The Observation of Remarkable Effects of Remotely Connected but Spatially Proximate Hydroxy-groups on the Rates and Regiochemistry of the Birch Reduction of Aromatic Rings and Double Bonds

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Product and competitive-rate studies of Birch reduction (Li, Bu^{t}OH, NH_3) of a series of alicyclic compounds, (**6**)—(**13**), are described. The hydrocarbons (**6a**)—(**8a**) and the *syn*-methoxy derivative (**6c**) are slowly reduced to give the unconjugated dienes such as (**16a**). In contrast the *syn*-alcohols (**6b**)—(**8b**) were rapidly reduced to give the monoenes (**17**), (**19**), and (**22**), respectively. Reduction of the *syn*-alcohol (**10b**) was also extremely rapid but that of the norbornenols (**11a**) and (**12a**) only showed moderate rate enhancements. Each of the above alcohols displays intramolecular OH ··· π bonding. Birch reductions of (**1**), (**6a**), (**10a**), (**11b**), and (**12b**), none of which possess intramolecular OH ··· π bonds, appear to obey third-order kinetics [equation (3)] whereas those of the OH ··· π-bonded alcohols (**6b**), (**10b**), (**11a**), and (**12a**) followed a combination of second- and third-order kinetics [equation (5)]. The rate and product data for the reduction of the alcohols (**6b**)—(**8b**), (**10b**), (**11a**), and (**12a**) are explained in terms of the presence of intramolecular OH ··· π bonding in these substrates. The observed second-order kinetics are explained in terms of intramolecular protonation of the anion-radical intermediate and is supported by the data for reduction of (**6c**) and (**9**). Geometric features which affect the efficacy of intramolecular proton transfer are discussed. Full STO-3G geometry optimisations on the anion radicals of (**11a** and **b**) reveal the presence of strong OH ··· π bonding in the anion-radical of (**11a**) amounting to some 27 kJ mol^{-1}.

Some 40 years of intensive research into the Birch reduction have led to the formulation of several generalisations, or rules, concerning this synthetically important reaction.[1,2] Three of these generalisations, which form the basis of this paper, are as follows.

(i) Carbon–carbon double bonds which are not in conjugation with other unsaturated centres undergo Birch reduction only with difficulty. For example it has been found that norbornene (**1**) is (Birch) reduced 36 times more slowly than toluene[3] and that less strained alkenes are reduced even more sluggishly.[4]

(ii) In the reduction of substituted aromatics to yield cyclohexa-1,4-dienes, donor substituents, such as alkoxy groups, tend to direct the reduction such that the major product has the maximum number of such groups attached to the residual double bonds and having the minimum of these groups located at the allylic sites.[5] Representative of this Birch rule[5,6] is the reduction of *o*-xylene to give mainly 1,2-dimethylcyclohexa-1,4-diene (**2**) and only a small amount of the isomeric 2,3-dimethylcyclohexadiene (**3**).[7,8] Over-reduction to give cyclohexenes is very unusual and is thought to occur only when sufficient quantities of strong base are generated during the reduction to effect isomerisation of the kinetically formed cyclohexa-1,4-diene to the more readily reducible 1,3-isomer.

(iii) Alkyl substituents markedly lower the rate of Birch reduction of aromatic substrates. Thus *o*-xylene and mesitylene are reduced respectively 20 and 60 times less rapidly than benzene.[7]

The first two generalisations are largely responsible for giving the Birch reduction its singular, and crucial, place in the synthetic organic chemist's methodology, whereas the third one is definitely a drawback in this respect.

Although a search for examples which contravene any of the three rules, and their explanation in terms of structural and substituent effects, would be beneficial from both mechanistic and synthetic points of view, only a few unequivocal cases have so far been reported. Thus we have found that isolated, *i.e.* non-conjugated, double bonds can, in fact, be reduced very rapidly if


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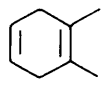
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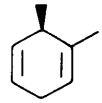
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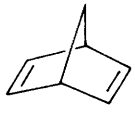
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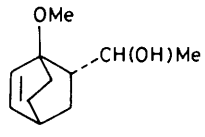
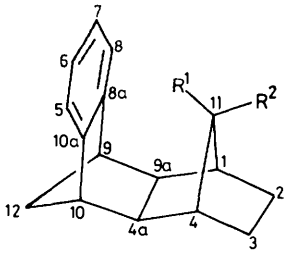


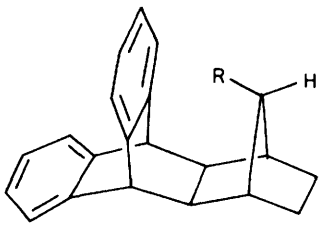
(5)

their π* MOs are able to interact with orbitals of remote substituents either through-space[3b] or through-bonds.[3a,9,10] A classic example of this type of violation of rule (i) is provided by norbornadiene (**4**) which undergoes Birch reduction (to give norbornene) *ca.* 3 500 times more rapidly than toluene.[3b,9] This result has been attributed to the consequences of through-space orbital interactions in (**4**) between the structurally enforced proximate double bonds.[3b] Examples of altered regiochemistry of reduction, *i.e.* exceptions to rule (ii), have been observed for sterically congested aromatic molecules:[11,12] a substituent, by virtue of its size, can over-ride the normally prevailing electronic influences to direct protonation of the intermediate anion to occur at an atypical site. The result is the formation of cyclohexa-1,3-diene (instead of the usual 1,4-isomer) which then undergoes further reduction. We are unaware of any exceptions to the third rule.

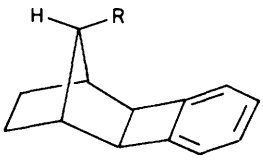
Several reports suggest that the normal stereochemical and regiochemical outcome of the Birch reduction of a variety of substrates, including styrene moieties,[13] aromatic rings,[12,14] and enones,[15–17] can be dramatically modified by the presence of hydroxy- or carboxy-groups spatially proximate to the



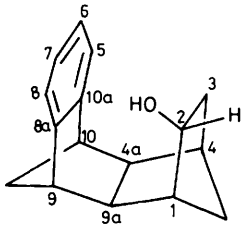
(6) a; R^1 = H, R^2 = H
b; R^1 = OH, R^2 = H
c; R^1 = OMe, R^2 = H
d; R^1 = OAc, R^2 = H
e; R^1 = H, R^2 = OH



(7) a; R = H
b; R = OH



(8) a; R = H
b; R = OH



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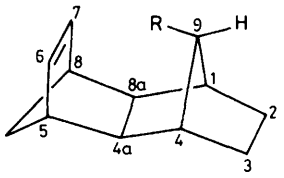
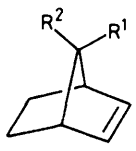
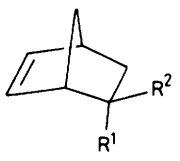


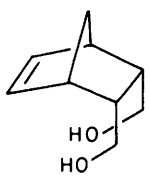
(10) a; R = H
b; R = OH



(11) a; R^1 = OH, R^2 = H
b; R^1 = H, R^2 = OH



(12) a; R^1 = OH, R^2 = H
b; R^1 = H, R^2 = OH



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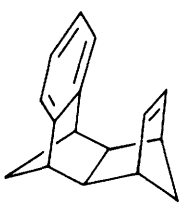

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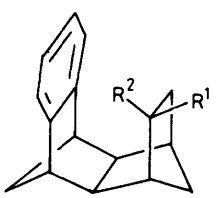


(15) a; R^1 = OH, R^2 = H
b; R^1 R^2 = =O

reduction site. In these cases it is thought that such a group serves as an intramolecular proton source or as a template to which the added proton source is bound, perhaps through the alkali-metal cation. The stereochemical and regiochemical outcome of the reduction is then determined, in a predictable way, by the geometrical relationship between the hydroxy- or carboxy-group and the possible sites of protonation.

It is likely, then, that exceptions to the three generalisations above could be found using substrates containing suitably located hydroxy-groups. Indeed Birch and Hutchinson have presented evidence which suggests that the reduction of the double bond in the *endo*-alcohol (**5**) is assisted by the hydroxy-group although no rate data were obtained.[18] In this paper we present a full account of our investigations[19] into the problem which, through a combination of product and rate studies of the Birch reduction of the series of substrates (**6**)—(**13**), together with model *ab initio* MO calculations, demonstrate quite unequivocally that neighbouring hydroxy-groups can strongly influence the course of the Birch reduction.

Results

Syntheses.—The synthesis of compounds (**6a**),[20] (**6b**),[20] (**7**),[10] (**8**),[21] and (**10**)[22] has been described elsewhere. The *syn*-methoxy- and *syn*-acetoxy-compound (**6c** and **d**) were prepared from (**6b**) using standard methods.

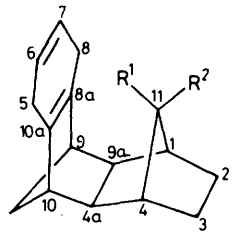
The hexahydrodimethanoanthracene[23] (**14**) served as a starting point for the synthesis of the *syn*-alcohol (**9**). Hydroboration of (**14**) and subsequent oxidation (OH^-, H_2O_2) of the resulting adduct gave the *anti*-alcohol (**15a**), the configuration of which followed from spectral data and from the most likely mode of attack of the BH_3 occurring on the less sterically hindered *exo*-face of the double bond of (**14**). The alcohol (**15a**) was readily oxidised to the ketone (**15b**), the reduction of which ($LiAlH_4$) led to the formation of the epimeric *syn*-alcohol (**9**). The assignment of structures (**9**) and (**15a**) to the respective alcohols was confirmed spectrally. The OH stretching frequencies for (**9**) and (**15a**) are respectively 3 567 and 3 617 cm^{-1} (CCl_4), the former being concentration independent. The wavenumber difference, $\Delta\bar{\nu}$, between these frequencies is 50 cm^{-1}. These data are consistent with the expectation that (**9**) should exist exclusively in the intramolecularly OH • • • π-bonded form[20,22] [*cf.* the $\bar{\nu}_{OH}$ values for *syn*-(**6b**) and *anti*-(**6e**) of 3 599 and 3 644 respectively;[20] $\Delta\bar{\nu}$ 44 cm^{-1}]. Finally the chemical shifts of H-2 in (**9**) and (**15a**) are respectively δ 3.8 and 3.2 ($CDCl_3$). The increased shielding of this proton in the latter compound is attributed to its more favourable location within the shielding zone of the aromatic ring.[20]

Birch Reduction Product Studies.—Unless stated otherwise all Birch reductions were carried out using a solution of lithium metal in a refluxing (*ca.* −33 °C) mixture of liquid ammonia, tetrahydrofuran (co-solvent), and t-butyl alcohol as a proton source.

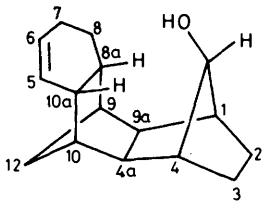
Birch reduction of the dimethanoanthracene (**6a**), with a large excess of lithium, proceeded very slowly to give, after 7 h, two products (7:1) and unreacted (**6a**) (40%) (g.l.c. analysis). Owing to the paltry amount of material available the products could not be isolated. The structure of the major product is believed to be (**16a**) on the basis of ^{1}n.m.r. and g.l.c.–m.s. analysis of the mixture (see Experimental section) and from the observation that it is readily rearomatised back to (**6a**) by treatment of the product mixture with dichlorodicyanobenzoquinone (DDQ) at room temperature. G.l.c.–m.s. studies on the minor product reveal that it has only one double bond. This product probably results from further reduction of (**16a**) at the disubstituted double bond.

