Orbital Interactions. 7. The Birch Reduction as a Tool for Exploring Orbital Interactions through Bonds. Through-Four-, -Five-, and -Six-Bond Interactions[1]

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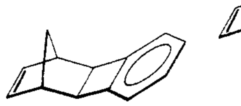
Abstract: Product and relative rate data have been obtained for the Birch reduction (Li, NH_3, *tert*-butyl alcohol) of compounds **3**, **4a**, and **5–8**. **3** is reduced to give exclusively **14** 44 times more rapidly than norbornene. Birch reduction of **4a** and **5** occurs exclusively at the double bond to give **15** and **17**, respectively. The rates of reduction of **4a** and **5** are respectively 554 and 1856 relative to norbornene. The enhanced rates of double-bond reduction in **4a** and **5** are attributed to the presence of through-four-bond interactions between the double bond π MO and the NLUMO of the aromatic ring and they constitute the first examples of the *chemical* consequences of orbital interactions through four bonds. Reduction of **6** and **7**, in which the unsaturated centers are separated by five σ bonds, occurred largely at the aromatic ring. The measured rates of double-bond reduction of these compounds showed little enhancement. The rate of reduction of the double bond in **8** is five times greater than in **14**. This result is tentatively attributed to the presence of through-six-bond interactions in **8**. Extended Hückel calculations were carried out on a series of α,ω-dehydropolyenyls, **27–30**, and the 1,6-dehydrohexa-1,3,5-trienes, **31–33**. The results of these calculations suggest that the magnitude of through-bond orbital interactions depends on both the length and the geometry of the σ bond relay; the all-trans configuration of the σ bonds is particularly efficacious in relaying orbital interactions.

Introduction

In the previous paper[1] we explained the enhanced rates of the Birch reduction[2] of the double bond of both **1** and **2** in terms of interactions operating between the π^* MO of this bond and ψ_5 (NLUMO) of the aromatic ring. Extended Hückel (EH) calculations revealed that these interactions were transmitted through three bonds[3,4] in the case of **1** and predominantly through space[3] in the case of **2**. We have applied the Birch reduction to study through-bond orbital interactions in the series of molecules **3**, **4a**, **5–8**, in which the unsaturated centers



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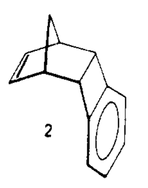

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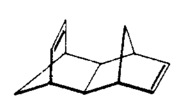

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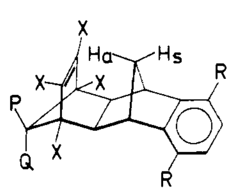

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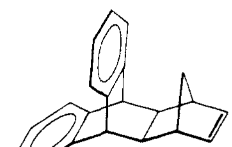

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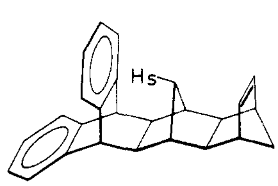
a P = Q = R = X = H
b P = Q = X = Cl ; R = H
c P = Q = X = H ; R = OCH_3
d P,Q = O ; R = X = H
e P = Q = OCH_3 ; R = X = H
f P = R = X = H ; Q = OH



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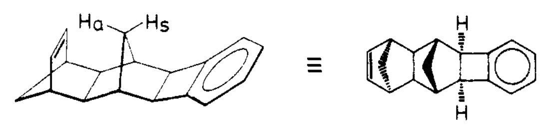
are separated by four (**3–5**), five (**6** and **7**), and six (**8**) σ bonds. This work is timely because, to the best of our knowledge, no reports demonstrating the *chemical* consequences of through-bond orbital interactions extending over more than three σ bonds have yet appeared. Indeed, there appear to be only two reports that attest to the *physical* consequences of through-four or more bond interactions.[5] Thus Martin and Schwesinger have rationalized the photoelectron spectrum of **3** in terms of two weak through-four-bond interactions between the π orbitals.[7] Verhoeven and his co-workers[8] have attributed



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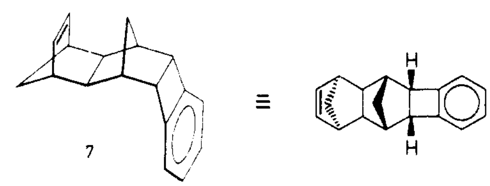

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the presence of a charge-transfer band in the UV spectrum of **9** to the operation of two through-five-bond interactions be-

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tween the sulfur nonbonding orbital and the π^* MO of the double bond.

Results

Syntheses. Reaction of cyclopentadiene with benzonorbornene[9] (1,4-dihydro-1,4-methanonaphthalene) in a sealed tube at 160 °C led to the formation of two cycloadducts in the ratio 1:12 (by GLC). The major component was shown to have the structure **4a** on the basis of its combustion analysis and its mass spectral, ^1H NMR, and ^{13}C NMR data. In particular the endo,exo[10] configuration was assigned to **4a** over the other three isomeric possibilities (i.e., endo,endo, exo,exo, and exo,endo) for the following reasons: (1) The endo,endo and exo,endo structures are eliminated because these compounds have been made unambiguously by other pathways[12,13] and their UV and ^1H NMR spectra are quite different from those of **4a**.[49] (2) Reductive dechlorination (Na/EtOH) of the adduct, **4b**, formed from the cycloaddition of hexachlorocyclopentadiene to benzonorbornene gave **4a** exclusively.[14] Diels-Alder reactions of hexachlorocyclopentadiene with norbornadienes have been studied extensively. Although cycloadducts having the endo,exo and endo,endo stereochemistries are formed,[15-17] none having the exo,exo stereochemistry, e.g., **10**,

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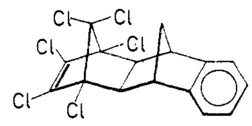

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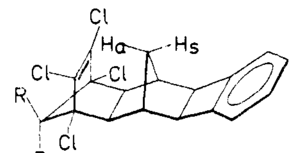
has been detected, presumably because of the adverse steric congestion which must occur in the exo,exo transition state. Therefore, from this and (1) above it follows that **4a** and **4b** both have the endo,exo stereochemistry. (3) Finally, the reaction between 3′,6′-dimethoxybenzonorbornene and cyclopentadiene has been reported to give exclusively adduct **4c** of endo,exo stereochemistry[18] whose UV and ^{1}H NMR spectra correspond closely with those of **4a**.[19]

The structure of the minor product resulting from the cyclopentadiene–benzonorbornene reaction has not been investigated. However, the ^{1}H NMR spectrum of the crude reaction product indicates that it is the endo,endo stereoisomer.

The reaction of cyclopentadiene with **1** or **2** did not give the respective adducts, **6** or **7**, but returned only intractable tars instead. The adduct, **11a**, of hexachlorocyclopentadiene and



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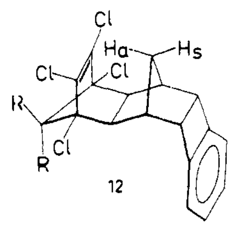

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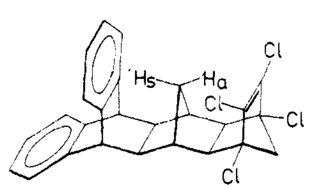
a R=Cl
b R=H

1 was formed in good yield at 150 °C.[22] Dechlorination of **11a** using the Winstein,[26] Gassman,[27] or metal-ammonia[2] reductions led only to polymeric material. However, Gassman reduction of **11b**, the cycloadduct of 1,2,3,4-tetrachlorocyclopentadiene and **1**, gave a good yield of **6**. The ^{1}H NMR spectrum of **6** reveals a deshielded resonance for the methano proton H_a, which is consistent with the proposed endo,exo,exo configuration.[20] In a similar manner **7** and **8** were prepared by the Gassman dechlorination of **12b** and **13**, respectively.



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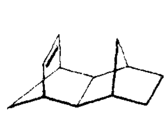
Birch Reductions. All Birch reductions described in this paper were carried out using a solution of lithium metal in a refluxing (ca. −33 °C) mixture of liquid ammonia, THF (cosolvent), and *tert*-butyl alcohol (proton source).

