracord, Model 137. The values are reported on the δ scale relative to internal Me_4Si. Although most NMR spectra were measured with a Varian spectrometer, Model A-60, some were obtained with a Varian Model HA-100.

Preparation and Purification of Reagents. Triphenylaluminum (8). This compound was prepared from aluminum metal and 0.20 mol of diphenylmercury in accord with a published procedure;[9] the product was recrystallized twice from xylene and then twice from toluene to give a 50% yield of densely packed colorless crystals, mp 240–242° (lit.[9] 243°).

Benzonorbornadiene (7a). This parent hydrocarbon and the 6-chloro-, 6-fluoro-, and 6-methylbenzonorbornadienes were prepared by the addition of the appropriate aryne to cyclopentadiene in accordance with the general method of Wittig and Knauss.[14]

Thus, into a 100-ml three-necked flask, which was fitted with a reflux condenser surmounted by a nitrogen inlet, a paddle-blade stirring assembly, and a 100-ml pressure-equalized dropping funnel, were placed 2 g (83 mmol) of magnesium turnings. Then a solution of 6.5 ml (4.9 g, 75 mmol) of freshly distilled cyclopentadiene and 13 g (75 mmol) of *o*-bromofluorobenzene (Penisular ChemResearch) in 45 ml of anhydrous tetrahydrofuran (freshly distilled from $LiAlH_4$) was slowly added to the magnesium; after 15 ml had been added, the flask was warmed slightly to initiate the reaction (light green color). The reaction proceeded smoothly as the balance of the THF solution was added over 30 min. The resulting solution was then heated to reflux for 30 min and thereafter the THF removed at a pressure of 25 mmHg. The residue was treated with 50 ml of saturated aqueous NH_4Cl solution and then extracted with ether. The ether extracts were dried with Na_2SO_4, freed of solvent and distilled to yield benzonorbornadiene: 5.9 g (55%); bp 45–46° (1 mm); $n^{20}D$ 1.5660 (lit.[14] $n^{20}D$ 1.5668); NMR (CCl_4) 2.20 (m, 2), 3.77 (m, 2), 6.66 (m, 2), 6.92 (m, 4). Analysis by GLC (F & M, Model 720, 6 ft Chromosorb P column with 10% silicone gum rubber) showed just one peak; the forerun fraction (bp 40–42°) contained 5% of *o*-bromofluorobenzene and a smaller amount of dicyclopentadiene.

6-Chlorobenzonorbornadiene (7b). The requisite 2-bromo-4-chlorofluorobenzene was prepared by a six-step sequence from *p*-chloroaniline. Thus, 2-bromo-4-chloroaniline (mp 65–67°, lit.[47] mp 69°) was prepared in 72% yield by the method of Chattaway and Clemo. This compound was then converted to the desired fluoro derivative by a modified Schiemann reaction in a 50% yield:[48] bp 88–89° (27 mm), $n^{20}D$ 1.5545 (lit.[48] $n^{19}D$ 1.5549). By repeating a run of the modified Schiemann procedure at a lower temperature

(155-160°) for the pyrolysis step than recommended (165-170°), the yield was improved to 60%.

By following the foregoing procedure for benzonorbornadiene, but using twice the amounts of reagents, the 6-chlorobenzonorbornadiene was obtained in 61% yield: bp 110-112° (10 mm); $n^{20}\mathrm{D}$ 1.5760 (lit.[14] $n^{21}\mathrm{D}$ 1.5763); NMR (C_6D_6) 2.08 (m, 2), 3.52 (bm, 2), 6.57 (bt, 2), 6.88 (d, 2), 7.13 (m, 1).

6-Methylbenzonorbornadiene (7c). 2-Bromo-4-methylaniline (Eastman) was converted into 2-bromo-4-methylfluorobenzene by a known procedure[48] [80% yield, bp 72-73° (25 mm)].

