

Preliminary communication

CATALYTIC ACTIVATION OF AROMATIC C—H BONDS

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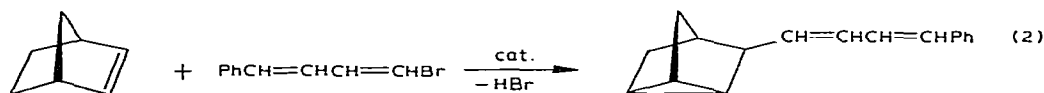
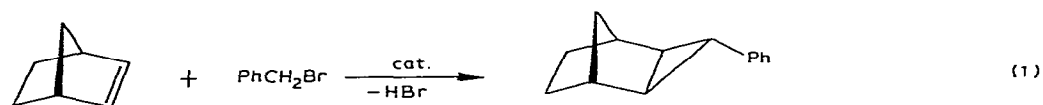
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Summary

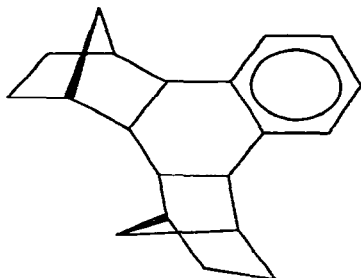
A new reaction is described, involving oxidative addition of aromatic bromides to palladium(0), two successive insertions of norbornene, and ring closure to the aromatic carbon *ortho* to the carbon originally bearing the bromine.

We previously described some reactions involving catalytic activation of a CH₂ group to form cyclopropane rings [1], for example eq. 1 and 2. In an attempt to extend the scope of these reactions we have found that catalytic activation of aromatic C—H bonds also is possible.



When bromobenzene (1 mol) is caused to react with norbornene (2 mol) under the catalytic influence of palladium(0) complexes (0.06 mol) with triphenylphosphine and in presence of an alkali acetate (1 mol) in anisole at 105–110°C for 22 h under N₂, the predominant product is one which corresponds to the addition of 1 mol of bromobenzene to 2 mol of norbornene (isolated yield 55% on the bromobenzene put in reaction, 9 mol per mol of

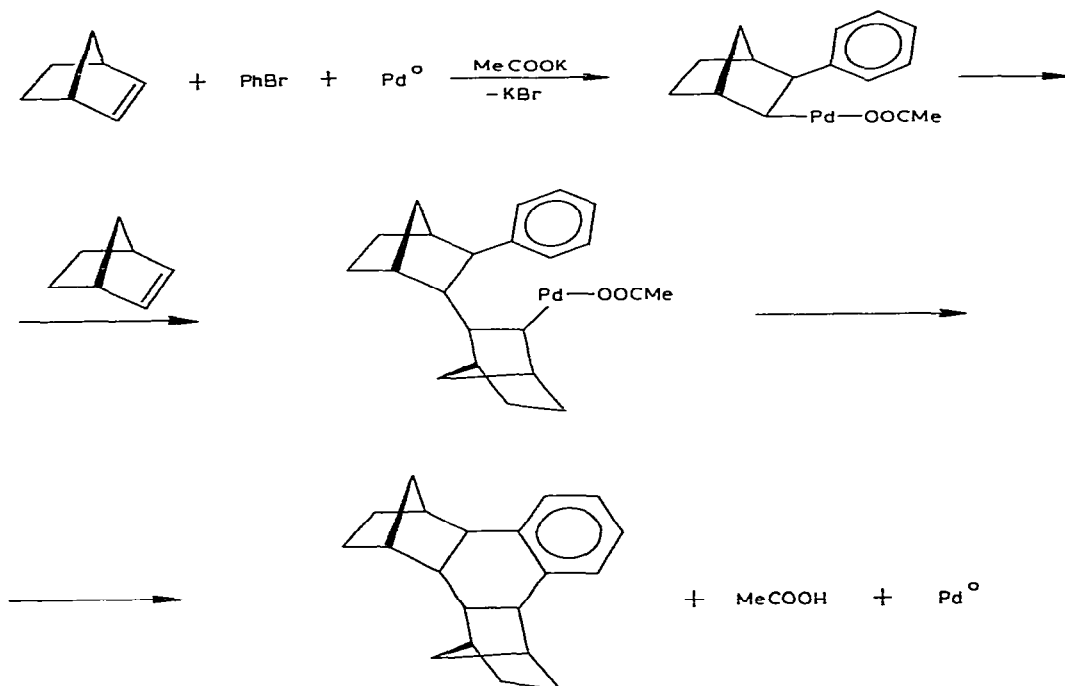
catalyst). Other isomers of the main product, along with small amounts of 1/1 and 1/3 adducts, are also present. We were able to isolate and characterize the major isomer, which has structure I, with the two norbornane rings mutually *trans*.