Birch reduction of **3** slowly led to the formation of a single product whose identity was shown to be **14**. In contrast to **3**, compounds **4a** and **5** were reduced quite rapidly to give **15** and **17**, respectively. No other products could be detected from these reactions. The absence of any products resulting from reduction of the aromatic ring, i.e., **16**, is remarkable. Indeed the aromatic rings of **15** and **17** were found to be reduced very slowly.



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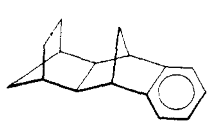

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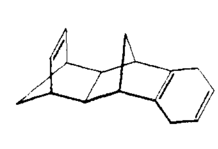

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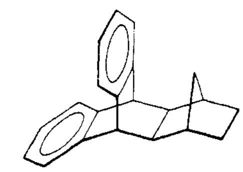

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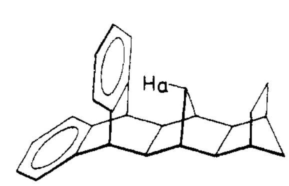
Birch reduction of **6** using a large excess of lithium gave a mixture of **18a** and **19a** in the ratio 19.5:1, respectively. The structural identities of **18a** and **19a** were confirmed by their ^{1}H NMR spectra and through their respective aromatization to **6** and **20a** with DDQ (Scheme I). Reduction of **6** using insufficient lithium led to the formation of **20a** in addition to **18a**, **19a**, and unreacted **6**. The formation of **19a** probably occurs via **20a** because it was observed that reduction of the latter compound, to give **19a**, was very slow compared with the overall rate of double-bond reduction of **6**. We conclude that the ratio of the yields of products, **18a:19a**, obtained from the reduction of **6** using a large excess of Li represents the ratio of the rate constants, k_A:k_D, for the reduction at the aromatic ring (k_A) and the double bond (k_D); i.e., k_A:k_D = 19.5:1.

The results of the reduction of **7** were similar to those obtained for the endo,exo,exo isomer, **6**. "Exhaustive" reduction (5 molar equiv of Li) of **7** led to the formation of **18b** and **19b** in the ratio 20:1, respectively. **20b** was also detected when the reduction was carried out using less Li (2 molar equiv). Using the same arguments that were applied to **6**, we conclude that k_A:k_D = 20:1 for **7**.

Birch reduction of **8** gave a mixture of **21**, **22a**, and **23a**. From the ratio of the product yields (**22a** + **23a**):**21**, we cal-



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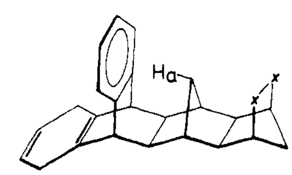

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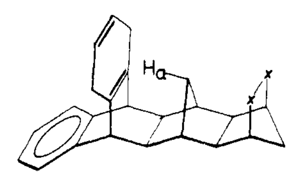

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a xx = HC=CH
b xx = H_2C–CH_2

culate that k_A/k_D = 1.46 (see Experimental Section for details). Similarly reduction of **21** slowly led to the formation of **22b** and **23b** in a 4:1 ratio (Experimental Section).

Competition Kinetic Studies. Relative rate constants for the Birch reduction of a series of substrates were determined by the competition method,[1,28] and are listed in Table I. The k^c values are measured with respect to the specified competitor whereas k^N have been adjusted to be relative to norbornene. Where applicable, $k_D{}^N$ and $k_A{}^N$ are the respective rate constants (relative to norbornene) of the reduction of the double

Scheme I

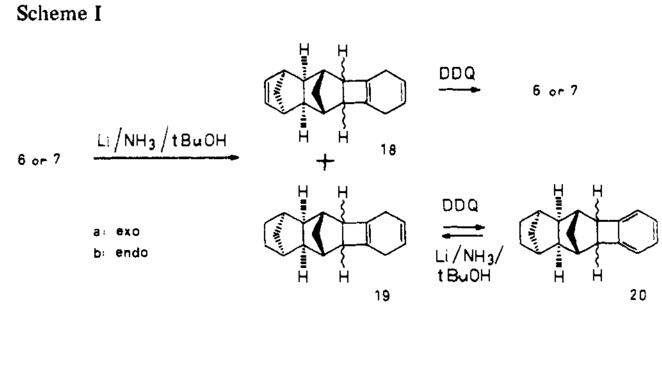


Table I. Relative Rate Constants for the Birch Reduction of Some Substrates

entry	substrate	competitor	$k^{c\ a}$	$k^{N\ b}$	$k_A:k_D$	$K_D{}^{N\ c}$	$k_A{}^{N\ d}$
1	**1**	toluene	24^e	696^e	3.94^e	141^e	555^e
2	**2**	toluene	14.7^e	426^e	4.5^e	78^e	348^e
3	**3**	toluene	1.5	43.5		43.5	
4	**4a**	toluene	19.1	554	0^f	554	
5	**5**	toluene	64	1856	0^f	1856	
6	**6**	toluene	11.6	337	19.5	16	321
7	**7**	toluene	14.1	409	20	20	389
8	**8**	**14**	11.9	69	1.46	28	41
9	**14**	toluene	0.2^e	5.7^e		5.7^e	
10	**17**	**14**	2.8	16.3			16.3
11	**20a**	toluene	11	319			319
12	**20b**	toluene	15	435			435
13	**21**	**14**	3	17.4			17.4
14	**24**	toluene	10.4^e	302^e			302^e
15	toluene	norbornene	29^e	29^e			29^e
16	**14**	norbornene	5.8^e	5.8^e		5.8^e	
17	**5**	**24**	5.6				
18	**20a**	**5**	0.21				
19	**20a**	**24**	1.1				

^{a} Overall rate constants relative to the specified competitor. ^{b} Adjusted rate constants relative to norbornene. ^{c} Rate constants for the reduction of the double bond of the substrates relative to norbornene. ^{d} Rate constants for the reduction of the aromatic ring of the substrates relative to norbornene. ^{e} Reference 1. ^{f} Reduction of the aromatic ring of this substrate could not be detected.

bond and the aromatic ring of the substrate. These were calculated from the quantities k^N $(= k_A{}^N + k_D{}^N)$ and k_A/k_D $(= k_A{}^N/k_D{}^N)$.

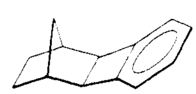
The consistency of the rate data may be gauged by checking how closely the k^c values fit the following relationships: $k_5{}^ck_{18}{}^c$ (13.4) $= k_{11}{}^c$ (11); $k_9{}^ck_{15}{}^c$ (5.7) $= k_{16}{}^c$ (5.8); $k_{14}{}^ck_{17}{}^c$ (58.3) $= k_5{}^c$ (64); $k_{14}{}^ck_{19}{}^c$ (11.4) $= k_{11}{}^c$ (11), where $k_n{}^c$ refers to the rate constant of the nth entry of Table I. The quantities in parentheses are the experimentally determined values of the terms. It can be seen from these values that the fit is quite good if an uncertainty of about ±10% is associated with each rate constant, and is quite acceptable for the purposes of this work.

Discussion

For reasons discussed elsewhere[1] orbital interactions involving the π^* MO of a double bond are expected to cause an enhanced rate of Birch reduction of that double bond compared with a suitable model substrate.

The diene **3** is reduced some 44 times more rapidly than norbornene. However, **3** is only 7.5 times more reactive than the more suitable model compound **14.** Although the double bonds are too distant to perturb one another inductively,[1] the small rate enhancement in **3** compared with **14** cannot be confidently attributed to the operation of through-four-bond interactions. It should be noted that the evidence for the presence of significant through-bond interactions in **3**, based on photoelectron spectral data,[7] is not particularly convincing.

The data for the reductions of **4a** and **5** were more encouraging. Thus the double bond of **4a** is reduced 96 times more rapidly than that of **14** and $k_D{}^N$ for **5** is 1856! The double bond of **5** is even 320 times more reactive than that of **14.** We are confident that inductive effects are chemically insignificant in **4a** and **5**.[1] It appears, then, that our data could constitute the first reported examples of the chemical consequences of through-four-bond orbital interactions.[29] The presence of an additional interacting (through-four-bond) aromatic ring in **5** would naturally enhance the double-bond reactivity of this compound compared with **4a.** It has been reported that the double bond of the endo isomer of **5**, i.e., **25,** is rapidly Birch reduced, although no rate data were reported.[30] We predict that **25** should be more reactive than **5** because the double bond in **25** is well situated to interact with the aromatic ring through space as well as through bonds.[31]



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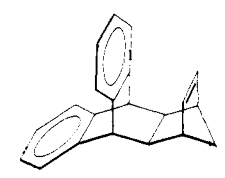

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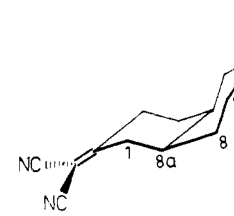

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An alternative explanation for these rate enhancements could be in some way the effects of ion pairing between the anion radical of the substrate and the lithium cation.