By the foregoing method applied to a 0.15-mol run, 6-methylbenzonorbornadiene was prepared in a 60% yield: bp 92-93° (9 mm); >99% pure by GLC; NMR (CCl_4) 2.23 (m, 5, CH_3 and CH_2 bridge), 3.74 (bm, 2, bridgehead protons), 6.69 (bt, 2, vinyl H), 6.58, 6.95, and 7.10 (3, benzo protons); ir (neat), strong bands at 590, 692, 705, 730, 800, 805, 1282, 1450, 2930, and 2980 cm^{-1}.

Anal. Calcd for $C_{12}H_{12}$: C, 92.25; H, 7.75; Found: C, 92.28; H, 7.62.

6-Fluorobenzonorbornadiene (7d). 2-Bromo-1,4-difluorobenzene (Peninsular ChemResearch) was converted on a 0.13 M scale to 6-fluorobenzonorbornadiene in a yield of 85%, by adherence to the above procedure, bp 77-78° (9 mm). Redistillation gave at least a 63% yield of a fraction >99% pure by GLC; NMR (CCl_4) 2.24 (bs, 2, methylene bridge), 3.82 (m, 2, bridgehead protons), 6.75 (t, 2, vinyl H), 6.30-7.30 (m, 3, benzo protons); ir (neat), strong bands at 590, 605, 702 (br), 738, 805, 820, 856, 925, 1100, 1145, 1210 (br), 1262, 1292, 1410, 1600, 2940, and 2980 cm^{-1}.

Anal. Calcd for $C_{12}H_{11}F$: C, 83.85; H, 5.95. Found: C, 84.01; H, 5.78.

Addition of Triphenylaluminum to Benzonorbornadienes. Benzonorbornadiene. A 100-ml two-necked flask fitted with a reflux condenser and nitrogen inlets was charged with 4.4 g (17 mmol) of triphenylaluminum (drybox), and then 50 ml of dry benzene was distilled (from sodium) directly into the flask. The benzonorbornadiene (2.4 g, 17 mmol, >99% pure) was introduced and thereupon the flask chilled in dry ice and alternately evacuated and refilled with nitrogen thrice. The solution was then heated at reflux for 4 h.

Under nitrogen, one-half of the mixture was transferred to a separate flask and then treated with 2 equiv of deuterium oxide (99.8%); the remaining half was hydrolyzed. After filtering from aluminum hydroxide and washing the latter with benzene, each portion was dried over Na_2SO_4, and the solvent was removed by rotary evaporation. Analysis of each fraction by GLC on a 6 ft column packed with 10% silicone gum rubber on Chromosorb P (used also in all succeeding analyses) showed no starting material and only one peak (programmed up to 300°).

Distillation of the hydrolysis fraction gave 1.6 g of colorless liquid: bp 114-115° (0.5 mm); ir (neat), strong peaks at 700, 750, 1275, 1450, 1475, 1500, 1600, 2875, 2965, 3050, and 3075 cm^{-1}; NMR ($CDCl_3$), 1.8 (m, 4, methylene bridge, 3-exo and 3-endo H), 2.75 (br d of d, 1; 2-endo benzylic H, coupled to 3-endo H with $J = 9$ Hz and to 3-exo H with $J = 5.5$ Hz), 3.3 (bd, 2, bridgehead protons), 6.9 (bm, 9, aromatic). Based upon these NMR spectral data, this compound is assigned the structure of *exo*-2-phenylbenzonorbornene (**11a**).

Anal. Calcd for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.68; H, 7.23.

Similar work-up of the D_2O-treated fraction gave 1.7 g of product whose infrared spectrum was identical with the hydrolysis product, except for an additional peak at 2190 cm^{-1} (C-D stretch); the NMR spectrum in $CDCl_3$ differed from that of *exo*-2-phenylbenzonorbornene in that the 2-benzylic proton was now a broadened doublet with $J = 9$ Hz, and the multiplet centered at 1.8 now had an area equivalent to 3 protons. Since the small trans coupling of the benzylic proton had now disappeared, this product is assigned the structure of exo-3-deuterio-*exo*-2-phenylbenzonorbornene (**11a**).

