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Preliminary communication

NEW TRANSITION METAL-CATALYZED C—C COUPLING REACTIONS INITIATED BY C—X BOND CLEAVAGE AND TERMINATED BY H-TRANSFER

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Summary

Reactions in the presence of rhodium or palladium catalysts involving C—X (X = Cl, Br, I) bond breaking, single and double insertion of unsaturated substrates, and finally H-transfer are reported.

Transition metal-catalyzed hydride transfer reactions leading to hydrogenolysis of C—X bonds have been described [1—5], but to our knowledge no report has dealt so far with catalytic reactions involving a "delayed" H-transfer, i.e. one not involving the original X-bonded carbon atom, but a new metal-bonded carbon atom formed by insertion of one or more molecules or groups of a substrate S:

$$RX + S + H^- \xrightarrow{\text{cat.}} RSH + X^-$$

A special case is presented by the reaction of aromatic halides with allylic alcohols [5], for which a hydride 1,2-addition—elimination mechanism has been postulated:

$$RX + CH_2{=}CHCH_2OH \xrightarrow{\text{cat.}} RCH_2CH_2CHO + HX$$

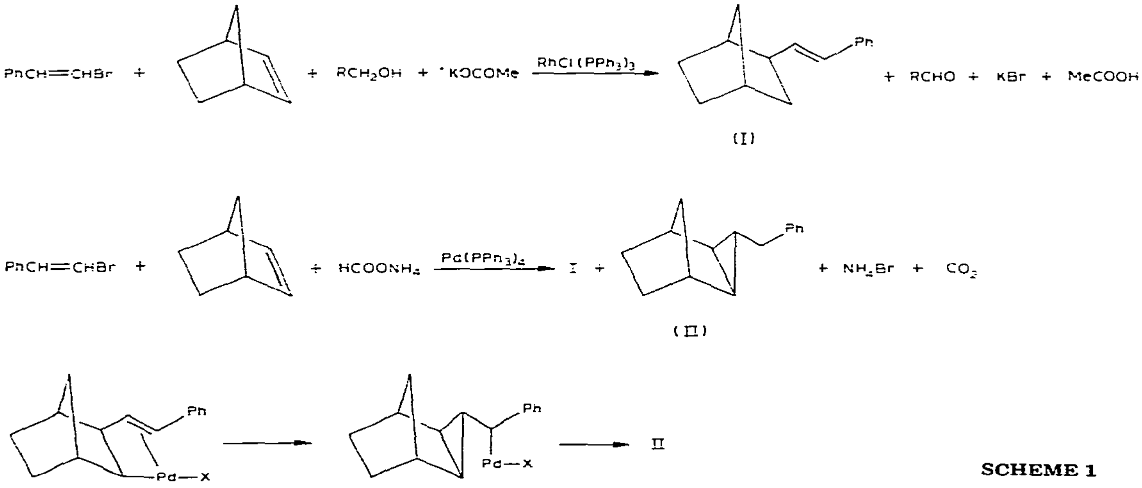
We have observed that delayed H-transfer reactions can be obtained catalytically with vinylic halides and strained olefins, in the presence of Rh or Pd catalysts and of H^- sources. A typical reaction is that of styryl bromide with norbornene, leading to product I. This reaction occurs readily with rhodium(I) complexes containing triphenylphosphine ligands at 80—120°C in alcohols. *exo*-Styrylnorbornane (fully characterized by ^1H and ^{13}C NMR spectroscopy and by oxidation to the known *exo*-norbornane-2-carboxylic acid [6] is selectively obtained.

Benzyl alcohol has proved effective in limiting the formation of heavier products. Thus equimolecular amounts of *trans*-β-bromostyrene, norbornene and potassium acetate were heated at 100—105°C in benzyl alcohol under nitrogen for 48 h in the presence of 0.0048 mol of $RhCl(PPh_3)_3$ per mol of bromostyrene. A 40% yield (based on bromostyrene) of *trans*-2-styrylnorbornane was obtained, styrene being the main by-product. The number of styryl bromide molecules transformed per molecule of Rh complex was 83, but optimization was not attempted.

The same reaction can be obtained with $Pd(PPh_3)_4$ but with a low selectivity. To obtain better results ammonium formate (2 mol per mol of bromostyrene) was used as H source [3] (not suitable with Rh) in place of alcohols and anisole was used as solvent. In this case another reaction, the extent of which increased with temperature, took place in addition to that leading to I. This involves a double highly stereoselective insertion with cyclopropane ring closure before final H-transfer. After 8 h at 80°C a 51.5% yield of product II (3-benzyl-1α,2β,-3α,4β,5α-tricyclo[3.2.1.0^{2,4}]octane) and 20.6% of I were obtained and 150 mol of bromostyrene per mol of Pd complex were converted. The ratio I/II varied from 1.7 at room temperature to 0.3 at 110°C.

Product II (M^+ 198) was obtained by an independent synthesis (norbornene + carbomethoxydiazomethane, saponification, reaction with phenyllithium and Wolff—Kischner reduction). It shows characteristic ^1H NMR absorptions (100 MHz, $CDCl_3$, TMS) τ 9.36 (m, 1H, HC(3)); 7.70 (m, 2H, HC(1), HC(5)); 7.57 ppm (d, 2H, CH_2—Ph). ^{13}C NMR (25.2 MHz, $CDCl_3$) (ppm from TMS, multiplicity is derived from off-resonance spectrum): 14.8 (d, C(3)); 23.2 (d, C(2), C(4)); 28.6 (t, C(8)); 29.6 (t, C(6), C(7)); 35.9 (d, C(1), C(5)); 37.6 (t, CH_2Ph); 125.5, 128.0, 142.0 (aromatic carbons).

The driving force for cyclopropane ring closure probably derives from double bond activation by palladium(II), which causes addition of the Pd—C bond formed in the initial insertion, as shown in Sheme 1. Similar reactions have been observed with other vinylic reagents such as 1-bromo-1-octene and with other strained olefins such as dicyclopentadiene.



SCHEME 1

Cyclopropane ring formation has been noticed only with Pd complexes as catalysts. The latter are known to be effective in cyclopropanation, though by an entirely different route, involving decomposition of diazo derivatives to carbenes [7].

The reactions described above also offer unequivocal evidence that H-transfer does not involve preliminary formation of conjugated double bonds, since hydrogen elimination to give a diene is unfavorable with norbornene and similar substrates [8].

Study of other substrates able to form metal-bonded species having greater tendency towards H-uptake than to H-elimination is in progress.

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