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Preliminary communication

PALLADIUM-CATALYZED SEQUENTIAL INSERTION OF DOUBLE BONDS FOLLOWED BY β,γ-CLEAVAGE OF A C—C BOND

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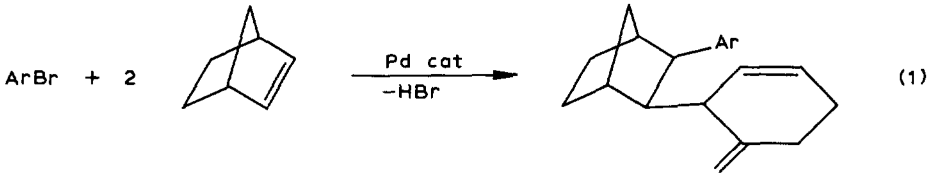
Summary

A termination process involving β,γ-cleavage of a C—C bond of a norbornane ring has been observed in the palladium-catalyzed reaction of bromobenzene with norbornene.

We recently described several pathways by which a Pd—C bond can terminate an insertion process [1,2]. We now report an example of β,γ-cleavage of a C—C bond which takes place after insertion of two norbornene double bonds into a Pd—C bond formed by oxidative addition of aryl bromides ArBr to palladium(0), according to eq. 1.



(I)

The reaction takes place under nitrogen in anisole at 100—110°C in the presence of $Pd(PR_3)_4$ as catalyst (R = aryl) and of alkali carboxylates or alkyl orthoformates in the amount required to neutralize the HBr formed. Reaction of ArBr and potassium acetate in a 10/1 molar ratio with respect to $Pd(PPh_3)_4$, followed by conventional work-up and separation on a SiO_2 column (n-hexane as eluent) gave compound I (Ar = Ph, one diastereoisomer) in moderate yield (16%), the main product being II, resulting from ring closure on the phenyl ring [2].

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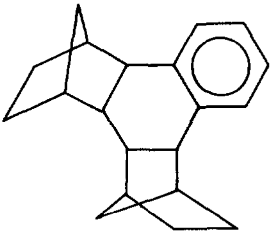


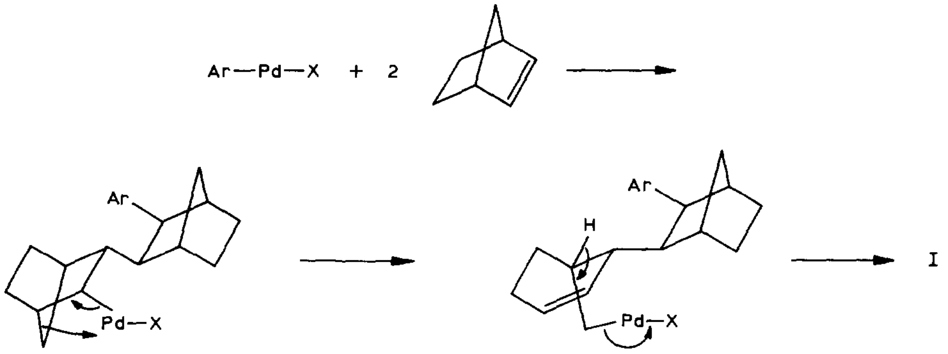
(II)

Compound I (Ar = Ph) could be obtained in higher yield by use of triethyl orthoformate (82% conversion and 41% selectivity). Besides II and minor products, other compounds containing three molecules of norbornene to one of aryl bromide were found in small amounts. Compound I (Ar = Ph), 2-phenyl-3-(2-methylencyclohex-5-en-1-yl)bicyclo[2.2.1]heptane, was fully characterized by spectroscopic techniques: MS (70 eV): M^+ 264, *m/e* 171, 129, 91, 67; IR (film): 1650, 890 cm^{-1}; UV (methanol): no conjugation of the two double bonds observed; ^{13}C NMR (25.2 MHz, $CDCl_3$, TMS): δ 148.7(s), 144.1(s), 131.8(d), 129.0(d 127.7(d); 125.7(d), 125.1(d), 107.9(t), 54.9(d), 52.1(d), 44.8(d), 43.6(d), 39.4(d), 35.4(t), 31.7(t), 29.0(t), 28.4(t), 28.2(t) ppm; ^{1}H NMR (270 MHz, $CDCl_3$, TMS): δ 7.40—7.10 (m, 5H, aromatic protons), 5.32 (d, further split, *J* 10.2 Hz, *J* 3.7 Hz, 1H, HC(5), cyclohexene), 4.72, 4.59 (2d, *J* 2.5 Hz, 2H, H_2C=), 4.66 (d, further split, *J* 10.2 Hz, *J* 4.8 Hz, 1H, HC(6), cyclohexene), 2.92 (br d, *J* 8.5 Hz, 1H, HC(2)), 2.37 (dd, *J* 10.8 Hz, *J* 4.8 Hz, 1H, HC(1), cyclohexene), 2.31 (br s, 1H, HC(1)), 2.20—2.30 (m, $H_2C(3)$, cyclohexene), 2.16 (br s, 1H, HC(4)), 2.15—2.00 (m, 2H, $H_2C(4)$, cyclohexene), 1.94 (dd, *J* 10.8 Hz, *J* 8.5 Hz, 1H, HC(3)), 1.87 br d, *J* 10.2 Hz, 1H, HC(7) *syn*), 1.70—1.30 (m, 4H, $H_2C(5)$, $H_2C(6)$), 1.23 (br d, *J* 10.2 Hz, 1H, HC(7) *anti*) ppm.