6-Chlorobenzonorbornadiene. Under the foregoing experimental conditions, 2.8 g (10 mmol) of triphenylaluminum was allowed to react with 1.9 g (10 mmol) of 6-chlorobenzonorbornadiene in 30 ml of refluxing benzene for 4 h. The cooled mixture was hydrolyzed with 1 ml of dilute aqueous HCl (2 equiv) and warmed to 50° for 1 h. Filtration of the aluminum hydroxide and drying of the filtrate with $MgSO_4$ gave an organic extract having only one peak upon GLC analysis. Removal of the solvent and distillation gave the 6- and 7-chloro-*exo*-2-phenylbenzonorbornenes: bp 149-150° (0.05 mm); NMR (CCl_4), 1.93 (m, 4, methylene bridge, 3-exo and 3-endo H), 2.82 (bd d, 1; 2-endo H), 3.40 (bd s, 2, bridgehead H), center at 7.4 (m, 8, aromatic); ir (neat), strong bands at 700, 730, 745, 802, 825, 875, 975, 995, 1075, 1160, 1450, 1475, 1495, 1590, 1610, and 3000 cm^{-1}.

Anal. Calcd for $C_{17}H_{15}Cl$: C, 80.13; H, 5.94. Found: C, 79.85; H, 6.30.

The product was expected to give the two exo regioisomers, 6- and 7-chloro-*exo*-2-phenylbenzonorbornenes. (**11b**) However, detection of these two isomers was not possible: (1) by GLC analysis on a 12-ft column packed with 10% silicone gum rubber on Chromosorb P, programmed at temperatures varying between 200 and 300°; or (2) by TLC on alumina or silica gel, with such developing solvents as C_6H_6-CCl_4-pentane (v/v 40:40:20), hexane-C_6H_6-ether (80:10:10), or hexane-C_6H_6-ethyl acetate (80:15:5).

6-Methylbenzonorbornadiene. In a similar manner, 4.35 g (17 mmol) of triphenylaluminum and 2.73 g (18 mmol. 99.8% pure) of 6-methylbenzonorbornadiene were heated at reflux in 50 ml of benzene for 4 h. Analysis by GLC showed that phenylation had occurred quantitatively. Usual work-up gave 6- and 7-methyl-*exo*-2-phenylbenzonorbornene (**11c**), bp 131-133° (1 mm). The NMR spectrum was measured with a Varian HA-100 spectrometer, in hopes of observing distinct methyl signals for the two expected regioisomers. However, no such peak resolution was observed even at a sweep width of 50 Hz. Spectra: NMR ($CDCl_3$), 1.8 (m, 4 H, methylene bridge, 3-exo and 3-endo H), 2.25 (s, 3 H, methyl), 2.77 (d of d, 1 H, 2-endo benzylic), 3.3 (s, 2 H, bridgehead), center at 7.0 (m, 8, aromatic); ir (neat), strong bands at 703, 732, 742, 775, 808, 825, 975, 995, 1029, 1040, 1450, 1475, 1600, and 2960 cm^{-1}.

Anal. Calcd for $C_{18}H_{18}$: C, 92.25; H, 7.75. Found: C, 92.00, H, 7.82.

6-Fluorobenzonorbornadiene. Analogously, 880 mg (3.4 mmol) of triphenylaluminum and 500 mg (3.2 mmol) of 6-fluorobenzonorbornadiene in 25 ml of refluxing benzene gave after 4 h a quantitative conversion to 6- and 7-fluoro-*exo*-2-phenylbenzonorbornene (**11d**): bp 121-122° (0.5 mm); NMR (CCl_4), 1.89 (m, 4 H, methylene bridge, 3-exo and 3-endo H), 2.80 (broadened d of d, 1 H, 2-endo benzylic H), 3.37 (bd d, 2 H, bridgehead H), 7.20 (s, 5, phenyl), and 6.5-7.3 (m, 3 H, aromatic); ir (neat) 703, 735, 745, 775, 810, 830, 875, 925, 1120, 1235, 1470, 1480, 1600, and 2960 cm^{-1}.