Birch reduction of the *syn*-methoxy-derivative (**6c**) was even more difficult to achieve than that of (**6a**): only 4% reduction had taken place after 5 h. G.l.c.–m.s. analysis of the reaction mixture revealed the presence of only one product whose structure probably corresponds to (**16c**).

In contrast to (**6a** and **c**) Birch reduction of the *syn*-alcohol (**6b**) was so rapid that the addition of the lithium to a solution of



(16) a; R^1 = H, R^2 = H
b; R^1 = OH, R^2 = H
c; R^1 = OMe, R^2 = H



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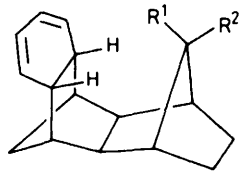
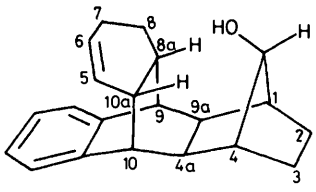


(18) a; R^1 = H, R^2 = OH
b; R^1R^2 = =O
c; R^1 = OH, R^2 = H



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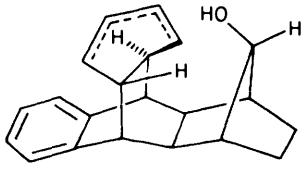

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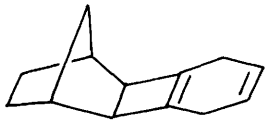

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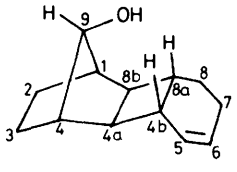

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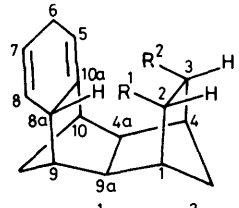
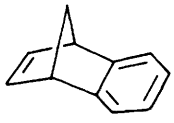


(23) a; R^1 = OH, R^2 = H
b; R^1 = H, R^2 = OH



(24)

(**6b**) in liquid ammonia simply resulted in its dissolution without turning the ammonia solution blue. The reduction came to an abrupt halt, as signalled by the development of the blue colour, only after 4 atom equiv. of metal had been consumed. The speed of this reduction is made more apparent by adding a solution of (**6b**) in THF to a solution of lithium in ammonia: addition of an excess of substrate all at once led to an immediate disappearance of the blue colour. It appears, therefore, that the rate of reduction of (**6b**) is determined by the rate of mixing of the reagents and could even be diffusion controlled!

A single product, resulting from the reduction of (**6b**) with 4 atom equiv. of lithium, was isolated in quantitative yield. Its elemental analysis and high-resolution mass spectrum corresponded to the molecular formula $C_{16}H_{22}O$, *i.e.* it is formed from the addition of 4 atom equiv. of hydrogen to the aromatic ring of (**6b**), a result which is also consistent with the observed stoicheiometry of the reduction. The following data served to establish the structure of the product as (**17**).

The hydroxy-group was still present but its $\bar{\nu}_{OH}$ value of 3 628 cm^{-1} (CCl_4) reveals the absence of any intramolecular OH···π bonding [*cf.* $\bar{\nu}_{OH}$ 3 599 cm^{-1} for (**6b**)]. Thus the double bond of the product cannot be located at C-8a or C-10a. The 13-line ^{13}C n.m.r. spectrum showed that the compound was devoid of any symmetry (three pairs of ^{13}C nuclei are accidentally isochronous) and that it has two tertiary vinylic carbon atoms. The location of the double bond in the product must therefore be at C-5 and C-6. This conclusion was also supported by the ^1H n.m.r. spectrum of the product which exhibited an AB quartet in the vinylic proton region: δ($CDCl_3$) 5.53 and 5.87 (*J* 11 Hz). That half of the doublet which appears at lower field is considerably broadened, presumably, through both vicinal and allylic coupling, and is assigned to H-6. The sharper, higher field half of the quartet is assigned to H-5.*

The stereochemistry at C-8a and C-10a was determined from the following sequence of reactions. Pyridinium chlorochromate oxidation of the *anti*-alcohol (**18a**), whose complete stereochemistry has been previously established unequivocally,[20] gave the ketone (**18b**), which was then reduced ($LiAlH_4$) to the *syn*-alcohol (**18c**). Birch reduction of this *syn*-alcohol gave (**17**) in quantitative yield which was identical in every respect with the product formed from the Birch reduction of (**6b**).

Birch reduction of the *syn*-alcohol (**6b**) with less than 4 atom equiv. of lithium gave only (**17**) and unreacted (**6b**). No dihydroaromatic intermediates such as (**16b**) could be detected.

Even carrying out the reduction in the absence of the proton source led only to mixtures of (**17**) and unreacted (**6b**). However, the results of this experiment should be treated with caution because the possibility of the presence of adventitious traces of water in the solution,† which would act as a proton source, cannot be excluded. Changing the reducing metal to sodium had no effect on the outcome of the reduction of (**6b**): the exclusive product was again (**17**).

The Birch reduction of the *syn*-acetoxy-derivative (**6d**) was very rapid and required *ca.* 8 atom equiv. of lithium before the ammonia solution turned blue. Perhaps not unexpectedly[2] the sole product was the alcohol (**17**). This reduction was then carried out using only 4 atom equiv. of lithium and omitting the t-butyl alcohol. In the absence of the proton source the reduction was extremely slow, taking some 5 h for the blue colouration of the solution (which immediately formed upon mixing of the reagents) to be discharged. G.l.c.–m.s. and ^1H n.m.r. analysis of the product mixture revealed the presence of the alcohols (**6b**) and (**17**) in the ratio of 2.5:1 respectively. That the alcohol (**6b**) had originated from the Birch reduction of the ester group of (**6d**) and not from a simple ammoniolysis reaction of that group was easily verified by leaving a solution of (**6d**) in liquid ammonia for 5 h. G.l.c. analysis of the material, after removal of the ammonia, revealed the presence of only acetate (**6d**) and no *syn*-alcohol (**6b**).

Birch reduction of the benzenomethanoanthracene (**7a**) has been reported to be so slow that the products could not be obtained in sufficient quantities to secure their identification.[10] In contrast, Birch reduction of the *syn*-alcohol derivative of this hydrocarbon, (**7b**), proceeded as rapidly as the rate of dissolution of the lithium, the blue colouration appearing only after 4 atom

* Molecular models of (**17**) suggest that H-6 should be more coupled than H-5 on the basis of the magnitudes of the dihedral angles between the C-6–H-6 (or C-5–H-5) bond and the C-7–H-7α (*ca.* 90°), C-7–H-7β (*ca.* 30°), and C-10a–H-10a (*ca.* 75°) bonds.

† Considering the scale on which these experiments were carried out (see Experimental section) it is estimated that the presence of only 10 mg of H_2O would be required for the complete reduction of (**6b**) to occur.

equiv. of metal had been consumed. A single product was isolated and high-resolution m.s. revealed that it was formed from the addition of 4 atom equiv. of hydrogen to (**7b**). The structure of the product has been assigned as (**19**) for the following reasons. The ^{1}H n.m.r. spectrum ($CDCl_3$) of the compound exhibited two broad singlets downfield at δ 7.07 (4 H, aromatic) and 5.42 (2 H, vinylic). It is evident, then, that one aromatic ring has survived the reduction and that the other has been reduced to a cyclohexene moiety in which the carbon atoms of the double bond are tertiary. Furthermore the ν_{OH} value of 3 629 cm^{-1} (CCl_4) demonstrates the absence of any intramolecular OH • • • π bonding in the product [*cf.* ν_{OH} 3 586 cm^{-1} for (**7b**)]. Therefore, reduction of the aromatic ring closer to the hydroxy-group must have taken place. That the compound lacked any molecular symmetry was demonstrated by its 16-line ^{13}C n.m.r. spectrum (five ^{13}C nuclei are accidentally isochronous) which also revealed (off-resonance decoupling) the tertiary character of both nonequivalent carbon atoms of the double bond.

The above data indicate that the only likely structures for the product are (**19**) and the three structures symbolised by (**20**), having a *trans*-fused C-8a–C-10a ring junction but differing in the location of the double bond.* Catalytic hydrogenation of the double bond of the product gave a compound whose ^{13}C n.m.r spectrum displayed only 10 lines, thereby indicating that the material must have C_s molecular symmetry.* This result is only consistent if the original product has structure (**19**) because catalytic hydrogenation of (**20**) would give a product still devoid of any molecular symmetry.

As in the case of the *syn*-alcohol (**6b**) attempts to detect less highly reduced compounds by carrying out the reduction of (**7b**) using fewer than 4 atom equiv. of lithium failed: only (**19**) and unreacted (**7b**) could be isolated.

Although Birch reduction of the methanobiphenylene (**8a**) slowly consumed only 2 atom equiv. of lithium to give (**21**),[3a] that of the *syn*-alcohol (**8b**) led to a rapid consumption of 4 atom equiv. of the metal to give the alcohol (**22**). Structural proof of this product rests on its 11-line ^{13}C n.m.r. spectrum (the compound therefore lacks any symmetry), the absence of intramolecular OH • • • π bonding (ν_{OH} 3 630 cm^{-1}), the presence of one disubstituted double bond (^{13}C off-resonance), and the seven-line ^{13}C n.m.r. spectrum of the compound formed from catalytic hydrogenation of (**22**). The latter result eliminates the possibility of a *trans* C-4b–C-8a-fused ring junction for (**22**). Finally the diastereoisomer of (**22**) in which the two rings fused to the cyclobutane ring are disposed *syn* with respect to each other [as opposed to their *anti* relationship in (**22**)] may be ruled out on steric grounds (see footnote †).

Reduction of (**8b**) using less than 4 atom equiv. of lithium gave mixtures containing only (**22**) and unreacted starting material.

It would seem from the above data that the extremely facile over-reduction of the *syn*-alcohols (**6b**)—(**8b**) is probably due to the proximity of the hydroxy-group to the two quaternary carbon atoms of the benzene ring in these molecules which should facilitate protonation of *both* these atoms. This would suggest that the Birch reduction of the *syn*-alcohol (**9**), in which the hydroxy-group is now proximate to only one quaternary site of the aromatic ring, should give a more conventional product, *i.e.* one containing a cyclohexa-1,4-dienyl ring.

Indeed, although Birch reduction of (**9**) proceeded very rapidly only *ca.* 2.1 atom equiv. of lithium were consumed. G.l.c.–m.s. analysis of the reaction mixture revealed the presence of two products of relative proportions 11:1 and having molecular ions of masses 228 and 230 Daltons respectively. Although we were unable to separate the products the following spectral data on the mixture are consistent with the structure of the major component being (**23a**). The ^{13}C n.m.r. spectrum showed the presence of two double bonds, one disubstituted and the other trisubstituted. A cyclohexadienyl ring, as shown in (**23**), is therefore present. The lack of OH • • • π bonding [ν (CCl_4) 3 628 cm^{-1}] eliminates from further consideration structure (**23b**) in which the hydroxy-group would be sufficiently close to the double bond to enter into OH • • • π bonding. The ^{1}H n.m.r. spectrum of the mixture exhibited a broad multiplet centred at δ 4.3 and the integrating for two (non-exchangeable) protons (assuming the vinylic resonances in the spectrum are due to three protons). This signal is attributed to H-2 and H-8a of (**23a**). The strong deshielding of the latter nucleus is a result of its proximity to the hydroxy-group. There is ample precedent for this effect[24] and its manifestation in the present case serves to confirm the stereochemistry of C-8a in (**23a**).