Decoupling experiments indicated that the proton at δ 2.92 ppm (HC(2)) was coupled to the proton at δ 1.94 ppm (HC(3)). The latter was also coupled to that at δ 2.37 ppm (HC(1)), cyclohexene). In its turn this latter proton was coupled to that at δ 4.66 ppm (HC(6), cyclohexene). Very small couplings with the allylic protons of the methylene group were also observed. The same proton (HC(6), cyclohexene) was coupled to that at δ 5.32 (HC(5), cyclohexene). The latter was coupled to the protons at δ 2.15—2.00 ppm ($H_2C(4)$, cyclohexene). This pattern is consistent only with the methylenecyclohexene structure shown.

The mechanism must involve formation of ArPdX (X = Br, carboxylate) followed by insertion of two norbornene units. At this point the system cannot undergo β-hydrogen elimination readily [1]. As an alternative, β,γ-cleavage of a C—C bond occurs, to generate I (Scheme 1).

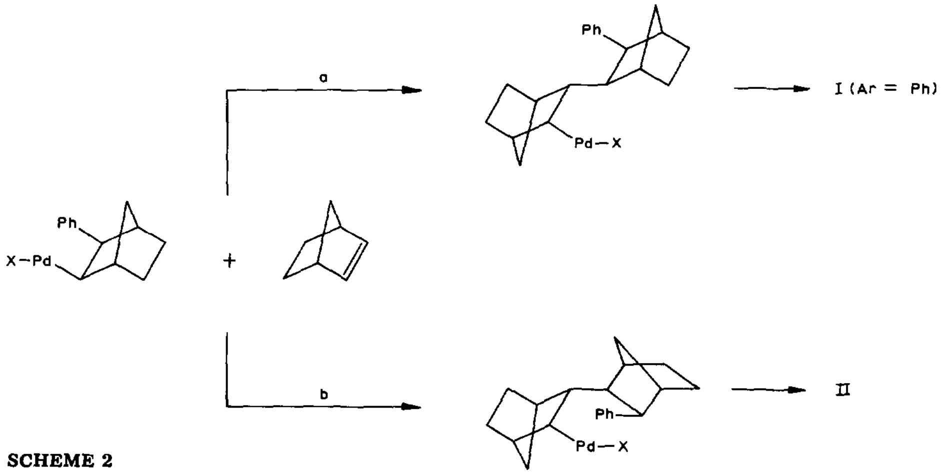
Examples of β,γ-cleavage of C—C bonds have been reported in the literature for some stoichiometric reaction of Pd complexes [3,4]. Furthermore other catalytic reactions, namely ring opening of a condensed cyclobutylmethylnickel ring [5], isomerization via cyclopropylalkylnickel intermediates [6], and dimerization of norbornadiene on a nickel catalyst, leading to *o*-tolylnorbornene [7] also imply β,γ-cleavage. The present result suggests that such behaviour is general



SCHEME 1

for transition metals (and possibly also for non-transition metals in the light of the ring-opening reaction of a condensed cyclobutylmethylmagnesium complex [8]) whenever β-elimination of hydrogen is difficult.

The reason why β,γ-cleavage to I is preferred under certain conditions to ring closure to II, is probably to be found in the steric arrangement of the second norbornene molecule: formation of the C—C bond between the phenylnorbornyl group and a new norbornene molecule can place the phenyl group in an unfavourable (way a) or favourable (way b) [2] position for ring closure on the aromatic ring (Scheme 2).



SCHEME 2

Further work is needed to clarify the effects of the ligand, the anion and the orthoformate on the formation of I and II.

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