Anal. Calcd for $C_{17}H_{15}F$: C, 85.67; H, 6.35. Found: C, 85.41, H, 6.27.

The individual expected regioisomers were not detectable by either GLC or TLC (cf. supra). In addition, examination of the product dissolved in perfluoro-*p*-xylene (which acted as a solvent and internal standard) with a Varian HA-100 spectrometer equipped with an ^{19}F probe revealed only one symmetrical eight-line signal at 7591 Hz downfield from the lock signal (first upper sideband of solvent). Such a signal is consistent with an ABCX splitting pattern arising from coupling between the ^{19}F nucleus and the three different benzo protons. Thus, even this spectrum failed to reveal any different signals for the 6- and 7-fluoro regioisomers of the product.

Determination of the Regioisomer Distribution. Attempted Reactions. First, a thermal ring opening of *exo*-2-phenyl-*exo*-3-diphenylaluminobenzonorbornene was attempted, with the hope that it might yield 1-diphenylalumino-2-phenyl-1,2-dihydronaphthalene. Such cleavage, together with subsequent hydrolysis and aromatization, might then produce 6- and 7-substituted 1-methyl-2-phenylnaphthalenes. However, when the adduct of benzonorbornadiene and triphenylaluminum was freed of solvent and then heated up to 250° for 4 h, hydrolysis and GLC analysis showed only 1% of a product at a higher retention time than *exo*-2-phenylbenzonorbornene.

Second, the formation of 3-bromo-*exo*-2-phenylbenzonorbornenes by the bromodealumination of the original aluminum adduct seemed promising as a route to isomeric hydroxy derivatives, which would be useful as substrates for NMR shift reagents. However, addition of 1 equiv of 6- and 7-methyl-*exo*-2-phenyl-*exo*-3-diphenylaluminobenzonorbornenes (3.4 mmol) in 10 ml of benzene to 3 equiv of bromine (10.5 mmol) in 15 ml of benzene, followed by 1 h of reflux, hydrolytic work-up, and GLC analysis, led to a mixture of 20% of 6- and 7-methyl-*exo*-2-phenylbenzonorbornenes and 80% of five other components. A repetition of the bromodealumination, in which the bromine in benzene was slowly added to the aluminum adduct, gave similar unpromising results.

Model Experiment with a Mixture of 6- and 7-Methyl-*exo*-2-benzonorborneol and Europium Shift Reagents. A mixture of 3.16 g (20 mmol) of 6-methylbenzonorbornadiene and 80 mmol of a 90% aqueous solution of formic acid was heated at incipient reflux for 4 h. Removal of the acid and water at reduced pressure and final distillation gave 3.8 g (95%) of the 6- and 7-methyl-*exo*-2-benzonorbornenyl formates: bp 104–105° (0.8 mm); GLC, product with 5% of unreacted olefin; ir (neat), strong bands at 825, 1020, 1150, 1500, 1730, and 3000 cm^{-1}.

The foregoing mixture of formate esters (2.1 g, 10 mmol) was allowed to stand for 2 h at 25° with a solution of 1.2 g (20 mmol) of KOH dissolved in 20 ml of ethanol. Dilution of the solution with water, extraction with pentane, drying of the extracts over Na_2SO_4, and solvent removal gave a colorless mixture of 6- and 7-methyl-*exo*-2-benzonorborneol: ir (neat) broad band at 3400 and complete absence of ester bands at 1150 or 1730 cm^{-1}; NMR (CCl_4), 1.66 (br d, 2 H, methylene bridge), 1.88 (br s, 1 H, 3-endo H), 2.05 (br s, 1 H, 3-exo H), 2.24 (s, 3 H, methyl), 3.16 (br s, 2 H, bridgehead H), 3.75–4.10 (m, 2 H, 2-endo H and OH), and 6.65–7.1 (m, 3 H, aromatic).