Identification of the minor product of the mixture could not be made owing to lack of material. We assume that it is formed from reduction of the C-7–C-8 double bond of (**23a**).

The ease of Birch reduction of the double bond of the compounds (**10**)—(**13**) was found to be highly dependent on the presence and stereochemical disposition of a hydroxy-group. Thus whereas the alkene (**10a**) and the alcohols (**11b**) and (**12b**) were reduced only with difficulty Birch reduction of the alcohols (**10b**), (**11a**), and (**12a**) proceeded quite briskly. This was particularly so for the reduction of (**10b**) which was so rapid that the ammonia solution did not turn blue until 2 atom equiv. of lithium had been consumed. Surprisingly the bis-*endo*-diol (**13**) was extremely resistant to Birch reduction: even after 45 min no product could be detected.

The stereochemistry of the reduction of the alkenes (**10**)—(**12**) is at present unknown although it could (and will) be determined through labelling experiments.

Competition Kinetic Studies.—Relative rate constants for the Birch reduction of the substrates (**6a—c**) and (**10**)—(**12**) were determined by the competition method[26] and the results are given in Table 1. The experimental procedure involved the g.l.c. analysis of the reaction product resulting from the partial reduction of a mixture of two substrates, s and s′, which had competed for a limited amount of lithium in the presence of a large (ten-fold) excess of t-butyl alcohol.

The k_c' values of Table 1 were obtained using equation (1) where the subscript zero refers to the concentrations of s and s′ at some initial time, t_0. If the rates of reduction of the two competing compounds, s and s′, obey the same rate law then the ratio of the corresponding rate constants, k_c [equation (2)], is equal to k_c'. This situation has been verified experimentally for competitive Birch reductions involving a variety of aromatic compounds and alkenes, such as benzene,[7,27] toluene,[27] anisole,[27] and (**10a**),[27] the rates of reduction of which were found to obey the third-order kinetic expression of equation (3),[7,27] where M is the reducing metal (Li or Na). Thus the k_c values for competitions involving these species are obtained directly from equation (1) (*i.e.* $k_c = k_c'$). It then follows that k_c is a dimensionless quantity and that k_c' is invariant to changes in the concentrations of the compounds appearing in equation (3).

$$k_c' = \frac{\text{Ln}\,([s]/[s]_0)}{\text{Ln}\,([s']/[s']_0)} \quad (1)$$

$$k_c = k_s/k_s' \quad (2)$$

$$-\,ds/dt = k_s[S][M][Bu^tOH] \quad (3)$$

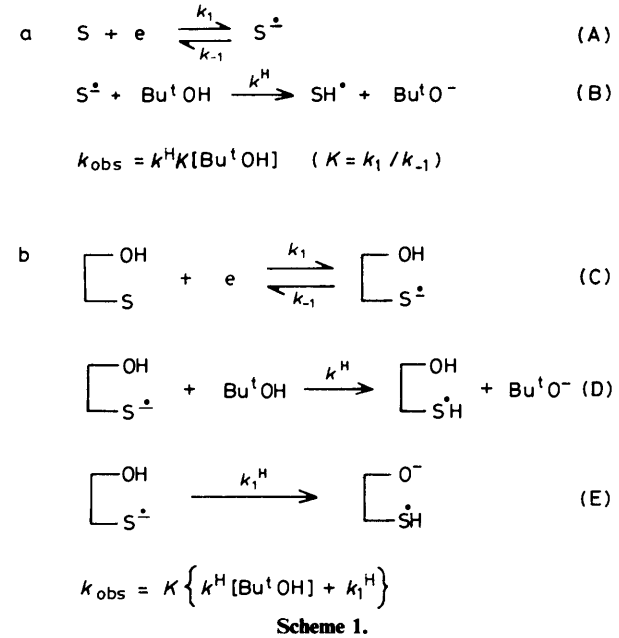
* Two pairs of ^{13}C nuclei are accidentally isochronous.

† The diastereoisomer of (**19**), in which the C-8a–C-10a ring junction is still *cis*-fused but in which the configurations of C-8a and C-10a have been inverted, can be eliminated because molecular models suggest its formation would generate prohibitively large steric congestion between the hydroxy-group and the cyclohexene ring. Also intramolecular OH • • • π bonding would have been observed in such a structure.

Table 1. Relative rate constants for the Birch reduction of some substrates[a]

Entry	Substrate	Competitor	k_c'[b]	k_c[c]	k_{c1}[d]	k_c^n[e]	k_{c1}^n[e]
1	(6a)	(10a)	0.55[f]				
2	(6a)	(10a)	0.57[g]	0.56[l]		1.06[l]	
3	(6b)	(24)	0.24[f,m]	0[n]	0.055	0[n]	6.10×10^3
4	(6c)	(6a)	0.025[f]	0.025		0.027	
5	(10a)	(1)	4.6[h]	4.6		1.89	
6	(10b)	(24)	0.89[f,m]	0[n]	0.203	0[n]	2.3×10^4
7	(11a)	(10a)	4.3[f]				
8	(11a)	(10a)	3.1[g]				
9	(11a)	(10a)	2.6[i]	2.35	0.45	4.43	0.85
10	(11a)	(11b)	8.3[f]	4.51	0.86		
11	(12a)	(12b)	171[f]				
12	(12a)	(12b)	70[g]				
13	(12a)	(12b)	41.7[i]	17.3	35.1	17.3	35.1
14	(12b)	(10a)	0.53[f]	0.53		1.0	
15	toluene	(1)	36[h,j]	36		14.8	
16	(24)	(4)	2.8[k]	2.8		1.11×10^5	
17	lithium benzoate	(4)	2.8[k]	2.8		1.11×10^5	
18	(4)	(1)	9.7×10^4[k]	9.7×10^4			

[a] Substrate and competitor both 6×10^{-3}M. [b] $k_c' = \ln\{[s]/[s]_0\}/\ln[c]/[c]_0)$ where s and c refer to substrate and competitor respectively. [c] Rate constant for third-order reduction (*i.e.* proceeding *via* step B, Scheme 1a) relative to that for the third-order reduction of the specified competitor (uncertainty ±6%). This is a dimensionless quantity. [d] Rate constant for second-order reduction (*i.e.* proceeding *via* step E, Scheme 1b) relative to that for the third-order reduction of the specified competitor. This quantity has dimensions of molarity. [e] Rate constant adjusted relative to (**12b**). k_c^n is dimensionless and k_{c1}^n has dimensions of molarity. [f] [Bu^{t}OH] 0.228M. [g] [Bu^{t}OH] 0.684M. [h] Ref. 25. [i] [Bu^{t}OH] 1.37M. [j] Ref. 3*a*. [k] Ref. 3*b*. [l] Average of entries 1 and 2. [m] Uncertainties of ±25%. [n] Assumed value.



Scheme 1.

We assume that the rates of Birch reduction of all aromatic and alkene substrates considered herein which do not contain a hydroxy-group capable of forming an intramolecular OH • • • π bond, *viz.* (**1**), (**4**), (**6a**), (**6c**), (**10a**), (**11b**), (**12b**), (**24**), and lithium benzoate, obey the rate equation (3). Therefore, $k_c = k_c'$ for competitions involving pairs of these compounds which constitute entries 1, 2, 4, 5, 14—17 of Table 1. Support for this assumption comes from previous studies on competition experiments carried out between the substrates (**10a**),[27] (**24**),[3b] and toluene.[27] That the reduction of (**6a**) also obeys the rate equation (3) is demonstrated by the observed invariance of k_c' for the competition between (**6a**) and (**10a**) to tripling the concentration of t-butyl alcohol (entries 1 *and* 2). Also g.l.c. analysis of quenched aliquot portions taken at various times during the course of the competitive reduction yielded the same k_c' value within experimental error. These observations demand that the reductions of both (**6a**) and (**10a**) (whose rate expression is known [27]) have identical kinetic orders with respect to M and Bu^{t}OH.

Mechanistic considerations led us to believe that the kinetic expression for Birch reduction of substrates containing hydroxy-groups that are known to be intramolecularly OH • • • π-bonded, such as the alcohols (**6b**),[20] (**10b**),[22] (**11a**),[28] and (**12a**),[29] could be more complicated than that given by equation (3).

The first two steps of the accepted mechanism [7] for the Birch reduction of simple substrates are given in Scheme 1a. These steps, which are consistent with the third-order kinetic expression of equation (3), result in the observed rate constant, k_s, being represented as a product of two quantities, *i.e.* equation (4) where K is the equilibrium constant for the formation of the anion radical and k^H is the second-order rate constant for the (intermolecular) protonation of that species.

$$k_s = Kk^H \quad (4)$$

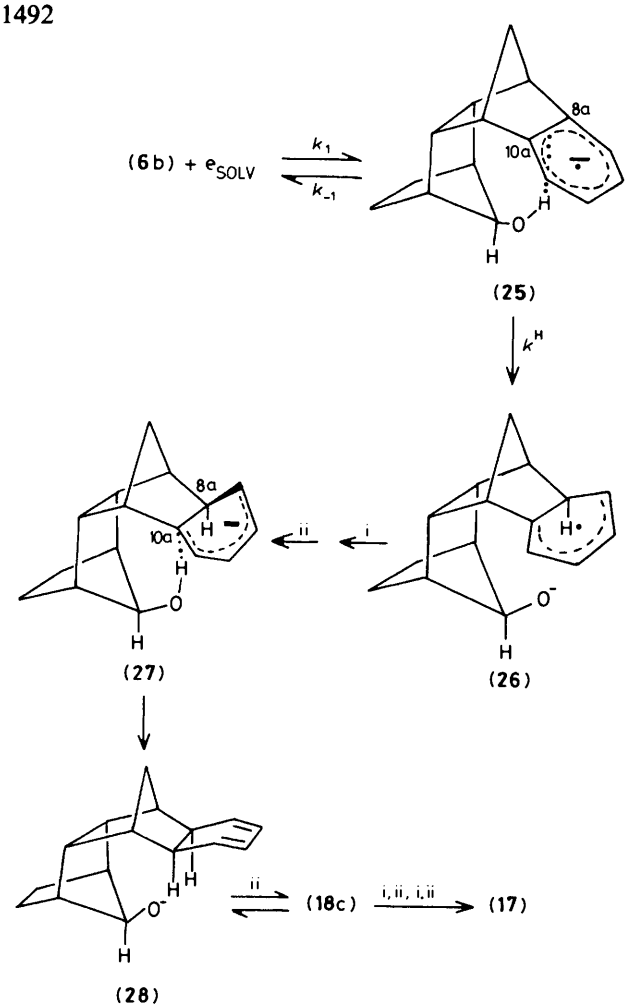
However, for the reduction of substrates exhibiting intramolecular OH • • • π bonding (Scheme 1b), protonation of the anion-radical intermediate can occur either intermolecularly (step D) or intramolecularly (step E). The overall rate of reduction of the alcohol is then given by equation (5) where equations (6) and (7) hold. If the concentration of the t-butyl alcohol proton source is held constant then it is easily demonstrated that, for a competition between two substrates, s and s′, whose rates of reduction obey respectively the kinetic expressions of equations (3) and (5), then equation (8) applies where $k_c = k_s/k_s'$ and $k_{c1} = k_{s1}/k_s'$ and k_c' is defined by equation (1). Note that, whereas k_c is dimensionless, k_{c1} has the dimensions of molarity, *i.e.* it is an effective molarity.[30]

$$-\mathrm{d}s/\mathrm{d}t = k_{s1}[M][S] + k_s[M][S][Bu^tOH] \quad (5)$$

$$k_s = Kk^H \quad (6)$$

$$k_{s1} = Kk_1^H \quad (7)$$

$$k_c' = k_c + k_{c1}/[Bu^tOH] \quad (8)$$



Scheme 2. *Reagents:* i, e $_{solv.}$; ii, Bu^{t}OH

The k_c and k_{c1} values of Table 1 for Birch reduction of the alcohols (**11a**) and (**12a**), relative to the specified competitors, were obtained by carrying out three competition experiments for each pair of substrates using different concentrations of t-butyl alcohol and applying the data to equation (8). In both cases the correlation between the data using equation (8) was good: r = 0.995 for (**11a**) *versus* (**10a**) (entries 7—9), and 0.999 for (**12a**) *versus* (**12b**) (entries 11—13). k_c and k_{c1} for (**11a**), relative to (**11b**), were calculated from the data of entry 9 and the k_c' value of entry 10.