For example, the nature of ion pairs, whether contact or solvent separated, markedly affects their rate of protonation[32] and therefore the overall rate of reduction.[33] This explanation is unlikely because the nature of the ion pair should be the same for a series of structurally similar compounds and using the same reducing metal.[34] Nevertheless, we are investigating this point further by studying the effect of crown ethers and cryptands on the Birch reduction.

The results for the reduction of **6–8** are more equivocal. Thus the double bond of **6** and **7** is respectively 2.8 and 3.4 times more reactive than that of **14.** Through-five-bond interactions do not appear to be important in these compounds.[35] The double bond of **8** is only five times more readily reduced than that of **14.** This enhancement is too small to be attributed unequivocally to the effects of through-six-bond interactions, although it should be noted that through-bond interactions are attenuated with distance.[4a]

The relatively small enhancement in the rates of reduction of the double bond in **6** and **7** is puzzling. However, it should be noted that the extent of through-bond coupling probably depends on the geometrical pattern of the intervening σ bonds.[4a] For example whereas through-five-bond interactions have been detected in **9,** they appear to be absent in the cis

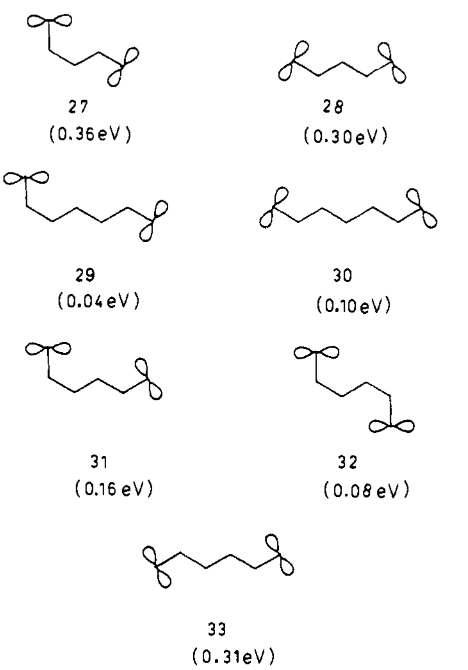

Figure 1. Some model arrangements of orbital lobes and intervening σ bonds. The numbers in parentheses are the splitting energies, Δ, in eV.

stereoisomer **26**.[8] Apparently the poor overlap of the C(1)–C(8a) and C(7)–C(8) bonds in **26** is not conducive to the transmission of through-bond interactions.[8] In order to determine whether geometrical factors could be responsible for the results of **6** and **7** some EH calculations[36,37] were carried out on the α,ω-dehydropolyenyls, **27–30**, and the 1,6-dehydrohexa-1,3,5-trienes, **31–35**.[39] The radical lobes of **27–33** (Figure 1) are p orbitals whose interactions are intended to mimic those between the π-type MOs of **3–8**. The σ bond relay patterns in **27, 31,** and **32** resemble those which occur in **3** (and **4**), **6,** and **7,** respectively. The splitting energies, Δ,[40] are shown in Figure 1. It is apparent from the Δ values for **27** and **28** that the *c-t*[41] and the *t-t* alignments of the σ bonds are efficacious in promoting through-four-bond interactions. However, Δ is much smaller for **31** and **32.** Interestingly, Δ for **33,** having the *t-t-t* geometry, is comparable to that for **27** and **28.** It appears, therefore, that the geometry of the σ framework *does* have an effect on Δ for the five-bond case and that a molecule having the *t-t-t* alignment of its intervening σ bonds might show increased double-bond reactivity toward Birch reduction compared with **6** and **7.**

Finally, EH calculations on **29** and **30** indicate that through-six-bond interactions are small, particularly in the case of **29.** The small enhanced rate of double-bond reduction of **8** is consistent with these calculations.

Experimental Section

Details concerning instrumentation have been described in the previous paper.[1]

The following columns were employed in the analytical preparative and GLC/MS phases of the work (the flow rates were 60 mL min^{-1} unless stated otherwise): A, 2 m × 3 mm stainless steel containing 3% OV 1 on Gas-Chrom Q 60/80; B, 2 m × 3 mm stainless steel containing Porapak Q 80/100; C, 8 m × 3 mm aluminum containing 7.5% Carbowax 20M on Chromosorb W (AW) 60/80; D, 2 m × 3 mm stainless steel containing 10% SE-30 on Chromosorb W (AW) 60/80; E, 4.2 m × 12 mm glass containing 10% SE-30 on Chromosorb W (AW) 60/80.

Microanalyses were performed by the Australian National University Micro Analytical Service under Miss B. Stevenson and Dr. J. E. Fildes.

***exo,endo*-1,4,4a,5,8,8a-Hexahydro-1,4:5,8-dimethanonaphthalene (3).** This compound was prepared by the method of Stille and Frey[24] but was purified by a modified procedure. The crude product (20 g, 0.13 mol) was added slowly to a stirred solution of saturated silver nitrate (20 mL). The resultant silver complex was removed by filtration and was recrystallized twice from absolute ethanol. The white powdery solid (45 g, 11 mmol) was dissolved in water (55 °C, 400 mL) followed by the addition of saturated sodium chloride solution (100 mL). The silver chloride precipitate was collected by filtration and triturated with petroleum spirit (bp 60–80 °C, 3 × 200 mL). The filtrate was also extracted with the same solvent (2 × 50 mL). The combined petroleum spirit extracts were dried (Na_2SO_4) and evaporated. Pure material (15 g, 75% yield) was obtained by fractional distillation, bp 36 °C (0.35 mmHg) (lit.[24] 108 °C, 25 mm).

***exo,endo*-1,4,4a,5,6,7,8,8a-Octahydro-1,4:5,8-dimethanonaphthalene (14)** was prepared by the method of Stille and Witherell,[42] bp 82 °C (5 mm) (lit.[42] 86 °C, 6 mm).

1,4-Dihydro-1,4-methanonaphthalene (benzonorbornene) was prepared by the method of Tufariello et al.,[43] bp 55 °C (5 mm) (lit.[43] 72–81 °C, 10 mm).

1,2,3,4-Tetrachlorocyclopentadiene was prepared by the method of McBee et al.,[44] mp 58 °C (lit.[44] 62–63 °C).

***exo*-1,4,4a,9,9a,10-Hexahydro-9,10(1′,2′)-benzeno-1,4-methanoanthracene (5).** A sealed glass tube containing anthracene (42 g, 0.23 mol) and norbornadiene (108 g, 1.2 mol) in a nitrogen atmosphere was heated at 175 °C for 27 h in an oil bath. On cooling, a yellow precipitate formed which was separated from the liquor by filtration (14 g). The norbornadiene was stripped from the reaction mixture at reduced pressure, giving a yellow residue (38 g). Pure product was obtained by extracting the combined precipitates with petroleum spirit (60–80 °C) in a Soxhlet apparatus, giving a crop of white, crystalline material (49 g, 78%), mp 144 °C (lit.[45a] 143 °C). ^{1}H NMR and mass spectral data for this product were in agreement with those quoted.[45]

***exo*-1,2,3,4,4a,9,9a,10-Octahydro-9,10(1′,2′)-benzeno-1,4-methanoanthracene (17).** Catalytic hydrogenation of **5** (1.0 g, EtOAc (10 mL), Pd (10%) on C) gave **17** in quantitative yield, mp 150 °C (from $CHCl_3/CH_3OH$) (lit.[45a] 151–152 °C).