The NMR spectra of this isomeric mixture of alcohols in CCl_4 and in $CDCl_3$ were almost identical, except that in CCl_4 the hydroxyl group occurs at 3.9 ppm, underneath the multiplet for the 2-endo H; in $CDCl_3$ this signal falls under the bridgehead signal at 3.25 ppm. To the chloroform solution of the alcohols was added a weighed amount of tris(dipivaloyl)methanato)europium(III) ($Eu(DPM)_3$) until the molar ratio of the shift reagent to alcohol was 0.07. A barely perceptible resolution of the methyl signal was achieved. Due to better solubility, the alcohols were dissolved in CCl_4 and $Eu(DPM)_3$ added, until a molar ratio of 0.154 (shift reagent:alcohols) was attained. Under these conditions, two distinct methyl signals, separated by 0.1 ppm, were observed: downfield: upfield signal = 1.6:1.0.

Oxidative Treatment of 6- and 7-Methyl-*exo*-2-phenyl-*exo*-3-diphenylaluminobenzonorbornene. The aluminum adduct from 4.5 g (30 mmol) of 6-methylbenzonorbornadiene and 7.8 g (32 mmol) of triphenylaluminum in 125 ml of benzene was treated with oxygen gas that was previously dried by passage through a 3 × 100 cm column of glass beads, upon which was dispersed granular P_2O_5. After an initial exotherm, during which the reaction mixture was cooled in an ice mixture, the stirred solution was oxidized at room temperature. Removal and GLC analysis of a hydrolyzed aliquot showed that ca. 60% of the aluminum adduct had oxidized after 1 h of treatment. After 2 additional hours of oxidation at 45°, conversion had risen to at least 80% (further oxidation caused a decrease in yield). Hydrolytic work-up with 150 ml of 1 N aqueous HCl, extraction with benzene, treatment of the benzene extracts with 10% aqueous Na_2CO_3 to remove the phenol, drying of the benzene extract with Na_2SO_4, and removal of the volatile components by rotary evaporation gave 7.55 g of yellow oil. Analysis by TLC on alumina with ether:hexane (v/v 20:80) showed four components: the *exo*-2-phenylbenzonorbornenes **11c**, the *exo*-3-phenylbenzonorbornen-2-ones **12c**, and the 3-phenyl-2-*exo*- and -2-*endo*benzonorborneols (**13c** and **14c**). The ketone(s) was ca. 10% of the product.

This yellow oil (5.5 g) was dissolved in 75 ml of spectral grade acetone and at 0° treated with 7.5 ml of freshly prepared 8 N Jones reagent. After standing overnight at 5°, the green suspension was treated with 2-propanol to remove excess H_2CrO_4 and then filtered. The dried filtrate yielded 5.0 g of yellow oil, which showed only two TLC spots: the borneols had disappeared and only the ketone and *exo*-2-phenylbenzonorbornenes remained. Column chromatography of the product on silica gel and successive elution with hexane and then hexane-ether yielded virtually all of the oxidation product (TLC monitoring), 4.35 g of colorless product, that solidified slowly upon standing. Recrystallization was not undertaken of either this ketone or its derivatives, since such purification might change the isomer ratio. Hence, melting points are not recorded here. Spectral data: ir (CCl_4) strong bands at 695, 710, 735, 805, 1070, 1450, 1475, 1745 (s, C=O) and 2925; NMR ($CDCl_3$), 2.32 (s, 3 H, methyl), 2.5 (m, 2 H, methylene bridge), 3.25 (bd, 1, 3-endo benzylic H), 3.59 (bs, 1 H, 4-bridgehead H), 3.84 (bs, 1 H, 1-bridgehead H), 7.20 (m, 3 H, benzo aromatic H), and 7.35 (s, 5 H, phenyl H). The compound mixture formed a 2,4-dinitrophenylhydrazone as yellow-orange needles. Based upon the above data, this product was assigned the structure of 6- and 7-methyl-*exo*-3-phenylbenzonorbornen-2-ones.

Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.49. Found: C, 86.93; H, 6.42.

NMR Analysis of the Isomer Ratio of 6- and 7-Methyl-*exo*-3-phenylbenzonorbornen-2-ones (12c) with Tris(perfluorobutyryl(pivaloyl)methanato)europium(III). The previously isolated ketone was freed of all traces of ether and hexane by rotary evaporation and then dissolved in $CDCl_3$. The NMR shift reagent was added in portions until the methyl signals were resolved. The ratio of the major downfield signal to the upfield signal was 53:47 by integration and by peak height. Since the major peak was shifted more by the europium complex, its structure was assigned as 7-methyl-*exo*-3-phenylbenzonorbornen-2-one.

Oxidative Treatment of 6- and 7-Fluoro-*exo*-2-phenyl-*exo*-3-diphenylaluminobenzonorbornene. The aluminum adduct from 3.0 g (18 mmol) of 6-fluorobenzonorbornadiene and 4.64 g (18 mmol) by triphenylaluminum in 75 ml of benzene (cf. supra) was treated with dry oxygen gas according to the above procedure. Analysis indicated ca. a 75% yield of oxidation products.

As in the methyl case, the 4.1 g of isolated yellow oil containing ca. 25% of the fluoro-*exo*-2-phenylbenzonorbornene was dissolved in 100 ml of spectral grade acetone and treated with 8 ml of 8 N Jones reagent. Usual work-up gave a product free of any benzonorborneols, as shown by TLC. Column chromatography on silica gel with elution by hexane and then by hexane-ether yielded the pure ketones, 3.1 g; ir (CCl_4) strong band at 1750 cm^{-1}; NMR (CCl_4) 2.39 (m, 2 H, methylene bridge), 3.02 (bd, 1 H, 3-endo H) 3.38 (bs, 1 H, 4-bridgehead H), 3.68 (bd, 1 H, 1-bridgehead H), and 6.9 (bm, 8, aromatic H). Again here, needles of a yellow-orange 2,4-dinitrophenylhydrazone were formed. Upon these data, the product is assigned the structure of 6- and 7-fluoro-*exo*-2-phenylbenzonornen-2-one (**12d**).

Anal. Calcd for $C_{17}H_{13}FO$: C, 80.93; H, 5.19. Found: C, 80.73; H, 5.57.

NMR Analysis of the Isomer Ratio of 6- and 7-Fluoro-*exo*-3-phenylbenzonorbornen-2-ones (12d) with Tris(perfluorobutyryl(pivaloyl)methanato)europium(III). The dried solvent-free oily ketone was dissolved in $CDCl_3$ and some allyl trifluoroacetate added as an internal standard. The ^{19}F NMR spectrum, which was recorded with a Varian HA-100 spectrometer, displayed two distinct octets (integrated ratio of 30:70) downfield from the lock signal of allyl trifluoroacetate, the minor octet being 111 Hz downfield from the major octet. Addition of the shift reagent caused both octets to broaden slightly and to move downfield, but the major octet shifted only 6 Hz and the minor octet 18 Hz. Therefore, the minor component was assigned the structure of 7-fluoro-*exo*-3-phenylbenzonorbornen-2-one.