Unfortunately, reliable values of k_c and k_{c1} for (**6b**) and (**10b**), both relative to (**24**), could not be obtained because these substrates are reduced so rapidly that their rates of reduction probably greatly exceed the rates of their mixing with the lithium–ammonia solution. The competition method is probably unreliable in this situation because product distribution is now dependent on both the reactivities of the substrates and their statistical availability.[26] Indeed we found a considerable variation of 25% in k_c' by changing the rate of addition of the substrates to the lithium in ammonia or by changing the mode of addition, *i.e.*, by adding the lithium–ammonia solution to the substrate.

Notwithstanding this problem of measurement we believe that the reduction of both *syn*-alcohols (**6b**) and (**10b**) proceeds exclusively *via* the intramolecular protonation pathway (Scheme 1b, path E) for two reasons. First, the extent of the contribution made by the intramolecular protonation route is found to increase with overall increasing reactivity of the substrate towards Birch reduction. Thus, using 0.228M-t-butyl alcohol, 46% of the reduction of the alcohol (**11a**) proceeds *via* the intramolecular pathway* whereas for the more reactive 5-norbornenol (**12a**) this route now constitutes 90% of the reduction.* The considerably greater reactivity of the *syn*-alcohols (**6b**) and (**10b**), compared with (**12a**), therefore implies the overwhelming preference of Birch reduction of the former two alcohols to take the intramolecular path. Secondly, the observed stereoselectivity of Birch reduction of (**6b**) is entirely consistent with the *syn*-hydroxy-group in the anion-radical of this species directing the protonation reaction.

The k_c^n and k_{c1}^n values of Table 1 are the rate constants for Birch reduction of the substrates adjusted relative to the *exo*-5-norbornenol (**12b**). This compound is a useful reference because its rate of reduction includes *all* effects of the hydroxy-group (*e.g.* inductive) except those due to intramolecular OH • • • π bonding. Since it is most likely that Birch reduction of (**12b**) follows third-order kinetics then k_{c1}^n has dimensions of molarity.

Since the k_{c1} (and k_{c1}^n) values for Birch reduction of the intramolecularly OH • • • π-bonded alcohols (**6b**), (**10b**), (**11b**), and (**12a**) involve the rate of intramolecular protonation of the anion-radical intermediate (step E of Scheme 1) relative to a substrate whose anion suffers exclusive intermolecular protonation, they shall henceforth be referred to as effective molarities (EM).[30] In the context of the present work the EM may be defined as the concentration of the t-butyl alcohol proton source required to make the Birch reduction of a substrate involving intermolecular protonation of its anion-radical proceed at the observed rate of that involving intramolecular protonation of the anion-radical.

Discussion

The product and rate data for Birch reduction of the aromatic *syn*-alcohols (**6b**)—(**8b**) and (**9**) convincingly demonstrate how the reductive behaviour of an *o*-xylene moiety can be dramatically modified by the presence of a spatially proximate hydroxy-group. Thus whereas the unperturbed *o*-xylene groups in the hydrocarbons (**6a**)—(**8a**) and the *syn*-methoxy-derivative (**6c**) display normal behaviour in their reduction in that they reluctantly take up only two equivalents of protons to form the cyclohexa-1,4-dienyl ring, in accordance with rules (i) and (ii) above, those in the *syn-alcohols* (**6b**)—(**8b**) are rapidly reduced, consuming four equivalents of protons, to form products containing the cyclohexene ring, *viz.* (**17**), (**19**), and (**22**), respectively. The reduction of (**7b**) is particularly impressive since, of the two *o*-xylene moieties present in the molecule, only that which is closer to the hydroxy-group undergoes reduction.

Just how rapid the reduction of the alcohols (**6b**)—(**8b**) and (**9**) are can be gauged from the EM values for Birch reduction of (**6b**): 5.8 × 10^{3}M relative to the hydrocarbon (**6a**), 4.1 × 10^{2}M relative to toluene, and 5.4 × 10^{3}M relative to xylene (assuming that *o*-xylene is 13 times less reactive than toluene[7]). Equally impressive is the EM value of 0.06M for the reduction of (**6b**) relative to lithium benzoate which is the most rapidly Birch-reduced substrate so far measured.[3b]

We attribute the extremely facile Birch reduction of the *syn*-alcohols (**6b**)—(**8b**) to the ability of the hydroxy-group to act as a very efficient intramolecular proton source by virtue of its proximity to the aromatic ring in each of these substrates. This proposal is supported by two observations. First, the large EM value of 2.3 × 10^{5}M for Birch reduction of (**6b**) relative to the *syn*-methoxy-derivative (**6c**) reveals that the proton, and not the oxygen atom, of the hydroxy-group is responsible for the

* This was calculated from the equation: % intramolecular pathway = $\frac{k_{c1}}{k_{c1} + k_c[\text{Bu}^t\text{OH}]} \times 100$

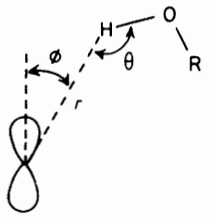
observed rate enhancements. Secondly, protonation of the quaternary aromatic carbon atoms occurs stereoselectively *syn* to the hydroxy-group in the alcohols (**6b**)—(**8b**).

A plausible mechanism for Birch reduction of the *syn*-alcohols (**6b**)—(**8b**), which satisfactorily accounts for their atypical behaviour, is shown in Scheme 2, using as an example the reduction of (**6b**). Addition of a solvated electron to the neutral substrate leads to the (reversible) formation of the anion-radical (**25**). This species is expected to be strongly intramolecularly OH • • • π bonded, with the OH bond vector bisecting the C-8a–C-10a bond because of the similar behaviour of the neutral precursor (**6b**).[20] The OH • • • π and O–H bonds should be respectively much stronger and weaker in (**25**) than in (**6b**) as a result of increased electrostatic interactions in the former species. This factor, together with the structurally enforced proximity of the (O)H atom to both C-8a and C-10a atoms* and the near collinearity of the O–H and the (O)H • • • C-8a (or C-10a) bond vectors in (**25**) should make intramolecular protonation of, say, C-8a by the OH group, to give (**26**), more favourable than the usually observed kinetic preference[2,32] for intermolecular C-8 protonation in substrates not containing a suitably located OH group such as (**6a**)—(**8a**). Rapid electron capture by (**26**), followed by protonation of the alkoxide group by t-butyl alcohol, gives the carbanion (**27**) which, by dint of strong intramolecular OH • • • π bonding, should suffer facile intramolecular protonation at C-10a to form (**28**), the conjugate base of (**18c**). The diene (**18c**) would then undergo rapid reduction to yield the observed product (**17**).

This mechanism is supported by the following observations: (i), the observed stereochemistry of the products (**17**), (**19**), and (**22**) is readily accounted for by the mechanism. (ii), The intermediacy of the diene (**18c**) in the reduction of (**6b**) is strongly implicated on the grounds that it was found to be readily Birch reduced to give exclusively (**17**). Also a competitive Birch reduction carried out between (**6b**) and (**18c**) led to the complete consumption of the latter compound and to the formation of only (**17**), together with unchanged (**6b**). The much greater reactivity of (**18c**) compared with (**6b**) readily explains why the reduction of (**6b**) using less than 4 atom equiv. of lithium gave only (**17**) and unchanged starting material but no dienes. (iii), The mechanism predicts second-order kinetic behaviour assuming that the protonation of (**25**) is rate determining and that the steady-state approximation holds for all intermediates. Extrapolation of the kinetic data for Birch reduction of (**11a**) and (**12a**) does indeed suggest second-order kinetic behaviour for Birch reduction of (**6b**)—(**8b**).

The Birch reduction of the *syn*-alcohol (**9**) is also consistent with the proposed mechanism. In this molecule the hydroxy-group is proximate only to C-8a and is certainly too far removed from C-10a to affect the reactivity at this site. Birch reduction of (**9**) should therefore proceed according to the first four steps of Scheme 1, to give the carbanion (**29**) but, unlike the related carbanions resulting from Birch reduction of (**6b**)—(**8b**), such as (**27**), it cannot undergo intramolecular protonation at C-10a to form eventually a monoene akin to (**17**). Instead it now follows the course of normal Birch reduction, *viz.*, kinetically favoured protonation at C-6[2,32] to give the unconjugated diene (**23a**).

The reason why Birch reduction of the *syn*-acetate (**6d**) readily gives (**17**) in the presence of t-butyl alcohol yet yields mainly the alcohol (**6b**) and only small amounts of (**17**) in the absence of added proton source is due to the difference in the acidity of the reaction medium in the two cases. Reductive cleavage of the acetoxy-group in (**6d**) generates the alkoxide (**6b**; $R^1 = O^-$). t-Butyl alcohol, but not ammonia, is sufficiently acidic to protonate extensively this alkoxide to give alcohol (**6d**) which then undergoes further reduction. In the absence of added proton source further reduction is greatly retarded owing to the low acidity of ammonia.



Substrate	r/Å	θ(°)	φ(°)
(11a)	2·5	107	20
(12a)	2·2	121	12
(10b)	1·8	171	15

Geometrical parameters r, θ, and φ, which largely determine the strength of an OH . . . π bond and their estimated values for (**10b**), (**11a**), and (**12a**)

Other examples in which a spatially proximate hydroxy-group influences the Birch reduction of an aromatic ring have been noted and explanations of the observations advanced.[12,14] In light of our results we suggest consideration of the following slight modifications to those explanations. Thus the observed regioselectivity of the reduction of a 1-arylcamphenilol, generated *in situ*, is more likely determined through intramolecular protonation of C-3 of the aromatic anion-radical instead of the cyclohexadienyl anion as was proposed.[12] The unusually high reactivity of Fujita's podocarpatrienols[14] [compounds (**12**) and (**13**) in that paper] is again more likely due to the influence of the hydroxy-group on the aromatic anion, rather than on the cyclohexadienyl anion,[14] because the formation and the subsequent protonation of the former species both influence the rate of reduction (see Schemes 1 and 2) whereas the latter ion, generated after the rate-determining step, cannot affect the reaction rate.