***endo,exo*-1,4,4a,9,9a,10-Hexahydro-1,4:9,10-dimethanoanthracene (4a).** A glass reaction tube was charged with benzonorbornene (10 g, 70 mmol), cyclopentadiene (5.3 g, 80 mmol), and 0.1 g of hydroquinone. The vessel was purged with nitrogen, sealed, and then heated at 160 °C for 20 h. Removal of the products from the tube with methylene chloride (3 × 50 mL) and fractionally distilling the mixture gave material (13.5 g, 60–80 °C, 65 mmol) whose GLC analysis (column A, 125 °C) indicated the presence of two components in the ratio 12:1. The major component was isolated by preparative GLC (column E, 125 °C) and was shown to be **4a** on the basis of its microanalysis and its spectral data: ^{1}H NMR ($CDCl_3$) δ 1.2–1.75 (3 H, m, 2 H_{11}, H_{12s}), 2.25 (2 H, br s, H_{4a}, H_{9a}), 2.83 (3 H, m, H_1, H_4, H_{12a}), 3.20 (2 H, s, H_9, H_{10}), 6.10 (2 H, t, olefinic protons), 6.80–7.20 (4 H, m, aromatic protons); ^{13}C NMR ($CDCl_3$) δ 152.5 (2 C, $C_{8a,10a}$), 136.4 (2 C, $C_{2,3}$), 125.2 (2 C, aromatic carbons), 119.2 (2 C, aromatic carbons), 54.9 (1 C, C_{11}), 48.9 (2 C, $C_{4a,9a}$), 45.6 (4 C, $C_{1,4,9,10}$), 42.3 (1 C, C_{12}); mass spectrum (70 eV) *m/e* (rel intensity) 208 ($M^{+\cdot}$, 5.5), 167 (8.0), 142 (100), 143 (14.5), 141 (28.5), 130 (10.5), 129 (38.5), 128 (53.5), 117 (15.8), 116 (24.7), 80 (21.5); UV (isooctane) λ_{max} (E_{max}) 259 nm (680), 265 (1070), 272 (1160). Anal. Calcd for $C_{16}H_{16}$: C, 92.25; H, 7.75. Found: C, 92.06; H, 7.50.

***endo,exo*-1,2,3,4,4a,9,9a,10-Octahydro-1,4:9,10-dimethanoanthracene (15).** A solution of the olefin **4a** (300 mg, 1.4 mmol) in absolute ethanol (20 mL) containing 10% Pd/C (25 mg) was shaken in an atmosphere of H_2 at 20 °C until no further uptake of gas occurred. The mixture was filtered through Celite, the filtrate poured into water (100 mL), and the resulting solution extracted with petroleum spirit (bp 30–40 °C, 2 × 50 mL). The combined extracts were dried (Na_2SO_4) and evaporated and the residue was sublimed (140 °C, 25 mm) to give 200 mg of product, **15** (66%): mp 31 °C; ^{1}H NMR ($CDCl_3$) δ 0.7–2.3 (12 H, m, H_1–H_4, H_{4a}, H_{9a}, H_{11}, H_{12}), 3.02 (2 H, s, H_9, H_{10}), 6.78–7.45 (4 H, m, aromatic protons); mass spectrum (70 eV) *m/e* (rel intensity) 210 ($M^{+\cdot}$, 19.1), 130 (100). The other peaks were less than 10%.

Anal. Calcd for $C_{16}H_{18}$: C, 91.40; H, 8.60. Found: C, 91.64; H, 8.50.

***endo,exo,exo*-1,2,3,4,11,11-Hexachloro-4a,5,5a,9b,10,10a-hexahydro-1,4:5,10-dimethanobenzobiphenylene (11a).** A mixture of hexachlorocyclopentadiene (1.4 g, 0.05 mol), **1**[1] (500 mg, 0.03 mol), and hydroquinone (20 mg) was heated for 5 min at 150 °C under an

N_2 atmosphere. The product was dissolved in CH_2Cl_2 (5 mL) and a solid was precipitated upon addition of methanol.

Repeated recrystallization of the solid from methanol yielded **11a** (600 mg, 50%): mp 153.5 °C; ^{1}H NMR ($CDCl_3$) δ 0.8 (1 H, d, J = 14 Hz, H_{12s}), 1.2 (1 H, d, J = 14 Hz, H_{12a}), 2.48 (2 H, s, H_5, H_{10}), 2.68 (2 H, s, H_{4a}, H_{10a}), 3.24 (2 H, s, H_{5a}, H_{9a}), 7.1 (4 H, m, aromatic protons). Exact mass: calcd for $C_{18}H_{12}{}^{35}Cl_6$, 437.907; found, 437.906.

***endo,exo,exo*-1,2,3,4-Tetrachloro-4a,5,5a,9b,10,10a-hexahydro-1,4:5,10-dimethanobenzobiphenylene (11b).** A mixture of 1,2,3,4-tetrachlorocyclopentadiene (4.8 g, 23 mmol), **1**[1] (2.0 g, 12 mmol), hydroquinone (20 mg), and *p*-xylene (10 mL) was heated in a sealed tube (nitrogen atmosphere) at 150 °C for 3 h. The xylene was removed under reduced pressure and the resulting tan-colored solid was purified by passing it down a column of silica (1 × 12 in.) and eluting with petroleum spirit (bp 60–80 °C). Recrystallization of the eluted solid from pentane gave **11b** as light tan crystals (2.5 g, 56%): mp 163.5 °C; ^{1}H NMR ($CDCl_3$) δ 0.70 (1 H, d, J = 12 Hz, H_{12s}), 1.05 (1 H, d, J = 12 Hz, H_{12a}), 2.2–2.6 (6 H, m, H_{4a}, H_5, H_{10}, H_{10a}, H_{11}), 3.13 (2 H, s, H_{5a}, H_{9b}), 6.8–7.3 (4 H, m, aromatic protons); mass spectrum (70 eV) m/e (rel intensity) 376 (10, 375 (1.0), 374 (2.2), 373 (1.2), 372 (3.5), 371 (1.0), 370 ($M^{+\cdot}$, 3.3), 337 (5.5), 335 (5.5), 178 (5.4), 169 (15.2), 168 (100), 167 (22.6), 153 (6.0), 129 (11.3), 128 (5.1). The other peaks were less than 5%. Exact mass: calcd for $C_{18}H_{14}{}^{35}Cl_4$, 369.9850; found, 369.9852.

***endo,exo,endo*-1,2,3,4-Tetrachloro-4a,5,5a,9b,10,10a-hexahydro-1,4:5,10-dimethanobenzobiphenylene (12b).** A mixture of 1,2,3,4-tetrachlorocyclopentadiene (8 g, 40 mmol), **2**[46] (4.8 g, 28 mmol), hydroquinone (20 mg), and *p*-xylene (10 mL) was heated in a sealed tube (N_2 atmosphere) at 150 °C for 3 h. Purification of the material in the manner described for the preparation of **11b** gave **12b** as white crystals: mp 155 °C (from isooctane); ^{1}H NMR ($CDCl_3$) δ 1.30 (1 H, d, J = 13 Hz, H_{12s}), 1.68 (1 H, d, J = 13 Hz, H_{12a}), 1.90–2.25 (4 H, m, H_{4a}, H_{10a}, H_{11}), 2.60 (2 H, br s, H_5, H_{10}), 3.55 (2 H, m, H_{5a}, H_{9b}), 6.95–7.25 (4 H, m, aromatic protons); mass spectrum (70 eV) m/e (rel intensity) 375 (1.0), 374 (2.2), 373 (1.3), 372 (3.2), 371 (1.0), 370 ($M^{+\cdot}$, 2.5), 178 (25.4), 169 (15.1), 168 (100), 167 (22.8): 129 (15.6). The remaining peaks were less than 10%. Anal. Calcd for $C_{18}H_{14}Cl_4$: C, 58.10; H, 3.79; Cl, 38.11. Found: C, 58.38; H, 3.89; Cl, 38.14.