Kinetics of Carbaluminating Benzonorbornadienes with Triphenylaluminum. Since the kinetic laws for the addition of aluminum alkyls to olefins and to acetylenes have already been determined, the relative reactivities of 6-substituted benzonorbornadienes toward triphenylaluminum were determined by the competitive method. The techniques, apparatus, and analytical methods for conducting such kinetic measurements with air- and moisture-sensitive systems have been described previously.[41]

Two types of runs were conducted: (1) a competitive addition of triphenylaluminum at 80.0 ± 0.2° to a mixture of benzonorbornadiene, 6-methylbenzonorbornadiene, and 6-chlorobenzonorbornadiene dissolved in benzene; and (2) a similar addition of the aluminum aryl at 80.0 ± 0.2° to a mixture of 6-chlorobenzonorbornadiene and 7-fluorobenzonorbornadiene. Through such choice of competing olefins, the starting olefins and the hydrocarbons obtained by hydrolysis were all completely separable on a 12-ft column of 10% silicone gum rubber on Chromosorb P. By use of gas-tight syringes, 0.5-ml aliquots were withdrawn and injected into 1.5 ml of 0.4 N aqueous HCl under a nitrogen atmosphere. After 1 h the sample was centrifuged and a 10-μl sample injected into the GC at 175° to monitor the disappearance of olefin; raising the temperature to 275° then permitted the product to be analyzed. Response factors were determined for all starting materials and products by use of known samples. Multiplication of such factors by disc-integrated peak areas put the analyses on a mole ratio basis.

Typical kinetic runs used the following proportions. First, a solution of 2.4237 g (9.39×10^{-3} mol) of triphenylaluminum in 40.00

± 0.5 ml of dry benzene was allowed to equilibrate in a thermostatic bath for 1 h at 80.0 ± 0.2°. Then 0.3 equiv of each olefin was added simultaneously: 439.7 mg (3.09×10^{-3} mol) of benzonorbornadiene, 503.7 mg (3.23×10^{-3} mol) of the 6-chloro derivative, and 552.3 mg (3.13×10^{-3} mol) of the 6-methyl derivative. The data resulting from analyzing the aliquots by GLC are given in Table I.

Secondly, a solution of 2.0145 g (7.8 mmol) of triphenylaluminum in 40.00 ± 0.05 ml of dry benzene was allowed to equilibrate for 1 h at 80.0 ± 0.2°. Then 0.5 equiv of each olefin was added simultaneously: 632.0 mg (3.95×10^{-3} mol) of 6-fluorobenzonorbornadiene and 688.8 mg (3.90×10^{-3} mol) of the 6-chloro derivative. The analytical data are given in Table II.

In calculating relative rates by the homocompetitive method, it is important to verify that the relative rates observed remain constant at all times during the reaction. In Table III the relative rates that were found at different times are given; after 10 min of reaction, such constancy in rates was observed.

In accordance with previous kinetic studies, it can be assumed that the reaction has a kinetic law of the form

$$-\mathrm{d}[\mathrm{olefin}]/\mathrm{d}t = k_{\mathrm{emp}}[\mathrm{olefin}][(\mathrm{C_6H_5})_3\mathrm{Al}]^{0.5}$$

Hence, for irreversible reactions of the same order, the expression for the relative rates of two olefins, A and B, with triphenylaluminum would be:

$$\frac{k_\mathrm{A}}{k_\mathrm{B}} = \frac{\log([\mathrm{olefin_A}]_t/[\mathrm{olefin_A}]_0}{\log([\mathrm{olefin_B}]_t/[\mathrm{olefin_B}]_0}$$

where k_A and k_B are the rate constants and $[\mathrm{olefin}]_t$ and $[\mathrm{olefin}]_0$ are the respective concentrations of the olefin at time t and initially.

Acknowledgments. The authors are indebted to The National Science Foundation for support of this research through Grant GP-35723. Fellowship support to N. E. Burlinson was also provided from The National Aeronautic and Space Administration and from The National Defense Education Act. Moreover, Dr. Ernest Lustig of The Food and Drug Administration was helpful in obtaining ^{19}F NMR spectra, as was Dr. Lloyd Kaplan of The Naval Ordnance Laboratory for ^{1}H and ^{19}F spectra.

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