Birch reduction of double bonds is also markedly influenced by suitably located hydroxy-groups, the most dramatic example being provided by (**6b**). This compound presumably is Birch reduced exclusively *via* the intramolecular protonations pathway, the EM for the reaction being 1.2×10^4M, relative to (**10a**), and 0.2M relative to lithium benzoate!

The results for the remaining two intramolecularly OH • • • π-bonded alcohols, (**11a**) and (**12a**) are less impressive but the following trends are noteworthy.

1. Birch reduction proceeding *via* intramolecular protonation by a hydroxy-group increases in importance along the series (**11a**), (**12a**), and (**10b**). For example the percentage of the reaction proceeding through this route for the reduction of (**11a**), (**12a**), and (**10b**), using 0.23M-t-butyl alcohol is 46, 90, and 100%, respectively.†

2. From the k_c^n values for (**11a**) and (**12a**) it may be concluded that the presence of intramolecular OH • • • π bonding accelerates Birch reduction proceeding *via* the *intermolecular* protonation route. For this pathway (**12a**) is some four times more reactive than (**11a**).

3. For the intramolecular protonation route the EM values increase very steeply along the series (**11a**), (**12a**), and (**10a**).

These trends can be understood in terms of the dependence of the strength of the intramolecular OH • • • π bond on the geometrical relationship between the hydroxy-group and the double bond (or aromatic ring for that matter) and how that OH • • • π bond influences both the formation of the anion radical intermediate and its subsequent protonation.

* The crystal structure of the *p*-nitrobenzoate derivative of (**10b**) gives the (C-9)–O–C-6 distance at *ca.* 2.8 Å.[31]

† See footnote *, p. 1492, for the equation used to calculate these data.

From equation (4) it can be seen that intramolecular OH • • • π bonding can accelerate the rate of Birch reduction in two ways. First, the presence of such bonding should stabilize the anion-radical more than the neutral precursor, through increased electrostatic interactions in the former species, and this will be manifested in an increased value of the equilibrium constant, K, for the formation of the anion-radical. Consequently this effect will even lead to accelerated rates of Birch reduction of substrates proceeding *via* the intermolecular protonation pathway, *viz.* path D, Scheme 1b. The enhanced k_c^n values for (**11a**) and (**12a**) support this view. Secondly, subject to geometric constraints, k^H for intramolecular protonation should be favoured over the corresponding intermolecular process on entropic, and possibly also energetic, grounds. The EM values (k_{c1}^n) for (**11a**), (**12a**), and (**10b**) convincingly verify this statement.

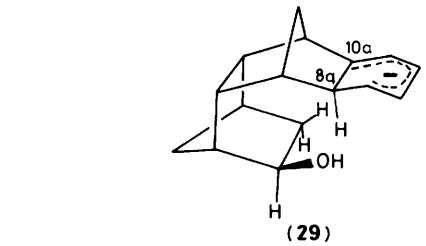
We suggest that the magnitude of the enhanced rate of Birch reduction depends on the strength, and therefore the geometry, of the OH • • • π bond. The three most important geometrical parameters in this respect are: (i), r, the (O)H • • • C(π) distance, (ii), θ, the O–H • • • C(π) angle, and (iii), φ, the angle between the (O)H • • • C(π) vector and the p orbital of the C(π) atom to which the O–H bond is pointing. These parameters are shown in the Figure.

The results of *ab initio* calculations on the water–ethene complex reveal[33] that the strongest OH • • • π bond results when θ = 180 and φ = 0°. This is to be expected because angular orbital overlap between the fragments is maximised for this configuration. It is also reasonable to expect that this configuration is also optimal for intramolecular proton transfer from O to C(π) in the corresponding anion-radical of the complex and that this process is further facilitated by a small value of r.

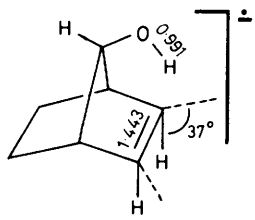
Approximate values of r, θ, and φ for (**10b**), (**11a**), and (**12a**) are given in the Figure and are based on the crystal structure of the *p*-nitrobenzoate derivative of (**10b**),[31] the STO-3G optimised structure of (**11a**),[34] and a partially optimised STO-3G structure, together with molecular models, of (**12a**).[35] The trends in these values indicate stronger OH • • • π bonding along the series (**11a**), (**12a**), and (**10b**) since r progressively diminishes, θ tends towards 180°, and φ [with the exception of (**12a**)] decreases. *If we assume that these trends are repeated in the corresponding anion-radicals* then the observation discussed in points 1—3 above are readily explained.

We propose that the required values of r, θ, and φ for a substrate to undergo Birch reduction predominantly *via* the intramolecular protonation path should resemble those for (**12a**). In particular, r should be smaller than 2.2 Å but with less stringent requirements for θ (greater than *ca.* 110°) and φ (less than *ca.* 20°). A cautionary note is sounded to the effect that the geometry of an anion-radical, which is the important species, does not necessarily resemble that of the neutral precursor. Notwithstanding this caveat molecular models suggest that the above criteria are reasonably well met, particularly with respect to r, for a variety of substrates which have been claimed to undergo Birch reduction *via* intramolecular hydroxy-group participation.[12-18]

The contrasting behaviour of the alcohols (**5**) and (**13**) towards Birch reduction is noteworthy. Although the values of r (*ca.* 1.7—2.0 Å), θ (*ca.* 180°), and φ (*ca.* 10°) for both compounds are optimal for the occurrence of intramolecular protonation of the corresponding anion-radicals, only (**5**) displays any evidence of an enhanced rate of reduction;[18] alcohol (**13**) is virtually inert to Birch reduction! However, it is probable that the hydroxy-groups in (**13**) are hydrogen bonded to each other and are therefore unavailable for OH • • • π bonding. This is supported by the persistence of a very intense, fairly broad, band at *ca.* 3 300 cm^{-1} in the i.r. spectrum of (**13**) even in very dilute solutions in CCl_4.*



(**29**)



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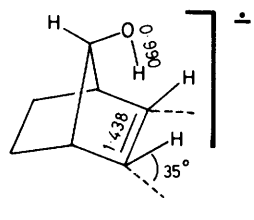
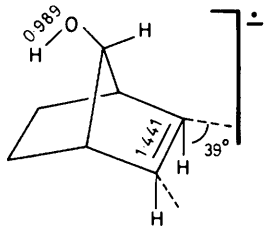
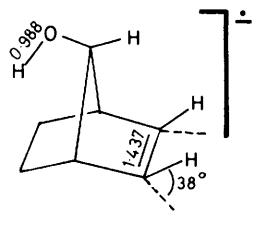


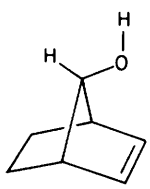
exo -(**30**)



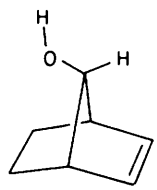
endo -(**31**)



exo -(**31**)



(**32**) anion radical
(**34**) uncharged

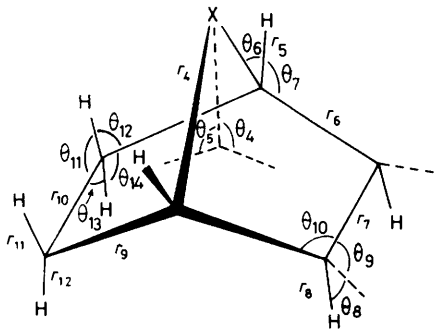


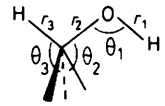
(**33**) anion radical
(**35**) uncharged

In order to gain a more detailed account of intramolecular OH • • • π bonding in anion-radicals full geometry optimisations of the anion-radicals of *syn*-7-hydroxynorbornene (**30**), and the corresponding *anti* isomer (**31**), were carried out using the UHF procedure and the STO-3G basis set and the GAUSSIAN 80 suite of programs.[36] To reduce the computing time C_s symmetry constraint was imposed on all geometries. The conformation of the hydroxy-group was staggered with respect to the C-1–C-7 and C-4–C-7 bonds as shown in (**30**) and (**31**). All optimised parameters and total energies are given in the Appendix. The choice of (**30**) and (**31**) for calculation was made because an STO-3G study on OH • • • π bonding in the corresponding neutral compounds (**11a** and **b**) has been reported.[34]

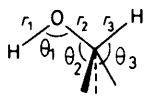
As in the case of the norbornene anion radical,[25] (**30**) and (**31**) each are predicted to have two stable geometries distinguished by the direction of bending of the olefinic C–H bonds, either *endo*, *viz.* *endo*-(**30**) and *endo*-(**31**), or *exo*, *viz.* *exo*-

* The actual conformation of (**13**) is most likely that in which the hydroxymethyl groups are rotated so that the hydroxy-groups are directed away from the *endo*-cavity of the ring. This would have the effect of minimising steric congestion and maximising OH • • • O bonding.





(36) a; X =



b; X =

(30) and *exo*-(31). The origin of the pyramidalization of alkenes[37] and their anion-radicals[25,38] has been discussed elsewhere. Interestingly the amount of out-of-plane *endo*- and *exo*-bending for (30) and (31) is comparable with that calculated for norbornene anion radical (*ca.* 39 and 38°, respectively)[25] and so the hydroxy-group, even in the OH • • • π bonding conformation, has little effect on this distortion.

For (30), (31), and the anion-radical of norbornene, the *endo*-isomer of each is preferred over the *exo*-isomer by 24.5, 14.6, and 18.3[25] kJ mol^{-1}, respectively.

A measure of the strength of the OH • • • π bond in (30) is provided by the energy of (30) relative to the *anti*-isomer (31),[34] a negative value implying stabilization. The values are −27.1 and −17.1 kJ mol^{-1} for *endo*- and *exo*-(30) respectively and are much larger than the OH • • • π bond energy of −7.0 kJ mol^{-1} calculated for the corresponding neutral precursor, (11a) relative to (11b).[34] This result nicely supports the qualitative prediction made earlier that OH • • • π bonding is much stronger in the anion-radical than in the corresponding neutral precursor.

The O–H and C=C bonds in both isomers of (30) are longer than the corresponding bonds in *endo*- and *exo*-(31) by *ca.* 0.003 and 0.002 Å, respectively. This result is, of course, entirely consistent with the presence of OH • • • π bonding in *endo*- and *exo*-(30), the resulting charge transfer from C=C to O–H causing a weakening of both bonds. However, although OH • • • π bonding in (11a) is some four times weaker than in (30) the same increments in the O–H and C=C bond lengths were calculated for (11a),[34] relative to (11b), as those for (30). Clearly, the strength of a hydrogen bond is not necessarily commensurate with the degree of bond length changes occurring in the donor and acceptor fragments.

That OH • • • π bonding is stronger in *endo*-(30) than in the *exo*-isomer (by 10 kJ mol^{-1}) is most likely due to the presence of improved OH • • • π orbital overlap and enhanced electrostatic interactions in the former isomer which are brought about by the large distortion of the π and π* MOs in the *exo*-direction.

Rotation of the hydroxy-group in *endo*- and *exo*-(30) by 180° leads to (32), the *endo*- and *exo*-forms of which lie respectively 64.8 and 51.4 kJ mol^{-1} higher in energy than the corresponding isomers of (30). These energy differences represent upper bounds because the geometries of *endo*- and *exo*-(32) were not optimised but were derived from those of (30) through rigid rotation of the hydroxy-group. The higher energy of both *endo*- and *exo*-(32), relative to the corresponding isomers of (30), is due to the replacement of a stabilizing OH • • • π bond with destabilizing oxygen lone pair–π repulsions and a torsional interaction which is probably only *ca.* 5 kJ mol^{-1} [34] and therefore relatively unimportant.