***endo,exo,exo*-1,2,3,4-Tetrachloro-4a,5,5a,6,11,11a,12,12a-octahydro-6,11(1′2′)-benzeno-1,4:5,12-dimethanonaphthacene (13).** A mixture of **5** (6 g, 22 mmol), 1,2,3,4-tetrachlorocyclopentadiene (7.5 g, 37 mmol), and *p*-xylene (10 mL) was heated in a sealed tube (N_2 atmosphere) at 150 °C for 3 h. Purification of the material in the manner described for the preparation of **11b** afforded **13** as white crystals (6.5 g, 62%): mp 287 °C (from isooctane); ^{1}H NMR ($CDCl_3$) δ −0.37 (1 H, d, J = 13 Hz, H_{14s}), 0.45 (1 H, d, J = 13 Hz, H_{14a}), 1.75 (2 H, s, H_5, H_{12}), 2.10–2.30 (6 H, m, H_{4a}, H_{5a}, H_{11a}, H_{12a}, H_{13}), 4.20 (2 H, s, H_6, H_{11}), 6.80–7.30 (8 H, m, aromatic protons); mass spectrum (70 eV) m/e (rel intensity) 475 (0.5), 474 (0.6), 472 ($M^{+\cdot}$, 0.6), 270 (2.0), 204 (14.0), 179 (15.4), 178 (100.0). The other peaks were less than 5%. Anal. Calcd for $C_{26}H_{20}Cl_4$: C, 65.83; H, 4.25; Cl, 29.90. Found: C, 65.46; H, 4.38; Cl, 29.84.

***endo,exo,exo*-1,4,4a,5,5a,9b,10,10a-Octahydro-1,4:5:10-dimethanobenzobiphenylene (6).** Dechlorination of **11b** was carried out using the Gassman method.[27] A solution of **11b** (5 g, 13.5 mmol) in THF (10 mL) was added to a refluxing solution of *tert*-butyl alcohol (15 g, 0.2 mol) in THF (90 mL) containing sodium wire (2.3 g, 0.1 mol). The resulting mixture was stirred under reflux (N_2 atmosphere) for 7 h, after which time it had turned a mauve color. The cooled solution was poured into water (200 mL) through a plug of glass wool (to trap any unreacted sodium). The aqueous solution was extracted with chloroform (3 × 50 mL). The combined extracts were dried (Na_2SO_4) and evaporated under reduced pressure. Sublimation of the residue (130 °C, 30 mm) gave **6** (1.3 g, 42%) as fluffy, white plates: mp 97.5 °C; ^{1}H NMR ($CDCl_3$) δ 0.34 (1 H, d, J = 12 Hz, H_{12s}), 1.35 (2 H, AB q, J = 8 Hz, H_{11}), 1.8–2.2 (5 H, m, H_{4a}, H_5, H_{10}, H_{10a}, H_{12a}), 2.9 (2 H, br s, H_1, H_4), 3.1 (2 H, s, H_{5a}, H_{9b}), 6.0 (2 H, t, J = 2 Hz: olefinic protons), 6.85–7.30 (4 H, m, aromatic protons); mass spectrum (70 eV) m/e (rel intensity) 234 ($M^{+\cdot}$, 3.5), 168 (100), 167 (67). All other peaks were less than 10%. UV (isooctane): λ_{max} (E_{max}) 271 nm (1600), 276 (2500): 282 (2550). Anal. Calcd for $C_{18}H_{18}$: C, 92.25;. H, 7.75. Found: C, 92.23; H, 7.81.

***endo,exo,endo*-1,4,4a,5,5a,9b,10,10a-Octahydro-1,4:5,10-dimethanobenzobiphenylene (7).** Dechlorination of **12b** (4 g, 10.7 mmol) under similar conditions employed for the dechlorination of **11b** afforded, after sublimation (0.5 mm, 75 °C), **7** as a white, waxy solid: mp 53.5 °C; ^{1}H NMR ($CDCl_3$) δ 0.70–1.80 (6 H, br m, H_{4a}, H_{10a}, H_{11}, H_{12}), 2.35 (2 H, br s, H_5, H_{10}), 2.75 (2 H, br s, H_1, H_4) 3.50 (2 H, m, H_{5a}, H_{9b}), 6.05 (2 H, t, olefinic protons), 7.0–7.35 (4 H, aromatic protons); mass spectrum (70 eV) m/e (rel intensity) 234 ($M^{+\cdot}$, 5.9): 193 (13), 168 (100), 167 (85), 153 (36), 141 (26), 120 (43), 128 (22), 102 (47), 66 (28). Anal. Calcd for $C_{18}H_{18}$: C, 92.25; H, 7.75. Found: C, 91.0; H, 7.68.

***endo,exo*-1,4,4a,5,5a,6,11,11a,12,12a-Decahydro-6,11(1′,2′)-benzeno-1,4:5,12-dimethanonaphthacene (8).** Dechlorination of **13** (5 g, 10.5 mmol) in the same way as described for the dechlorination of **11b** afforded **8** (3 g, 85%): mp 140.5 °C (from isooctane); ^{1}H NMR ($CDCl_3$) δ −0.9 (1 H, d, J = 12 Hz, H_{14s}), 1.0–1.5 (3 H, m, H_{14a}, H_{13}), 1.65–1.85 (6 H, m, H_{4a}, H_5, H_5, H_{11a}, H_{12}, H_{12a}), 2.73 (2 H, br s, H_1, H_4), 4.22 (2 H, s, H_6, H_{11}), 5.80 (2 H, t, J = 2 Hz, olefinic protons), 6.92–7.40 (8 H, m, aromatic protons); mass spectrum (70 eV) m/e (rel intensity) 336 ($M^{+\cdot}$, 1.7), 270 (8.3), 204 (3.6), 178 (100); UV (isooctane) λ_{max} (E_{max}) 215 nm (2270), 267 (1430), 273 (1702). Anal. Calcd for $C_{26}H_{24}$: C, 92.81; H, 7.19. Found: C, 92.65; H, 7.22.

***endo,exo,exo*-1,2,3,4,4a,5,5a,9b,10,10a-Decahydro-1,4:5,10-dimethanobenzobiphenylene (20a).** Hydrogenation of **6** (1 g, 4.3 mmol), in the manner described above for the preparation of **15**, gave **20a** (0.85 g, 84%): mp 84.5 °C (from ethanol); ^{1}H NMR ($CDCl_3$) δ 0.67 (1 H, d, J = 10 Hz, H_{12s}), 1.0–1.85 (9 H, m, H_2, H_3, H_{4a}, H_{10a}, H_{11}, H_{12a}), 2.10 (2 H, s, H_5, H_{10}), 2.25 (2 H, br s, H_1, H_4), 3.0 (2 H, s, H_{5a}, H_{9b}), 6.75–7.30 (4 H, m, aromatic protons); mass spectrum (70 eV) m/e (rel intensity) 236 ($M^{+\cdot}$, 5.1), 208 (10.2), 207 (13.4), 168 (12.8), 167 (16.3), 142 (14.8), 141 (16.3), 130 (14.8), 129 (93.7), 128 (100), 80 (15.6). The other peaks were less than 10%. Anal. Calcd for $C_{18}H_{20}$: C, 91.5; H, 8.5. Found: C, 91.42; H, 8.66.

***endo,exo,endo*-1,2,3,4,4a,5,5a,9b,10,10a-Decahydro-1,4:5,10-dimethanobenzobiphenylene (20b).** Hydrogenation of **7** (1 g, 4.3 mmol), in the manner described above for the preparation of **15**, gave **20b** (1 g, 98.5%): mp 53.5 °C (sublimation: 75 °C, 0.5 mm); ^{1}H NMR ($CDCl_3$) δ 0.85–2.35 (14 H, br m, H_1–H_{4a}, H_5, H_{10}, H_{10a}, H_{11}, H_{12}), 3.55 (2 H, m: H_{5a}, H_{9b}), 6.95–7.35 (4 H, m, aromatic protons); mass spectrum (70 eV) m/e (rel intensity) 236 ($M^{+\cdot}$, 9) 208 (10.7), 168 (15.7), 167 (18.1), 155 (11.4), 153 (13.0), 142 (19.4), 141 (17.4), 130 (16.1), 129 (83.9), 128 (100.0), 116 (13.4), 111 (11.0), 97 (11.4), 95 (13.7), 91 (11.0), 80 (14.0), 71 (12.4), 70 (11.7), 67 (15.1), 57 (16.4), 55 (10.7). The other peaks were less than 10%. UV (isooctane): λ_{max} (E_{max}) 262 nm (1360), 274 (2200), 200 (1600). Anal. Calcd for $C_{18}H_{20}$: C, 91.5; H, 8.5. Found: C, 91.43; H, 8.71.

