Journal of Organometallic Chemistry, 301 (1986) C62–C64
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

NICKEL-CATALYZED COUPLING OF ACTIVATED ALKENES WITH ORGANIC HALIDES

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(Received November 13th, 1985)

Summary

Alkenenickel complexes catalyze the coupling of activated olefins with aryl or vinyl halides. Substitution or conjugate-addition products are obtained depending on the activating group in the alkene and on the nature of the organic halide.

The coupling of alkenes with organic halides, the Heck reaction [1], is generally accomplished by the catalytic action of a zero-valent palladium complex formed "in situ" by the reduction of a palladium salt. We recently reported the ability of highly dispersed palladium on graphite (Pd-Gr) to catalyze this reaction [2]. Although zero-valent nickel complexes readily undergo oxidative addition with organic halides [3], only few examples of nickel-catalyzed Heck reactions have been described [4].

We now report that coupling of activated olefins with aryl and vinyl halides can be brought about by using a catalytic amount of dichlorobis(triphenylphosphine)nickel and an excess of zinc powder in tetrahydrofuran (THF). The active catalyst is the (η^2-alkene)bis(triphenylphosphine)nickel complex (1), which is first formed by the reaction between the alkene, dichlorobis(triphenylphosphine)nickel and zinc (eq. 1) (see ref. 5). The organic halide is then added to the mixture to give three main products; the substitution product **2**, and/or the conjugate addition (saturated) product **3**, and the homocoupling product of the organic halide **4** (eq. 2).

$$NiCl_2(Ph_3P)_2 + CH_2{=}CHR' \xrightarrow{Zn} \underset{(1)}{(CH_2{=}CHR')Ni(Ph_3P)_2} \qquad (1)$$

0022-328X/86/$03.50

$$\mathrm{RX} + \mathrm{CH_2{=}CHR'} \xrightarrow[\mathrm{Zn(excess)}]{\mathbf{1}\mathrm{(cat)}} \underset{(\mathbf{2})}{\mathrm{RCH{=}CHR'}} + \underset{(\mathbf{3})}{\mathrm{RCH_2CH_2R'}} + \underset{(\mathbf{4})}{\mathrm{R{-}R}} \qquad (2)$$

Depending on the activating group of the alkene (phenyl or ethoxycarbonyl) and on the organic halide (aryl or vinyl; iodide or bromide), preferential formation of **2** or **3** is observed (Table 1).

TABLE 1

REACTION CONDITIONS AND YIELDS OF PRODUCTS (eq. 2)

R′	RX	T (°C)	t (h)	Product yields (%)		
				1	**2** [b]	**3**
Ph	PhI	25	4	31	—	44
Ph	PhI	25	6.5 [c]	59	—	32
Ph	PhI	25	20 [d]	52	—	20
Ph	PhBr	66	3	25	—	55
Ph	PhCl	66	4	15	—	48
CO_2Et	PhI	66	1	54	6	5
CO_2Et	PhBr	66	17	3	45	3
CO_2Et	PhCl	66	40 [e]	—	7	2
CO_2Et	$4\text{-}(CH_3)C_6H_4I$	66	5	51	—	8
CO_2Et	$4\text{-}(CH_3)C_6H_4Br$	66	15	7	25	8
CO_2Et	$4\text{-}(CH_3O)C_6H_4I$	25	3.5	42	—	10
CO_2Et	$4\text{-}(CH_3O)C_6H_4Br$	66	15	10	20	9
CO_2Et	C_3H_5Br [f]	66	15	41	15	n.d.

[a] Typical procedure: a mixture of the alkene (15 mmol), $NiCl_2(Ph_3P)_2$ (1 mmol) and zinc (30 mmol) in THF (10 ml) is stirred at room temperature for 1/2 h, then the organic halide (10 mmol) is added and the mixture is kept at the temperature reported until GLC analysis shows that the halide has disappeared. After treatment with water (2 ml) and extraction with ether the products are purified by flash column chromatography and identified through IR, ^1H NMR, ^{13}C NMR, and mass spectra. [b] Yield of **3** refers to 5 mmol maximum yield. [c] Water (0.1 ml) was added. [d] Water (0.2 ml) was added. [e] Only 20% of the halide reacted. [f] The 1-bromo-1-propene was a 1/1 *cis/trans* mixture; no attempt was made to determine the amount of hexadiene.

The substitution product **2** is formed almost to the exclusion of **3** in the reaction of styrene with either iodo- or bromo-benzene, although the formation of biphenyl is even more important [5]. The presence of a little water increases the yield of **2** but also lowers the reaction rate. The reaction of ethyl acrylate with aryl iodides similarly affords **2** as the main product, but with the corresponding bromides the saturated product **3** predominates; in all cases the homocoupling product **4** is formed to some extent. In contrast, in the reaction between ethyl acrylate and 1-bromo-1-propene **2** is again the main product.

The product **2** is obtained in *E* configuration of the double bond, no traces of the *Z* isomer being detected by capillary GLC analysis of the product mixtures.

We believe that the mechanism of the reaction leading to the substitution product **2** is similar to that of the Heck reaction, apart for the need to have zinc present to regenerate the nickel(0) catalyst in a reductive manner, since in basic conditions (triethylamine) there is no reaction. We do not yet understand the formation of the saturated compound **3**, because we have not been able to obtain convincing evidence for possible ionic or radical pathways which would provide the source, of the hydrogen incorporated into 3 at the carbon atom bearing R′. From reactions between ethyl acrylate and bromobenzene in octadeuterated tetrahydrofuran, a source of deuterium atoms, or after quenching the reaction with electrophiles (deuterium oxide, benzaldehyde), we were never able to detect deuterated or condensation products.

We have demonstrated that nickel complexes can be used in place of the more expensive palladium catalysts in coupling activated alkenes with organic halides.

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