The magnitude of the oxygen lone pair–π repulsion energy in (32), which is taken as the energy difference between (32) and (33),[34] is calculated to be 20.0 and 15.1 kJ mol^{-1} for *endo*- and *exo*-(32), respectively. These values are considerably larger than that estimated (5 kJ mol^{-1} [34]) for the uncharged analogue (34), relative to (35), and is obviously due to the presence of the negative charge in (32).

This effect, *i.e.* increased oxygen lone pair–π repulsions upon anion-radical formation, is probably responsible, at least in part, for the observed 40-fold reduction in the rate of Birch reduction of the *syn*-methoxy compound (6c) relative to the unsubstituted analogue (6a) (entry 4, Table 1). Steric factors would force the methoxy-group in (6c) to adopt a conformation, similar to that shown by the hydroxy-group in (32), in which an oxygen non-bonding orbital is directed towards the aromatic ring. The anion-radical from (6c) should therefore be considerably destabilized relative to that from (6a).

From the data of Table 1 (entries 5, 7, 10, and 14) it is calculated that the rates of Birch reduction of (11b) and (12b) show comparable enhancements of respectively 2.40 and 2.44 both relative to norbornene. These enhancements are most likely caused by the inductive effect of the hydroxy-group which should stabilize the anion-radical, thereby leading to an increase in the value of K of equation (4). The magnitude of this inductive stabilization may be estimated from the energy change for the model reaction (9) which is calculated (STO-3G) to be −22.3 and −26.0 kJ mol^{-1} for the *endo*- and *exo*-isomer respectively.* The related reaction (10) involving the OH • • • π-bonded conformation of (11a) is even more exothermic, −42.3 and −36.1 kJ mol^{-1} for the *endo*- and *exo*-isomer respectively, as a consequence of hydrogen bonding.

$$(1)^- + (11b) \longrightarrow (1) + (31) \quad (9)$$

$$(1)^- + (11a) \longrightarrow (1) + (30) \quad (10)$$

That the observed rate enhancements for Birch reduction of (11) and (12), proceeding *via* the intermolecular protonation route, are only modest in comparison with the large calculated exothermicities for the above reactions might seem surprising. However it should be realised from equation (4) that the observed rate constant could very well be only modestly enhanced because stabilization of the anion-radical by inductive and hydrogen-bonding effects of the hydroxy-group will, in general, lead to an *increase* in K but to a corresponding *decrease* in k^H for intermolecular protonation. For Birch reduction of OH • • • π-bonded alcohols proceeding *via* intramolecular protonation of their anion-radicals the observed enhancements are larger because k^H is no longer as sensitive to the actual stability of the anion-radical as it is to geometric factors and to the ease of O–H bond scission.

Conclusions

The following important points emerge from this study.

1. The presence of intramolecular OH • • • π bonding can markedly influence the regio- and stereo-chemistry and the rate of Birch reduction of aromatic rings and double bonds.

2. The reduction of such substrates can proceed according to either second-order or third-order kinetics, with the former corresponding to intramolecular protonation of the anion-

* STO-3G energies were calculated for the reported optimised geometries for (1), *endo*- and *exo*-(1)$^-$, and (11b).[25,34,39]

radical and the latter to the corresponding intermolecular process.

3. Both intra- and inter-molecular paths show rate enhancements due to OH • • • π bonding although the former are much more dramatically affected.

4. The degree by which Birch reduction proceeds *via* the intramolecular protonation route depends critically on the geometry of the O–H • • • π moiety as defined by r, θ, and φ in the Figure. The predicted values for substantial occurrence of intramolecular protonation are: $r < 2.2$ Å, $\theta > 110°$, and $\varphi < 20°$.

5. The results of model *ab initio* calculations indicate that intramolecular OH • • • π bonds are much stronger, by *ca.* 20 kJ mol^{-1}, in anion-radicals than in the uncharged analogues. Indeed it seems that OH • • • π bonds in anion-radicals are as strong as those in uncharged OH • • • O systems.[40]

6. Model calculations also suggest that oxygen lone pair–π repulsions are much stronger, by *ca.* 15 kJ mol^{-1}, in anion-radicals than in the uncharged precursors.

7. Conclusions 5 and 6 imply that anion-radicals of unsaturated substrates containing either hydroxy-groups or other groups having lone pairs of electrons proximate to the π system will be subject to much stronger conformational requirements than the uncharged analogues.

Finally we draw attention to the possibility of promoting hydroxy-group-assisted Birch reductions of substrates devoid of such a group in template-directed reactions. For example cyclodextrins,[41] flush with OH groups, and able to bind aromatic substrates into their cavities, could profoundly affect the regiochemistry and the rates of Birch reduction of aromatic systems.

Note added in proof: The ranges of values for r and θ for O to C proton transfer found in this study are in remarkable agreement with those reported recently by Menger [42] for C to O proton transfer in base-catalysed elimination reactions: $r \leqslant 2.2$ Å, $\theta > 106°$! This excellent agreement between the conclusions derived from the results of two entirely different reactions strongly suggests that proton-transfer reactions in general are *not* required to proceed *via* linear X–H • • • Y transition states as is commonly believed.[43]

Experimental

General.—M.p.s are uncorrected and were recorded on an electrothermal m.p. apparatus in capillary tubes. B.p.s are also uncorrected.

^{1}H N.m.r. specra were run at 60 MHz on a JEOL model PMX-60 spectrometer; deuteriochloroform was used as a solvent with tetramethylsilane employed as the internal standard. Chemical shifts are reported relative to $SiMe_4$. ^{13}C N.m.r. spectra were obtained on a JEOL PS 100 instrument operating at 25.15 MHz in the pulse Fourier mode. Deuteriochloroform was employed as the solvent and internal lock with chemical shifts being measured relative to $SiMe_4$.

I.r. spectra were run on a Perkin-Elmer model 621 spectrometer in 1 mm cells using CCl_4 as a solvent.

G.l.c. analyses were performed on a Shimadzu model GC-RIA attached to a microprocessor model RPR-G1. All g.l.c. peak areas were obtained electronically using the microprocessor. The following columns were employed in the analytical, preparative, and the g.l.c.–m.s. phases of the work, the flow rates being 35 ml min^{-1} unless otherwise stated: A, 25 m by 0.2 mm containing 100% OV-101 on vitreous silica; B, 25 m by 0.2 mm containing 100% SE-30 on vitreous silica.

Mass spectra were measured on an A.E.I. MS902–Pye 105 g.l.c.–m.s. system operating at 75 eV.

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

(1β,4β,4aα,9α,9aα,10α)-syn-11-*Acetoxy*-1,2,3,4,4a,9,9a,10-*octahydro*-1,4:9,10-*dimethanoanthracene* (**6d**).—A mixture of the *syn*-alcohol (**6b**)[20] (2.5 g), acetic anhydride (3.0 g), and dry pyridine (3.0 g) was heated on a steam-bath under nitrogen for 2 h. The mixture was poured into ice–water (50 g) and extracted with dichloromethane (3 × 50 ml). The combined CH_2Cl_2 extracts were washed with H_2SO_4 (10 ml, 1M), saturated aqueous $NaHCO_3$ (10 ml), dried (Na_2SO_4), and evaporated. The solid was recrystallized from light petroleum to give the syn-*acetoxy derivative* (**6d**) (2.75 g, 94%), m.p. 112—113 °C (Found: M^+, 268.1466. $C_{18}H_{20}O_2$ requires M, 268.1463). The purity of the compound was judged to be >99.8% by g.l.c. analysis (column A; 150—210 °C), $\tilde{\nu}_{max.}$ 1 572s (C=O) cm^{-1}; $\delta_H(CDCl_3)$ 1.13 (2 H, dd, H-2, -3), 1.40 (3 H, s, CH_3), 1.70 (4 H, m, H-2, -3, -12), 2.15 (2 H, m, H-1, -4), 2.50 (2 H, m, H-9a, -4a), 3.30 (2 H, m, H-9, -10), 4.07br (1 H, s, H-11), and 7.00 (4 H, m, aromatic).

(1β,4β,4aα,9α,9aα,10α)-1,2,3,4,4a,9,9a,10-*Octahydro*-syn-11-*methoxy*-1,4:9,10-*dimethanoanthracene* (**6c**).—To a stirred suspension of sodium hydride (1.0 g), freed from mineral oil, in dioxane (20 ml) was added slowly a solution of the *syn*-alcohol (**6b**)[20] (0.85 g) in dioxane (15 ml). The resulting mixture was refluxed under nitrogen for 18 h. Methyl iodide (5.0 g) was added to the cooled solution which was then refluxed for 6 h. The mixture was cooled to 0 °C, treated with ice–water, and extracted with petroleum spirit (4 × 50 ml). The combined extracts were washed with water (2 × 50 ml), dried (Na_2SO_4), and evaporated under reduced pressure. The solid was recrystallized from light petroleum to give (**6c**) (0.87 g, 87%), m.p. 106—108 °C (Found: M^+, 240.1511; $C_{17}H_{20}O$ requires M, 240.1514). The compound was >99.9% pure by g.l.c. (column A; 150—230 °C), $\delta_H(CDCl_3)$ 0.87—2.03 (8 H, m, H-1, -2, -3, -4, -12), 2.40 (3 H, s, OCH_3), 2.48 (2 H, m, H-4a, -9a), 2.88br (1 H, s, H-11), 3.33 (2 H, m, H-9, -10), and 7.03 (4 H, m, aromatic.).

(1α,4α,4aα,9α,9aα,10α)-1,2,3,4,4a,9,9a,10-*Octahydro*-1,4:9,10-*dimethanoanthracen*-syn-11-*ol* (**9**).—To a stirred solution of (**14**)[23] (0.25 g, 1.15 mmol) in THF (10 ml) was added slowly diborane (1M, 3.45 ml, 3.45 mmol) in THF under nitrogen. The resulting mixture was stirred at 50 °C for 1 h. The cooled solution was treated with NaOH (3 ml) and H_2O_2 (3 ml, 33%) and then heated for 1 h at 50 °C. The ether phase was separated and the aqueous phase was saturated with NaCl and extracted with ether (3 × 50 ml). The combined ether extracts were washed with saturated NaCl (25 ml), dried (Na_2SO_4), and evaporated to give the *exo*-alcohol (**15a**) (0.25 g, 74%), $\nu_{max.}(CCl_4)$ 3 617s (OH) cm^{-1}.

The crude *exo*-alcohol (**15a**) (0.25 g, 1.10 mmol) was added in one portion to a magnetically stirred suspension of pyridinium chlorochromate[44] (0.59 g, 2.74 mmol) in dry dichloromethane (5 ml). The mixture was stirred for 2.5 h, after which time ether (100 ml) was added and the black solid triturated. The ether was decanted from the black residue. The residue was further triturated with ether (4 × 25 ml). The combined ether extracts were passed through a small column of alumina and then evaporated under reduced pressure to give the ketone (**15b**) (0.23 g, 93%), $\nu_{max.}(CCl_4)$ 1 754s (C=O) cm^{-1}.