***endo,exo,exo*-1,2,3,4,4a,5,5a,6,11,11a:12,12a-Dodecahydro-6,11(1′,2′)-benzeno-1,4:5,12-dimethanonaphthacene (21).** Hydrogenation of **8** (1 g, 3 mmol), in the manner described above for the preparation of **15**, gave **21** (0.95 g, 95%): mp 151.5 °C (from isooctane); ^{1}H NMR ($CDCl_3$) δ −0.52 (1 H, d, J = 10 Hz, H_{14a}), 0.88 (1 H, d, J = 10 Hz, H_{14s}), 1.0–2.35 (14 H, m, H_1–H_{5a}, H_{11a}, H_{12}, H_{12a}, H_{13}), 4.23 (2 H, s, H_6, H_{11}), 6.90–7.25 (8 H, m, aromatic protons); mass spectrum (70 eV) m/e (rel intensity) 338 ($M^{+\cdot}$, 0.7), 179 (15), 178 (100). All other peaks were less than 2%. UV (isooctane): λ_{max} (E_{max}) 274 nm (1600), 267 (1340), 204 (3400). Anal. Calcd for $C_{26}H_{26}$: C, 92.25; H, 7.78. Found: C, 92.37; H, 7.78.

Birch Reductions. Reagents and Equipment. The equipment and the purification of the reagents used for the Birch reductions have been described in the preceding paper.[1]

Individual Birch Reductions. The general procedure as described in the preceding paper[1] was used for performing the Birch reductions. Unless stated otherwise the following quantities of reagents were used: liquid NH_3 (150 mL), THF (5 mL), and *tert*-butyl alcohol (TBA) (1.4 g). Also, unless stated otherwise, $CHCl_3$ was used to extract the organic products of the Birch reduction during the workup procedure.[1]

A. Reduction of 3. Treatment of **3** (1.0 g, 6.3 mmol) with a large excess of Li (0.21 g, 30 mmol) in liquid ammonia: THF, and TBA for 3 h and subsequent workup[1] (extracting solvent pentane) led to the formation of a single product. Thus GLC analysis (column A, 90 °C) revealed the presence of a single peak which was attributed to **14** through comparison of its GLC retention time, its mass spectral cracking pattern, and its ^{1}H NMR spectrum with those of authentic **14**.

B. Reduction of 4a. This compound (1.0 g, 4.8 mmol) was treated with Li (0.1 g, 14.3 mmol) in liquid NH_3, THF, and TBA for 3 h, after which time the mixture was worked up[1] (pentane extracting solvent). GLC analysis of the mixture (column C, 190 °C) revealed the presence of a single product which was identified as **15** through comparison of its ^{1}H NMR and mass spectral data with those of authentically prepared **15** (vide supra). Treatment of the product with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) followed by GLC analysis of the resulting mixture did not reveal any trace of **4a.** It was concluded that **16** is completely absent from the product resulting from the Birch reduction of **4a.**[48]

C. Reduction of 5. The reduction of **5** (1.0 g, 3.7 mmol) with Li (65 mg, 9.3 mmol) in liquid NH_3, THF (30 mL), and TBA was complete within 6 min. The crude product, after workup,[1] was analyzed by ^{1}H NMR and TLC (silica gel, variety of solvents) and was found to consist of a single product. The identity of the product as **17** was confirmed through comparison of its ^{1}H NMR and mass spectral data with those of authentically prepared **17** (vide supra).

D. **Reduction of 17. 17** (1.0 g, 3.7 mmol), Li (155 mg, 22.2 mmol), liquid NH_3, THF (30 mL), and TBA were reacted for 3.5 h, after which time the mixture was worked up in the usual procedure.[1] The examination (silica gel plates, 50% chloroform in petroleum ether (bp 60-80 °C)) revealed two spots, the more prominent of which was found to be unreacted **17.** Identification was made through TLC comparison with known material, removal of the spot from the plate, and obtaining a ^{1}H NMR spectrum. There was insufficient material for a useful spectrum of the remaining spot, but DDQ oxidation yielded a product with identical TLC properties with **17.**

E. Reduction of 6. Treatment of **6** (0.5 g: 2.1 mmol) with a large excess of Li (74 mg, 10.5 mmol) in liquid NH_3, THF (35 mL), and TBA for 3.2 h gave, after workup, two products in the ratio 19.5:1 (GLC analysis: column C, 190 °C). A small quantity of the major product was collected at the exit port of the analytical gas chromatograph and identified as ***endo,exo,exo*-1,4,4a,5,5a,6,9,9b,10,10a-decahydro-1,4:5,10-dimethanobenzobiphenylene (18a):** ^{1}H (PFT) NMR ($CDCl_3$) δ 0.59-1.80 (6 H, m, H_{4a}, H_{10a}, H_{11}, H_{12}), 2.41 and 2.47 (6 H, pair s, H_5, H_6, H_9, H_{10}), 2.83 and 3.67 (4 H, pair s, allylic protons, H_1, H_4, H_{5a}, H_{9b}), 5.72 (2 H, s, olefinic protons H_7, H_8), 5.95 (2 H, t, J = 4 Hz, olefinic protons H_2, H_3); mass spectrum (70 eV) m/e (rel intensity) 236 ($M^{+\cdot}$, 5.2), 207 (10.0), 195 (24.6), 170 (37.4), 169 (22.0), 168 (18.3): 167 (17.2), 156 (18.7), 155 (50.01), 154 (12.6), 153 (11.7), 143 (26.5), 142 (29.1), 141 (33.5), 131 (17.6), 130 (27.6), 129 (79.8), 128 (26.3), 118 (14.3), 117 (28.0), 116 (89.8), 115 (13.0), 106 (14.3), 105 (30.4), 104 (27.2), 93 (16.3), 92 (100.0), 91 (42.0), 79 (72.4), 78 (16.1), 67 (17.4), 66 (32.6). The other peaks were less than 10%.

Treatment of **18a** in benzene with excess DDQ at 20 °C rapidly led to the exclusive formation of rearomatized material **6,** as judged through comparison of its GLC/MS data with those of authentic material.

Lack of material precluded isolation of the minor component of the reduction product mixture. However, its identify was readily proved to be **19a** through comparison of its GLC/MS data with those of authentic material (vide infra).

Treatment of the reduction product mixture in benzene with excess DDQ at 20 °C led to the formation of **6** and **20a** in the ratio 19.5:1 (GLC, column C, 200 °C). It is concluded that **19a** must be the source of **20a.**

Reduction of **6** (0.5 g, 2.1 mmol) using less Li (14 mg, 2 mmol) led to the formation of **20a** in addition to **18a, 19a,** and unreacted **6** (GLC, column C, 190 °C). The identity of **20a** was confirmed through comparison of its GLC/MS data with those of authentic material.

F. Reduction of 20a. Reduction of **20a** (0.5 g, 2.1 mmol) with Li (67 mg, 9.5 mmol) in liquid NH_3, THF (35 mL), and TBA for 3 h and subsequent workup led to the quantitative formation of ***endo,exo,exo*-1,2,3,4,4a,5,5a,6,9,9b,10,10a-dodecahydro-1,4:5,10-dimethanobenzobiphenylene (19a)** as a white, waxy solid which resisted attempts at recrystallization or sublimation: ^{1}H NMR ($CDCl_3$) δ 1.1-2.2 (14 H, m, methine and methylene protons), 2.32 (2 H, s, H_{5a}, H_{9b}), 2.44 (4 H, s, H_6, H_9), 5.67 (2 H, s, olefinic protons H_7, H_8); mass spectrum (70 eV) m/e (rel intensity) 238 ($M^{+\cdot}$, 6.9%), 209 (11.1), 169 (11.3), 167 (12.0), 155 (12.4), 143 (23.8), 142 (12.9), 141 (15.8), 132 (13.6), 131 (100.0), 130 (60.5), 129 (57.3), 128 (32.0), 117 (16.2), 116 (16.4), 109 (19.5), 108 (10.0), 95 (34.9), 93 (12.4), 92 (17.3), 91 (30.2), 81 (14.7), 80 (48.7), 79 (17.5), 67 (29.3). The other peaks were less than 10%. Exact mass: calcd for $C_{18}H_{22}$, 238.1721; found, 238.1720.