(I)

The mass spectrum (70 eV) shows the expected fragmentation leading to m/e 128 (naphthalene) after the loss of 67, 68 and 1 fragments. ^1H NMR (100 MHz, CDCl_3 , TMS): δ 7.3–6.9 (m, 4H), 2.72 (br d, $J = 8$ Hz, 2H), 2.22 (m, 2H), 2.05 (m, 2H), 1.8–0.8 (m, 14H) ppm; ^{13}C NMR (25.2 MHz, CDCl_3 , TMS): δ 138.1, 129.2, 124.9, 47.7, 47.6, 46.4, 45.5, 33.4 (t, C(7) in a 2,3-*cis,exo* arrangement of the norbornane ring), 30.7, 28.8 ppm.

An alternative structure with the two methylene bridges on the same side of the tetrahydronaphthalene ring can be excluded on account of the large steric hindrance in the palladium complex undergoing ring closure.

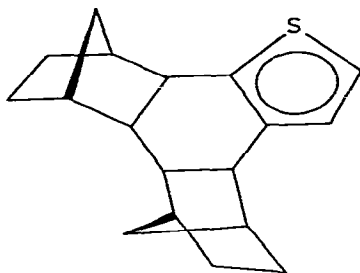


SCHEME 1

The other isomers probably correspond to double insertion of norbornene with a different type of termination, not involving aromatic C—H activation but rather ring opening of the second molecule of norbornene.

The main reaction appears to conform to a general pattern involving oxidative addition of the aromatic halide to palladium(0), insertion of two molecules of norbornene in sequence (this process being favored by the acetate anion), and substitution [2] (possibly electrophilic [3]) at the aromatic carbon. Since the last step liberates a proton, which is taken up by the anion present in the complex, palladium(II) initially formed by oxidative addition reverts to palladium(0) and a catalytic cycle is established. This is the observation of catalytic C—H activation of the aromatic ring, although, under the conditions used (which were not optimized) only a few molecules per Pd atom are transformed (Scheme 1).

We have examined the scope of this reaction with other aromatic and heterocyclic compounds and found analogous behaviour. In particular, under the conditions described for bromobenzene, 2-bromothiophene gives II, which exhibits NMR and mass spectral behaviour analogous to that of I.



(II)

Mass spectrum (70 eV): M^+ 270, m/e 203, 147, 135, 134, 67; ^1H NMR (270 MHz, CDCl_3 , TMS): δ 7.02 (d, J 5 Hz, 1H), 6.67 (d, J 5 Hz, 1H), 2.76 (br d, J 8 Hz, 1H), 2.60 (br d, J 8 Hz, 1H), 2.22 (m, 1H), 2.16 (m, 1H), 2.03 (m, 2H), 1.64 (ddd, J 2 Hz, J 4 Hz, J 8 Hz, 1H), 1.61 (ddd, J 2 Hz, J 4 Hz, J 8 Hz, 1H) (protons at the C—C juncture of the two norbornane rings in *trans* configuration), 1.57–1.23 (m, 8H), 1.16, 1.10, 0.95, 0.90 (4d quintets, J 2 Hz, J 10 Hz) ppm.

The scope and mechanism of this new reaction are currently investigated.

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References

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