The crude ketone (**15b**) (0.17 g, 0.75 mmol) was added to a magnetically stirred slurry of $LiAlH_4$ (0.06 g, 1.58 mmol) in anhydrous ether (10 ml) under nitrogen. The resulting mixture was refluxed for 2 h, after which time the excess of $LiAlH_4$ was destroyed through the cautious addition of saturated aqueous sodium sulphate. The ether layer was separated and washed with water, dried (Na_2SO_4), and evaporated. The residue was recrystallized from light petroleum to give (**9**) (0.18 g, 76%), m.p. 75—77 °C (Found: M^+, 226.1355. $C_{16}H_{18}O$ requires M, 226.1358). The purity of (**9**) was >99.8% by g.l.c. (column A; 135—230 °C), $\tilde{\nu}_{max.}(CCl_4)$ 3 567s (OH) cm^{-1}; $\delta_H(CDCl_3)$ 0.07—

0.46 (1 H, dd, H-3 *syn*), 0.70 (1 H, d, *J* 12.0 Hz, OH, D_2O exchange), 1.27—1.57 (3 H, m, H-3-*endo*, -12), 2.02 (2 H, m, H-11), 2.27 (2 H, m, H-1, -4), 2.87 (2 H, m, H-4a, -9a), 3.30 (2 H, m, H-9, -10), 3.75br (1 H, m, H-2), and 7.15 (4 H, m, aromatic).

(1β,4β,4aα,8aβ,9α,9aα,10α,10aβ)-1,2,3,4,4a,8a,9,9a,10,10a-*Decahydro*-1,4:9,10-*dimethanoanthracen*-syn-11-*ol* (**18c**).—To a magnetically stirred suspension of pyridinium chlorochromate[44] (2.5 g, 11.5 mmol) in dichloromethane (25 ml) was added, in one portion, a solution of the *anti*-alcohol (**18a**)[20] (1.0 g, 4.38 mmol) in dichloromethane (10 ml). The mixture was stirred for 2.5 h, after which time ether (100 ml) was added and the black solid triturated. The ether was decanted from the black residue. The residue was further triturated with ether (4 × 50 ml). The combined ether extracts were passed through a small column of alumina and then evaporated under reduced pressure to give the ketone (**18b**) (0.7 g, 70%), $\bar{\nu}_{max.}(CCl_4)$ 1 775s and 1 742m,sh (C=O) cm^{-1}

A solution of the crude ketone (**18b**) (0.7 g, 3.13 mmol) in ether (10 ml) was added to a magnetically stirred slurry of $LiAlH_4$ (0.59 g, 15.6 mmol) in anhydrous ether (50 ml) under nitrogen. The resulting mixture was refluxed for 1.5 h, after which time the excess of $LiAlH_4$ was destroyed through the cautious addition of saturated aqueous sodium sulphate. The ether layer was separated and washed with water, dried (Na_2SO_4), and evaporated. The residue was recrystallized from light petroleum to give the *syn*-alcohol (**18c**) (0.5 g, 71%), m.p. 117—118 °C (Found: M^+, 228.1513. $C_{16}H_{20}O$ require *M*, 228.1514).

The purity of (**18c**) was >99.9% (column A; 150—230 °C), $\bar{\nu}_{max.}(CCl_4)$ 3 629s (OH) cm^{-1}; $\delta_H(CDCl_3)$ 0.85—2.40 (13 H, m, H-1—4, -4a, -9, -9a, -10, -12, OH, D_2O exchange), 3.08 (2 H, s, H-8a, -10a), 3.96 (1 H, s, H-11), and 5.22—5.65 (4 H, m, H-5—8).

Catalytic Hydrogenation of (**19**).—A solution of (**19**) (0.2 g, 0.69 mmol) in ethyl acetate (20 ml) containing a catalytic amount of platinum oxide was hydrogenated at 25 °C and 1 atm. pressure until no more uptake of hydrogen was observed. Filtration of the mixture, followed by evaporation of the filtrate, and recrystallization of the residue from hexane gave (1β,4β,4aα,8aβ,9α,9aα,10α,10aβ)-*perhydro*-9,10-*benzeno*-1,4-*methanoanthracen*-syn-11-*ol* (0.19 g, 94%), m.p. 115—117 °C (Found: M^+, 294.1980. $C_{21}H_{26}O$ requires *M*, 294.1984). The purity of the product was >99.7% by g.l.c. (column A: 150—240 °C), $\delta_H(CDCl_3)$ 0.9—2.99 (21 H, m, H-1—8, -8a, -9, -9a, -10, -10a, OH), 3.98 (1 H, s, H-11), and 6.98 (4 H, s, aromatic), $\delta_C(CDCl_3)$ 144.74 (2C), 125.52 (4C), 80.23 (COH), 50.82 (2C), 44.99 (2C), 43.88 (2C), 34.32 (2C), 29.61 (2C), 25.19 (2C), and 20.34 p.p.m. (2C).

Catalytic Hydrogenation of (**22**).—A solution of (**22**) (50 mg, 2.6 mmol) in ethyl acetate (20 ml), containing 10% palladium on charcoal, was hydrogenated at 25 °C and 1 atm. pressure until no more uptake of hydrogen was observed. Filtration of the mixture, followed by evaporation of the filtrate, and recrystallization from hexane gave (1α,4a,4aβ,4bα,8aα,8bβ)-*perhydro*-1,4-*methanobiphenylen*-syn-9-*ol* (48 mg, 96%), m.p. 135—136 °C (Found: M^+, 192.1511. $C_{13}H_{20}O$ requires *M*, 192.1514). The purity of hydrogenated product is >99.9% by g.l.c. (column A: 150—200 °C), $\delta_H(CDCl_3)$ 0.85—2.13 (19 H, m, H-1—4, -4a, -4b, -5—8, -8a, -8b) and 4.15 (1 H, s, H-9), $\delta_C(CDCl_3)$ 82.51 (COH), 48.68 (2C), 43.29 (2C), 34.75 (2C), 25.82 (2C), 25.48 (2C), and 18.49 p.p.m. (2C).

Birch Reductions: Reagents and Equipment.—The general techniques for carrying out the Birch reductions, and for the purification of the reagents, are described elsewhere.[3b]

Individual Birch Reductions.—The general procedure is as follows. To a magnetically stirred solution of the appropriate quantity of lithium metal in refluxing liquid ammonia (*ca.* 50 ml) was added the substrate (*ca.* 0.35 mmol) dissolved in a mixture of THF (15 ml) and Bu^{t}OH (800 mg, 10.8 mmol). The resulting mixture was stirred under reflux for the required period after which the reaction flask was cooled to −78 °C. Saturated aqueous ammonium chloride (*ca.* 50 ml) was added dropwise over 1 h followed by addition of dichloromethane (10 ml). The mixture was warmed to −10 °C and the organic layer collected. The aqueous layer was again extracted with dichloromethane (2 × 50 ml) and the organic extracts were combined, washed with water (2 × 50 ml), dried (Na_2SO_4), and evaporated. The following reductions were carried out. [Although the amount of substrate used in the reduction varied from experiment to experiment the ratio of the amounts of substrate (mol): Bu^{t}OH (mol): ammonia (ml) did not change from that stated above.]

(a) *Reduction of* (**6a**). The hydrocarbon (**6a**) (75.8 mg, 0.36 mmol) was treated with an excess amount of lithium (38 mg, 5.4 mmol) under the usual conditions for 7 h. G.l.c. analysis of the reaction mixture indicated that 60% reduction had occurred to give two products (7:1). Attempts to separate these products were unsuccessful but the major component is believed to be (**16a**) on the basis of the following data: *m/z* 212 (M^+) and 118 (M^+ − norbornene); $\delta_H(CDCl_3)$ 0.50—1.92 (14 H, m, H-1—4, -4a, -9, -9a, -10, -11, -12), 2.56 (4 H, m, H-5, -8), and 5.67 (2 H, s, H-6, -7).

The product mixture was treated with DDQ (0.2 g) in $CHCl_3$ (10 ml). The solution was stirred at room temperature for 30 min and then filtered and the residue washed with $CHCl_3$ (10 ml). The resulting filtrate was washed with saturated aqueous NaCl, dried (Na_2SO_4), and evaporated to give a single product whose m.p. and spectral properties were identical to those of (**6a**).

G.l.c.—m.s. studies of the minor product revealed that it only had one double bond: *m/z* 213 (M^+) and 120 (M^+ − norbornene).

(b) *Reduction of* (**6b**). This compound was reduced in four runs, two of which were carried out using different amounts of Li and another in competition with the diene (**18c**). The remaining run was carried out in the absence of Bu^{t}OH.

The *syn*-alcohol (**6b**) (82 mg, 0.36 mmol) was treated with lithium (10 mg, 1.43 mmol) under the usual conditions until a blue colour developed. The isolated product was recrystallized from petroleum spirit to give (**17**), m.p. 118—119 °C (Found: C, 83.6; H, 9.6. $C_{16}H_{22}O$ requires C, 83.4; H, 9.6%); $\bar{\nu}_{max.}(CCl_4)$ 3 628s (OH) cm^{-1}; $\delta_H(CDCl_3)$ 0.77—1.30 (4 H, m), 1.48—1.93 (13 H, m), 2.20—2.30 (2 H, m), 3.88br (1 H, s, H-11), 5.53 (1 H, d, *J* 11 Hz), and 5.87br (1 H, d, *J* 11 Hz); $\delta_C(CDCl_3)$ 133.38, 128.14, 80.09 (COH), 54.31, 53.73, 48.05, 47.76, 41.21 (2C), 38.44 (2C), 37.42, 29.66 (2C), 28.59, and 23.20 p.p.m.

In the second run the *syn-alcohol* (**6b**) (82 mg, 0.36 mmol) was treated with lithium (5.0 mg, 0.72 mmol) under the usual conditions. G.l.c. analysis of the reaction mixture indicated that 49% reduction had occurred to give only one product. The product was unambiguously identified as (**17**) through comparison of its g.l.c. retention time and mass spectral data with those of authentic material.

In the third run a mixture of the *syn*-alcohols (**6b**) (17.8 mg, 0.079 mmol) and (18c) and (18.0 mg, 0.24 mmol) was treated with lithium (1.65 mg, 0.24 mmol). G.l.c. analysis of the reaction mixture revealed the presence only of unchanged (**6b**) and reduced product (**17**) in the ratio 0.6:1, respectively.

In the fourth run the *syn*-alcohol (**6b**) (82 mg, 0.36 mmol) was treated with lithium (5.0 mg, 0.72 mmol) under the usual conditions in the absence of the proton source Bu^{t}OH. Analysis of the reaction mixture by ^1H n.m.r. spectroscopy revealed the

presence only of starting material (**6b**) and product (**17**) in the ratio 1:5 respectively.

(c) *Reduction of* (**6c**). The *syn*-methoxy-compound (**6c**) (51.4 mg, 0.21 mmol) was treated with lithium (3.0 mg, 0.43 mmol) under the usual conditions for 3 h. G.l.c. analysis and the ^{1}H n.m.r. spectra of the reaction mixture indicated that only 4% reduction had occurred. The appearance of a sharp singlet at δ 5.28 in the ^{1}H n.m.r. spectrum of the mixture indicates that the reduced product probably has the structure (**16c**).

(d) *Reduction of* (**6d**). This compound was reduced in two runs, one with Bu^{t}OH and the other without. In the presence of Bu^{t}OH the *syn*-acetate (**6d**) (87.4 mg, 0.33 mmol) was treated with lithium (18.5 mg, 2.64 mmol) under the usual conditions. ^{1}H N.m.r. spectral analysis of the reaction mixture revealed the presence only of alcohol (**17**).