A solution of **19a** in benzene was treated with excess DDQ at 20 °C. The solution was filtered, washed with dilute NaOH followed by saturated aqueous NaCl, dried (Na_2SO_4), and evaporated. The residue was shown to be **20a** through comparison of its ^{1}H NMR and mass spectral data with those of authentic material (vide supra).

G. Reduction of 7. Reduction of **7** (0.2 g: 0.84 mmol) with excess Li (30 mg, 4.3 mmol) in liquid NH_3, THF (35 mL), and TBA for 3 h and subsequent workup led to the formation of two products in the ratio 20:1 (GLC, column C, 200 °C). A very small sample of the major product was isolated by GLC (column C, 200 °C) and was shown to be ***endo,exo,endo*-1,4,4a,5,5a,6,9,9b,10,10a-decahydro-1,4:5,10-dimethanobenzobiphenylene (18b):** ^{1}H (PFT) NMR ($CDCl_3$) δ 0.62-2.40 (8 H, m, H_{4a}, H_5, H_{10}, H_{10a}, H_{11}, H_{12}), 2.63 (4 H, s, allylic protons H_6, H_9), 2.77 (4 H, m, allylic protons: H_1, H_4, H_{5a}, H_{9b}), 5.75 (2 H, s, olefinic protons H_7, H_8), 5.95 (2 H, t, J = 2 Hz, olefinic protons H_2, H_3); mass spectrum (70 eV) m/e (rel intensity) 236 ($M^{+\cdot}$, 7.1), 207 (7.7), 196 (10.5), 195 (36.2), 171 (11.1), 170 (43.3), 169 (28.8), 168 (18.5), 167 (17.4), 156 (19.4), 155 (51.0), 154 (16.0), 153 (10.8), 143 (47.3), 142 (31.6), 141 (35.0), 131 (28.2), 130 (36.8), 129 (4.6), 128 (32.6), 118 (17.7), 117 (32.3), 116 (68.9), 115 (17.1), 106 (13.1), 105 (32.5), 104 (24.2), 93 (19.7), 92 (100.0), 91 (54.1), 79 (76.9), 78 (21.7), 93 (19.7), 92 (100.0), 91 (54.1), 79 (76.9), 78 (21.7), 67 (20.2), 66 (61.5). The other peaks were less than 10%.

Treatment of a benzene solution of **18b** with excess DDQ led to the quantitative formation of **7** as judged by GLC/MS and ^{1}H NMR spectroscopy.

The minor component of the Birch reduction product could not be isolated owing to lack of sufficient material. However, its identity was found to be **19b** through comparison of its GLC and GLC/MS data with those of authentic material (vide infra). Also treatment of the Birch reduction product, containing both compounds (in the ratio 20:1), with DDQ led to the formation of **7** and **20b** in the ratio 20:1, respectively. The identification of **7** and **20b** rests through comparison of their GLC and GLC/MS data with those of authentic specimens.

Reduction of **7** (0.1 g, 0.4 mmol) using less Li (ca. 3 mg, 0.4 mmol) led to the formation of **20b** in addition to **18b, 19b,** and unreacted **7** (GLC, column C, 190 °C). The identity of **20b** was confirmed through comparison of its GLC/MS data with those of authentic material.

H. Reduction of 20b. Reduction of **20b** (0.1 g, 0.4 mmol) with excess Li (ca. 14 mg, 2 mmol) under the usual conditions (2 h) led to the formation of ***endo,exo,endo*-1,2,3,4,4a,5,5a,6a,9,9b,10,10a-dodecahydro-1,4:5,10-dimethanobenzobiphenylene (19b)** as a waxy material (ca. 100 mg) which resisted attempts at sublimation or recrystallization. However, GLC analysis (column C, 190 °C) revealed that it was pure: ^{1}H NMR ($CDCl_3$) δ 0.70-2.40 (14 H, m, methine and methylene protons), 2.60 (4 H, s, allylic protons H_6, H_9), 2.85 (2 H, d, J = 4 Hz, allylic protons H_{5a}, H_{9b}), 5.69 (2 H, s, olefinic protons H_7, H_8); mass spectrum (70 eV) m/e (rel intensity) 238 ($M^{+\cdot}$, 13.2), 207 (12.7), 168 (16.5), 167 (13.7), 156 (9.4), 146 (15.6), 144 (61.8), 143 (27.4), 142 (31.3), 141 (19.8), 132 (18.9), 131 (21.2), 130 (21.2), 129 (100.0), 117 (16.5), 95 (15.6), 94 (30.7), 92 (15.1), 91 (20.8), 84 (16.0), 79 (19.8). The other peaks were less than 15%. Exact mass: calcd for $C_{18}H_{22}$, 238.1721; found, 283.1721.

Treatment of a benzene solution of **19b** with DDQ, in the manner described above for the reaction between **19a** and DDQ, led to its quantitative rearomatization to **20b,** as judged by GLC, MS, and ^{1}H NMR spectroscopy.

I. Reduction of 8. Treatment of **8** (1.0 g, 2.9 mmol) with Li (105 mg, 15 mmol), under the usual conditions, for 3 h led to a mixture of four components (TLC). The major component (ca. 40%) was shown to be unreacted **8** through comparison of its TLC and ^{1}H NMR spectral data with those of authentic material. The remaining components could not be separated. They are believed to be **21, 22a,** and **23a** for the following reasons. Treatment of the Birch reduction product mixture with excess DDQ in benzene at 20 °C led to the formation of a mixture of **8** and **21.** The identification of these compounds rests on their TLC data and on the ^{1}H NMR spectrum of the mixture—in particular the presence of the two high-field doublets at δ −0.9 and −0.5 (or the aromatic and vinylic signals) gave **8:21** = 3.2:1.

The ^{1}H NMR spectrum of the original product mixture from the Birch reduction of **8** displayed three vinylic resonances at δ 5.95, 5.8, and 5.67. The multiplet at δ 5.8 is attributed to the vinylic H resonances of **8** and (probably) **22a** and **23a.** The signals at δ 5.95 and 5.67 are tentatively assigned to the vinylic proton resonances of the cyclohexadienyl rings of **22a** and **23a,** respectively, by analogy with similar assignments made for **22b** and **23b** (vide infra). Integration of the aromatic and vinylic signals led to the following composition: **8** (42.5%), **21** (23.4%): **22a** + **23a** (34.1%). Note that the ratio (**8** + **22a** + **23a**):**21** is 3.27:1. This ratio should, and does, agree with the ratio of the products, **8:21**, resulting from the aforementioned DDQ oxidation reaction (**22a** and **23a** are rearomatized to **8** by DDQ). From the ratio of product yields, (**22a** + **23a**):**21**, we calculate that k_A/k_D = 1.46.

J. Reduction of 21. Treatment of **21** (1 g, 2.9 mmol) with Li (0.08 g, 11.4 mmol) in the usual way led to the formation of unreacted **21** (ca. 40%) and to two products (by TLC analysis). The products are believed to be **22b** and **23b** for the following reasons. The ^{1}H NMR spectrum of the product mixture displayed vinylic resonances at δ 5.96 and 5.68 of relative areas 4:1, respectively. A single high-field doublet at δ −0.5 was also present which is probably a superposition of the resonances of the methano proton, H_a, of **22b** and unreacted **21**. Integration of the aromatic, vinylic, and the high-field doublet signals allows the following product composition to be determined: **21** (38%), **22b** (49.6%), **23b** (12.4%). From their relative areas the vinylic proton resonances at δ 5.96 and 5.68 are assigned to those of **22b** and **23b**, respectively.[47] Finally treatment of the product mixture with DDQ led to the exclusive formation of **21**.

