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Extraordinary Effect of Remote Aromatic Rings on the Birch Reduction of Isolated Double Bonds: a Chemical Manifestation of Orbital Interactions through Bonds

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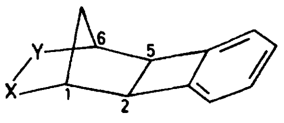
Summary The presence of remote aromatic rings in (**1**) and (**2**) dramatically enhance the Birch reduction of the norbornene double bond by factors of 180 and 210 respectively and these results have been explained in terms of orbital interactions through bonds.

Normally isolated carbon–carbon double bonds are reduced with difficulty under Birch conditions[1] (metal, liquid ammonia, proton source). However the close proximity of an unsaturated group may greatly enhance their reactivity by orbital interactions through space (OITS).[2] This proximity effect has been used to explain the rapid reduction of norbornadiene to norbornene.[3]

We report on the remarkably easy Birch reduction of the isolated double bond in both *exo*-3,4-benzotricyclo-$[4.2.1.0^{2,5}]$nona-3,7-diene (**1**) and the *exo*-anthracene–norbornadiene adduct (**2**) which is unprecedented because the remoteness of the aromatic groups [3.8 Å in (**1**) and 4·5 and 5·2 Å in (**2**)] precludes their interactions with the double bond *via* OITS and/or inductive effects.

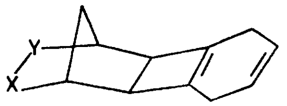
The exhaustive reduction[†] of (**1**)[4] gave (**4**) and (**5**) in the ratio 2·1 : 1,[‡] the structures of which were confirmed by ^{1}H n.m.r. and mass spectral analyses and by their smooth oxidation to (**3**)[4] and (**1**), respectively, by dichlorodicyanobenzoquinone.

The following observations demand that the first step in the formation of (**4**) is the reduction of the isolated double bond of (**1**) to give (**3**). Firstly, partial reduction of (**1**) (2 g equiv. Na) resulted in a mixture of (**3**), (**4**), and (**5**) with



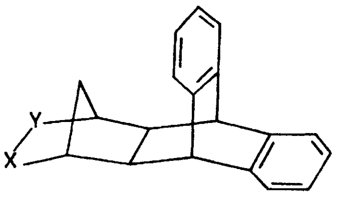
(1) XY = HC=CH

(3) XY = H_2C—CH_2



(5) XY = HC=CH

(4) XY = H_2C—CH_2



(2) XY = HC=CH

(6) XY = H_2C—CH_2

[†] Typical conditions: substrate (0·75 mmol), ammonia (150 cm^3), dioxan (20 cm^3), t-butyl alcohol (2 cm^3), and the appropriate quantity of sodium.

[‡] Yields were determined by ^{1}H n.m.r. spectroscopy and the products were ioslated by g.l.p.c. (SE30 or Carbowax on Chromosorb W; 180 °C).

(**3**) predominating. Secondly, (**3**) is readily (Birch) reduced to give (**4**) whereas (**5**) is essentially unreactive under the same conditions. Thus the reduction of (**1**) occurs at the double bond to the extent of 68%.

An even more dramatic example of this effect is provided by the *exo*-anthracene–norbornadiene adduct (**2**).[5] In this case reduction occurred almost exclusively at the double bond to give (**6**)[5] (> 90%).

Finally under a set of conditions which effected reduction of the double bond in (**1**) (*ca.* 60%) and (**2**) (*ca.* 70%) respectively, essentially no reduction (< 0·3%) of norbornene to norbornane occurred. Thus the presence of aromatic rings in (**1**) and (**2**) enhances the reactivity of the double bond by factors of *ca.* 180 and 210 respectively.

These results may be explained in terms of orbital interactions through bonds[2,6] (OITB) which operate between the unsaturated sites in (**1**) and (**2**) *via* three and four σ-bonds respectively.§ Although there are numerous reports of the influences of OITS on the spectroscopic states[2,7] and chemical reactivities[2,3,8] of molecules, evidence on the chemical consequences of OITB is scarce.[2a,6,9,10] In this respect our report describes the first example of the chemical consequences of OITB which extends over four intervening σ-bonds.¶

The relevance of OITB to the present study is easily explained if we accept the reasonable assumptions that the ease of the Birch reduction of a substrate and the site at which the reduction takes place is determined by the respective stability and electron density distribution of the radical anion of the substrate.[1] Thus our extended Hückel (EH) calculations on (**1**) reveal the presence of OITB [operating *via* the C(1)–C(2) and C(5)–C(6) σ-bonds] which results in a lowering in the energy of the LUMO of (**1**) by 0·2 and 0·4 eV with respect to the LUMO's of (**3**) and norbornene. Therefore the radical anion of (**1**) should be more stable than either of the latter two systems and this is manifested in a more rapid rate of reduction of (**1**).** In addition, the LUMO of (**1**) contains a significant contribution from the 'isolated' double bond which implies that the electron density of the corresponding radical anion will be high in this region.** Appreciable reduction of the double bond is therefore expected.

EH calculations on model systems[11] indicate that the LUMO of (**5**) should likewise be perturbed as a result of OITB. However the LUMO remains energetically higher than that of (**1**) or (**3**) which is in full accord with the lack of reduction of (**5**).

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§ A referee has suggested that the increased reactivity of (**1**) over norbornene may be due to the strain arising from the two additional ring systems. Compound (**5**), however, is essentially unreactive towards Birch conditions.

¶ This type of interaction has been recently demonstrated using photoelectron spectroscopy.[10b]

** We assume that the LUMO of (**1**) reflects the properties of the radical anion (the formation of which involves the addition of an electron to this MO).

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[2] (a) Reviews: R. Hoffmann, *Accounts Chem. Res.*, 1971, **4**, 1; R. Hoffmann and W.-D. Stohrer, Specl. Lecture XXIII Internat. Congr. Pure Appl. Chem., Vol. 1, Butterworths, London, 1971, p. 157; (b) R. Hoffmann, E. Heilbronner, and R. Gleiter, *J. Amer. Chem. Soc.*, 1970, **92**, 706.

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[7] In particular through photoelectron spectroscopy: H. Bock and B. G. Ramsey, *Angew. Chem. Internat. Edn.*, 1973, **12**, 734, and references therein.

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[9] C. W. Rees and R. C. Storr, *Chem. Comm.*, 1965, 193; R. Gleiter, W.-D. Stohrer and R. Hoffmann, *Helv. Chim. Acta.*, 1972, **55**, 893, and references therein; E. Haselbach and W. Eberbach, *ibid.*, 1973, **56**, 1944; W. Schmidt and B. T. Wilkins, *Tetrahedron*, 1972, **28**, 5649.

[10] Photoelectron spectral demonstrations of OITB are plentiful: (a) F. Brogli, W. Eberbach, E. Haselbach, E. Heilbronner, V. Hornung, and D. M. Lemal, *Helv. Chim. Acta.* 1973, **56**, 1933; H.-D. Martin, S. Kagabu, and R. Schwesinger, *Chem. Ber.*, 1974, **107**, 3130; R. Gleiter, E. Heilbronner, M. Hekman, and H.-D. Martin *ibid.*, 1973, **106**, 28; (b) H.-D. Martin and R. Schwesinger, *ibid.*, 1974, **107**, 3143.

[11] M. N. Paddon-Row, unpublished results.