In the second run the *syn*-acetate (**6d**) (144 mg, 0.54 mmol) was treated with lithium (15.0 mg, 2.1 mmol) under the usual conditions in the absence of Bu^{t}OH. After 2 h the reaction mixture was worked up and then analysed by ^{1}H n.m.r. which revealed the presence of *syn*-alcohol (**6b**) and reduced product (**17**) in the ratio 2.3:1 respectively.

(e) *Reduction of* (**7b**). The *syn*-alcohol (**7b**) (82.3 mg, 0.29 mmol) was treated with lithium (8.4 mg, 1.2 mmol) under the usual conditions until a blue colour developed. The isolated product was recrystallized from ethanol at 0 °C to give (**19**), m.p. 140—141 °C (Found: C, 85.9; H, 8.4. $C_{21}H_{24}O$ requires C, 86.3; H, 8.3%); $\tilde{\nu}_{max.}$(CCl_4) 3 629s (OH) cm^{-1}; δ_H($CDCl_3$) 0.92—1.85 (11 H, m, H-1—4, -4a, -8, -9a, OH, D_2O exchange), 2.32br (2 H, s, H-8a, -10a), 2.83—3.10 (4 H, m, H-7, -9, -10), 3.98 (1 H, s, H-11), 5.42 (2 H, m, H-5, -6), and 7.07 (4 H, s, aromatic), δ_C($CDCl_3$) 145.08, 144.01, 132.99, 128.00, 125.76 (2C), 125.47, 124.93, 80.23 (COH), 50.77 (2C), 45.29 (2C), 43.97, 43.78, 34.22 (2C), 29.56 (2C), 27.96, and 23.54 p.p.m.

(f) *Reduction of* (**8b**). The *syn*-alcohol (**8b**)[21] (55 mg, 0.30 mmol) was treated with lithium (5.2 mg, 0.74 mmol) under the usual conditions until a blue colour developed. The solid product was recrystallized from petroleum spirit to give (**22**), m.p. 113—114 °C (Found: C, 83.8; H, 9.7. $C_{13}H_{18}O$ requires C, 82.1; H, 9.5%); $\tilde{\nu}_{max.}$(CCl_4) 3 630s (OH) cm^{-1}; δ_H($CDCl_3$) 0.82—2.30 (13 H, m, H-1—4, -4a, -4b, -8, -8a, -8b, OH, D_2O exchange), 2.93br (2 H, s, H-7), 4.15 (1 H, s, H-9), and 5.58—6.00 (2 H, m, H-5, -6); δ_C($CDCl_3$) 132.94, 127.36, 82.37 (COH), 50.92, 45.72, 43.39 (2C), 34.61, 33.68, 26.36, 25.82 (2C), and 21.11 p.p.m.

(g) *Reduction of* (**9**). The *syn*-alcohol (**9**) (80 mg, 0.35 mmol) was treated with lithium (6.2 mg, 0.88 mmol) under the usual conditions until a blue colour developed. G.l.c. analysis of the reaction mixture revealed the presence of two products of relative proportions 11:1. Attempts to separate the two products were unsuccessful, but the major component was identified as (**23a**) on the basis of the following data: $\tilde{\nu}_{max.}$(CCl_4) 3 628s (OH) cm^{-1}, δ_H($CDCl_3$) 1.17—2.93 (14 H, m, H-1, -3, -4, -4a, -6, -9, -9a, -10, -11, -12, OH, D_2O exchange), 4.33br (2 H, m, H-2, -8a), and 5.53—6.05 (3 H, m, H-5, -7, -8); δ_C($CDCl_3$) 151.17, 133.06, 126.12, 113.12, 75.93 (COH), 48.50, 48.21, 47.74, 46.81, 45.31, 44.53, 43.22, 40.40, 39.44, 27.79, and 27.44 p.p.m.

(h) *Reduction of* (**10b**). The *syn*-alcohol (**10b**)[22] (80.4 mg, 0.46 mmol) was treated with lithium (7.9 mg, 1.1 mmol) under the usual conditions until a blue colour developed. The isolated product was recrystallized from petroleum spirit to give the fully reduced perhydrodimethanonaphthalen-*syn*-9-ol whose m.p. and spectral properties were identical with those of authentic material.[22]

(i) *Reduction of* (**11a**). The *syn*-alcohol (**11a**)[45] (150 mg, 1.36 mmol) was treated with lithium (23.8 mg, 3.4 mmol) under the usual conditions for 2 h. G.l.c. analysis of the reaction mixture indicated 53% reduction had occurred to give 7-norbornanol which was unambiguously identified through comparison of its g.l.c. retention time and mass spectral data with those of the authentic material.

Table 2. UHF STO-3G fully optimised geometries[a] (C_s symmetry constraint) and the corresponding energies for *endo*-(30), *exo*-(30), *endo*-(31), and *exo*-(31).

Energy (a.u.) parameter	*endo*-(30) −341.271 71	*exo*-(30) −341.262 37	*endo*-(31) −341.261 41	*exo*-(31) −341.255 86
r_1	0.991	0.990	0.989	0.988
r_2	1.429	1.430	1.439	1.441
r_3	1.096	1.097	1.092	1.093
r_4	1.558	1.565	1.556	1.564
r_5	1.092	1.091	1.092	1.091
r_6	1.534	1.540	1.535	1.542
r_7	1.443	1.438	1.441	1.437
r_8	1.086	1.085	1.087	1.086
r_9	1.564	1.560	1.568	1.563
r_{10}	1.559	1.560	1.560	1.560
r_{11}	1.091	1.091	1.091	1.091
r_{12}	1.088	1.087	1.087	1.086
θ_1	100.0	100.9	104.4	104.3
θ_2	127.1	126.8	133.0	134.0
θ_3	125.8	126.7	121.8	121.1
θ_4	122.9	127.0	122.7	125.7
θ_5	120.8	119.2	122.2	121.3
θ_6	115.1	115.2	115.1	115.4
θ_7	117.5	117.1	118.0	117.3
θ_8	37.1[b]	35.4[c]	38.6[b]	38.4[c]
θ_9	131.2	131.6	131.6	132.0
θ_{10}	105.5	105.5	105.6	105.4
θ_{11}	110.7	110.6	111.0	111.0
θ_{12}	112.2	112.1	112.9	112.7
θ_{13}	112.0	111.9	111.8	111.8
θ_{14}	111.8	111.8	111.3	111.4

[a] Bond lengths in Å. [b] The vinylic hydrogens are pointing in the *endo*-direction. [c] The vinylic hydrogens are pointing in the *exo*-direction.

(j) *Reduction of* (**11b**). The *anti*-7-norbornenol[46] (**11b**) (150 mg, 1.36 mmol) was treated with lithium (23.8 mg, 3.4 mmol) under the usual conditions for 2 h. G.l.c. analysis of the reaction mixture indicated 8% reduction had occurred to give 7-norbornanol which was unambiguously identified through comparison of its g.l.c. retention time and mass spectral data with those of the authentic material.

(k) *Reduction of* (**12a** and **b**). A 4:1 mixture of (**12a**)[47] and (**12b**)[47] (200 mg, 1.8 mmol) was treated with lithium (31.8 mg, 4.5 mmol) under the usual conditions for 10 min. G.l.c. analysis of the reaction mixture revealed that only the *endo*-isomer (**12a**) had undergone reduction, to an extent of 68%. The product, *endo*-2-norbornanol, was identified through comparison of its g.l.c. retention time and mass spectral data with those of authentic material.

(l) *Reduction of* (**13**). The diol (**13**)[48] (150 mg, 0.97 mmol) was treated with lithium (17 mg, 2.44 mmol) under the usual conditions for 45 min. G.l.c. analysis of the reaction mixture revealed no reduction had occurred.

(m) *Reduction of* (**18c**). The *syn*-alcohol (**18c**) (80 mg, 0.35 mmol) was treated with lithium (6.4 mg, 0.91 mmol) under the usual conditions until a blue colour developed. The isolated product was recrystallized from petroleum spirit to give exclusively (**17**) which was identical in every respect to that prepared by the Birch reduction of (**6b**).

Competition Kinetics.—The same equipment was used for the competition kinetics as for the individual reductions (see above)

with the exception that the reaction vessel was a graduated 250 ml Erlenmeyer flask into which side, immediately above the bottom, was attached a short outlet and stopcock. The general procedure for carrying out the competition work is as follows.

A solution of approximately equimolar amounts of the competing substrates (0.5 mmol each) in a mixture of THF (20 ml) and Bu^{t}OH (1.4 g, 19 mmol) was added to a magnetically stirred solution of lithium metal (1 mg-atom) in refluxing liquid ammonia (75 ml). At various time intervals, *ca.* 5 ml aliquot portions of the reaction mixture were drawn off, *via* the stopcock, into a quenching mixture consisting of sodium benzoate (*ca.* 250 mg) and ether (5 ml) at −78 °C. A final aliquot portion was taken at the end of the reaction, *i.e.* when the blue colour of the solution had faded. Between five and six aliquot portions were sampled for each competition reaction with the exception of that between (**6b**) and (**24**) and between (**10b**) and (**24**). In these cases the reduction was so rapid that only the final aliquot portions could be taken.

The quenched aliquot portion from a competition reaction were then analysed by g.l.c. and the product compositions were obtained from the peak areas. Thus from each quenched aliquot portion k_c' was obtained using equation (1). The value of k_c', averaged over all aliquot portion, is given in Table 1. The method of obtaining relative rate constants from k_c' values is described in the text.

The competitions involving (**6b**), (**10b**), and (**24**) are unreliable owing to the very rapid rate of their Birch reduction. The competitions were carried out in duplicate but consistent values of k_c' could not be obtained. The average k_c' values for these competitions (uncertainty of ±25%) are given in Table 1.

The mixtures containing the pairs of competitors and their reduced products (which are not shown below) resulting from the competition experiments were analysed as follows: (i) (**6a**) against (**10a**) (column A, 150—230 °C at 5 °C min^{-1}); (ii) (**6b**) against (**24**) (column A, 80—240 °C at 5 °C min^{-1}); (iii) (**6c**) against (**6a**) [as for (i) above]; (iv) (**10b**) against (**24**) [as for (ii) above]; (v) (**11a**) against (**10a**) (column A, 80—250 °C at 10 °C min^{-1}); (vi) (**11a**) against (**11b**) (column A, 70—150 °C at 1 °C min^{-1}); (vii) (**12a**) against (**12b**) (column B, 60—70 °C at 1 °C min^{-1}); (viii) (**12b**) against (**10a**) (column B, 60—150 °C at 1 °C min^{-1}).

Appendix

The fully optimised UHF geometries (C_s symmetry constraint) and energies of the four norborn-2-en-7-ol anion-radicals, *endo*-(**30**), *exo*-(**30**), *endo*-(**31**), and *exo*-(**31**) are given in Table 2. The parameters of Table 2 refer to those shown in (**36a**), for *endo*- and *exo*-(**30**), and (**36b**), for *endo*- and *exo*-(**31**).

The UHF STO-3G energies for (**32**) and (**33**) are:

endo-(**32**)	−341.247 04 a.u.
exo-(**32**)	−341.242 81 a.u.
endo-(**33**)	−341.254 66 a.u.
exo-(**33**)	−341.248 55 a.u.

The geometries of these species were unoptimised and were obtained by rigid rotation of the OH group in the corresponding optimised structures (**30**) and (**31**).

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