Competition Kinetics. The general procedure for carrying out the competition studies is described in the preceding paper.[1] GLC analyses of the mixtures were carried out in triplicate. Areas under ^{1}H NMR signals were averaged over ten separate integrations. The mixtures containing the pairs of competitors and their products of reduction (which are not given below) resulting from the competition experiments were analyzed as follows: (1) **3** (column A, 90 °C, isothermal) vs. toluene (column A, 30 °C, isothermal); (2) **4a** (column A, 30–250 °C, 7 °C min^{-1}) vs. toluene (as for 1); (3) **5** (^{1}H NMR) vs. toluene (as for 1) (The mixture was first analyzed for toluene and dihydrotoluene by GLC and then evaporated under reduced pressure at 100 °C. The residue, containing only **5** and **17**, was analyzed by ^{1}H NMR. The relative proportions of **5** and **17** were obtained from the relative areas of the aromatic and olefinic regions of the NMR spectrum.); (4) **6** (column C, 190 °C, isothermal) vs. toluene (as for 1); (5) **7** (column C, 190 °C, isothermal) vs. toluene (as for 1); (6) **8** (^{1}H NMR) vs. **14** (column A, 90 °C, isothermal) (The mixture was first analyzed for toluene and its reduced products. The volatiles were removed under reduced pressure and the residue, which contained only **8** and its reduced products, was analyzed by ^{1}H NMR as explained in the text.); (7) **14** (as for 6) vs. toluene (as for 1); (8) **17** (^{1}H NMR) vs. **14** (as for 6) (GLC analysis of the mixture, followed by evaporation under reduced pressure at 100 °C (to remove **14** and its reduced product) and ^{1}H NMR analysis. The proportions of **17** and its reduced products were obtained from the relative areas of the aromatic and olefinic regions of the ^{1}H NMR spectrum.); (9) **20a** (column C, 190 °C, isothermal) vs. toluene (as for 1); (10) **20b** (column C, 190 °C, isothermal) vs. toluene (as for 1); (11) **21** (^{1}H NMR) vs. **14** (as for 6) (GLC analysis of the mixture followed by evaporation under reduced pressure at 100 °C (to remove **14** and its reduced product). ^{1}H NMR analysis of the residue, as outlined in the text, enables the relative amounts of **21** and its reduced products to be determined.); (12) toluene (as for 1) vs. norbornene (column D, 25 °C, isothermal, flow rate 10 mL min^{-1}); (13) **5** (^{1}H NMR) vs. **24** (column C, 150 °C, isothermal); (14) **20** (as for 9) vs. **5** (^{1}H NMR); (15) **20a** (as for 9) vs. **24** (as for 13).

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(35) The small rate enhancements observed for **6**–**8** could be the result of the observed (relative) rate constant being a product of K, the equilibrium constant for the formation of the anion radical, and k_D, the rate constant for the protonation of the double bond of the same species.[1] The presence of orbital interactions is expected to increase K yet decrease k_D.[1] Therefore the whole reactivity scale is compressed and it is possible that the small rate enhancements observed for the double bond reduction of **6**–**8** result from an accidental canceling of the effects on K and k_D. Clarification of this problem must await the determination of separate measurements of K or k_D (absolute or relative), which would be a major undertaking. We thank a referee for bringing aspects of this problem to our attention.
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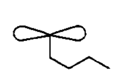
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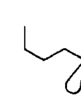
ii

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(49) Note Added in Proof. We are indebted to Professor H. Prinzbach for sending us a copy of the ^{1}H NMR spectrum of the endo,endo isomer.

Conversion of Benzo- and Naphthonorcaradien-7-yl to Benzo- and Naphthotropyl Radicals

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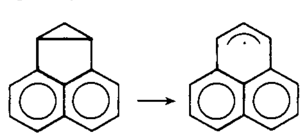
Abstract: Thermal decompositions of *tert*-butyl 2,3-benzonorcaradiene-7-percarboxylate (**7**), *tert*-butyl 2,3-(2′,3′-naphtho)norcaradiene-7-percarboxylate (**8**), bis(2,3-benzonorcaradiene-7-carbonyl) peroxide (**9**), and bis[2,3-(2′,3′-naphtho)norcaradiene-7-carbonyl] peroxide (**10**) have been studied with particular attention paid to the hydrocarbon products, 2,3-benzonorcaradiene (**11**) and 1,2-benzotropilidene (**12**) from **7** and **9**, and 2,3-(2′,3′-naphtho)norcaradiene (**14**) and 1,2-(2′,3′-naphtho)tropilidene (**15**) from **8** and **10**. The variation of product ratio with solvent from **7** and **8** suggests that the intermediate benzo- and naphthonorcaradien-7-yl radicals competitively abstract a hydrogen atom or undergo ring opening to the corresponding tropyl radical. A similar study of **9** and **10** suggests that there is an additional, polar component to formation of seven-membered ring products **12** and **15**. Since the hydrocarbon products are free radical in origin, it is suggested that the intermediates, whether highly polarized species or free cations, must revert back to free radicals before giving these products. It is further suggested that the greater degree of ring opening from the diacyl peroxides, **9** and **10**, is due to the greater allowedness of the ring opening of the norcaradienyl type cations relative to the corresponding radicals. It is also demonstrated that benzonorcaradienyl intermediates undergo ring opening more readily than the corresponding naphthonorcaradienyl intermediates.

Introduction

Our interest in the reactions of tropyl and benzotropyl radicals[1] has led us to explore the possibility of the electrocyclic ring opening of norcaradien-7-yl radicals to provide the corresponding tropyl radicals.

While a number of thermal ring openings of cyclopropyl radicals have been reported,[2,3] calculations indicate that the reaction, at least of the cyclopropyl radical to allyl itself, is forbidden.[4] The calculations further point out that, of the two possible modes of ring opening, conrotatory and disrotatory, the latter is preferred, although both modes should have large activation energies. In general, liquid phase reactions of simple cyclopropyl radicals show few, if any, products of ring opening. This is not surprising considering the activation energy for ring opening, estimated to be 22 kcal/mol for the cyclopropyl to allyl conversion in the gas phase,[5] is considerably higher than that for hydrogen abstraction, reported to be 7.3 kcal/mol.[6]

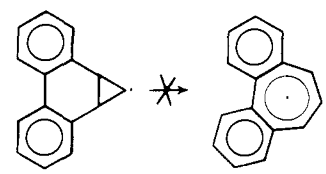
When phenyl substituents are put on the 2 and 3 positions of the cyclopropyl radical, the ring opening seems to be more facile.[3] Thus, for example, the 2,3-diphenylcyclopropyl radical has been observed to open in competition with hydrogen abstraction.[2b] Consistent with these observations is the report that free radical **1** readily undergoes ring opening to the radical shown, even using ethylbenzene as solvent and as hydrogen



1

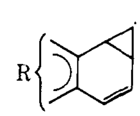
donor.[7] What appears quite puzzling, however, is the report[7] that the dibenzonorcaradien-7-yl radical **2**, under the same conditions, does not open to the dibenzotropyl radical. This is in spite of the known aromaticity of the tropyl radical.[8]

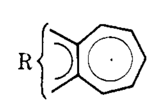
This paper describes our attempts to observe the ring



2

opening of the 2,3-benzonorcaradien-7-yl radical (**3**) to produce the benzotropyl radical (**4**) and also the ring opening of the 2,3-(2′,3′-naphtho)norcaradien-7-yl (**5**) radical to produce the naphthotropyl radical (**6**). We felt that ring opening might





3, R = benzo
5, R = 2,3-naphtho

4, R = benzo
6, R = 2,3-naphtho

be observable under an appropriate set of conditions since these should be highly exothermic reactions. Not only is the strain inherent in the three-membered ring being lost, but also the resonance energy associated with the tropyl radical[8] is being gained in these ring opening reactions.

Results and Discussion

In an attempt to observe the ring opening of norcaradienyl radicals, we have studied the thermal decomposition of *tert*-butyl 2,3-benzonorcaradiene-7-percarboxylate (**7**), *tert*-butyl 2,3-(2′,3′-naphtho)norcaradiene-7-percarboxylate (**8**), bis(2,3-benzonorcaradiene-7-carbonyl) peroxide (**9**), and bis[2,3-(2′,3′-naphtho)norcaradiene-7-carbonyl] peroxide (**10**) at 180 °C in a variety of solvents. We examined the hydrocarbon products, 2,3-benzonorcaradiene (**11**) and 1,2-benzotropilidene (**12**) from **7** and **9**, and 2,3-(2′,3′-naphtho)norcaradiene (**14**) and 1,2-(2′,3′-naphtho)tropilidene (**15**) from

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