Rhodium-catalysed Diene–Allylamide Coupling Reaction and Palladium Catalysis of Formation of the Active Rhodium Species

Gian Paolo Chiusoli,* Mirco Costa, and Antonio Fiore
Istituto Chimica Organica dell'Università, Viale delle Scienze, I-43100 Parma, Italy

Diene–allylamide carbon–carbon coupling reaction occurs regioselectively under the catalytic action of a rhodium complex, whose formation is catalysed by palladium(0).

We report a new rhodium-catalysed regioselective reaction of butadiene (and other dienes) with allylamides of organic acids [equation (1), R = alkyl, aryl] at 90—95 °C in 99.5% ethyl alcohol.

$$CH_2{=}CHCH{=}CH_2 + CH_2{=}CHCH_2NHCOR \xrightarrow{\text{Rh cat.}} CH_3CH{=}CH(CH_2)_2CH{=}CHNHCOR \quad (1)$$

The reaction leads to linear unsaturated amides, only the terminal carbon atom of the allylamide is involved in the coupling. With $RhCl_3$–Na_2CO_3 and 0.2—0.5 mol of triphenylphosphine as catalyst and butadiene in 5:1 excess of the benzoic acid allylamide (R=Ph) and a ratio of allylamide to rhodium of 100:1 ([Rh] = 0.01 M), a 60% conversion is obtained after stirring the mixture at 94 °C for 24 h in a closed, glass vessel under nitrogen or argon. The 1-*E*-5-*E* stereoisomer of (**1**)† was formed in 50% yield, and the 1-*Z*-5-*E* and 2-*E*-5*E* stereoisomers in *ca.* 7%. A small amount of a complex isomeric mixture, deriving from the addition of two molecules of butadiene per molecule of allylamide was also obtained. Butadiene oligomers were also found in the reaction mixture. The presence of allylic chain substituents reduced the yield remarkably (less than 10% yield with *N*-crotylbenzamide).

The regioselectivity must be attributed to the chelating effect of the amido group, on the basis of previous reports on the non-regioselectivity of the reaction of dienes with alkenes.[1,2] Double-bond insertion into a rhodium(III)-hydride bond was postulated as being the initial step with $RhCl_3$ in ethanol.[2] In our case this method gave the branched isomer of (**1**), $MeCH{=}CHCH_2C({=}CH_2)CH_2NHCOR$, predominantly.

Under our conditions the formation of rhodium(I) hydrides seems to be favoured.[3] Complex $RhH(PPh_3)_4$ slowly reacted in toluene to give 10% of the amide (**1**), together with a large amount of the propenylamide, which tends to inhibit the reaction.

With the same substrate and under the same conditions (η^4-butadiene)rhodium(I) tetraphenylborate gives the coupling reaction in ethanol at a remarkably higher rate (44%

---

† *Characterization of compounds* (**1**). All compounds (1) exhibited spectroscopic data in accord with the assigned structures and gave the corresponding amide of heptylamine by hydrogenation on Pd/C.

allylamide conversion in 6 h, 96% in 24 h). The 1-*E*-5-*E* stereoisomer of (**1**) is the major product (52% of total products) (1-*Z*-5-*E*, 28% and 2-*E*-5-*E*, 7%); also formed were isomeric products, deriving from the addition of two molecules of butadiene to one of allylamide. The reaction also takes place in toluene and even *N*-methylallylamide undergoes reaction, although at a reduced rate. We suggest that the initial step consists of phenyl transfer from tetraphenyl borate[4—6] to the diene [equation (2)]. This involves a phenylbutenylrhodium complex, analogous to the alkylbutenyl complex described by Su.[2]

$$(\eta^4\text{-}C_4H_6)Rh^+\ BPh_4^- \rightarrow PhCH{=}CHCH{=}CH_2 + Rh\text{-}H + BPh_3 \quad (2)$$

Accordingly, we could detect phenylbutadiene (and analogous phenyldienes working with other dienes such as isoprene or 1,3-hexadiene) among the reaction products. Rhodium hydride could not be revealed by NMR spectroscopy, nevertheless the hydrogen from reaction (2) must attack the diene according to reaction (3).

$$Rh\text{-}H + CH_2{=}CHCH{=}CH_2 \rightarrow (\eta^3\text{-}C_4H_7)Rh$$

$$(\eta^3\text{-}C_4H_7)Rh + CH_2{=}CHCH_2NHCOR \rightarrow (\mathbf{1}) \quad (3)$$

Since reaction (1) required a long induction period even with the rhodium tetraphenyl borate complex (5% conversion was reached only after 3 h), we attempted to reduce the induction by the addition of a catalyst [$Pd(PPh_3)_4$] that had proven ability in phenyl transfer reactions.[5] Using 100:1 allylbenzamide to rhodium and 10:1 rhodium to palladium molar ratios, we obtained a complete conversion in 6 h (5% conversion was reached in 1.5 h). The yield was >95%, product distribution being essentially the same as in the absence of palladium. Analogous results were obtained in toluene, although with longer times (50% conversion with the rhodium catalyst and *ca.* 90% with the rhodium–palladium system in 24 h). We believe that the palladium catalyst promotes the reaction by helping the decomposition process of the tetraphenyl borate anion shown in equation (**2**). The process should, thus, be regarded as a 'catalysis of catalysis.'

We thank Consiglio Nazionale delle Ricerche and Ministero della Ricerca for financial support, and Centro Interfacoltà de Misure of the University of Parma for NMR spectroscopy and mass spectrometer facilities.

Received, 23rd April 1990; Com. 0/01794I

References

1 T. Alderson, E. L. Jenner, and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, 1965, **87**, 5638.

2 R. Cramer, *J. Am. Chem. Soc.*, 1967, **89**, 1633. A. C. L. Su, *Adv. Organomet. Chem.*, 1979, **17**, 269.

3 R. Grigg, T. R. B. Mitchell, and N. Tongpenyai, *Synthesis*, 1981, 442; H. Brume, J. Unsin, R. Henner, and M. Reichardt, *J. Organomet. Chem.*, 1989, **369**, 335.

4 A. Segnitz, E. Kelly, S. H. Taylor, and P. M. Maitlis, *J. Organomet. Chem.*, 1977, **124**, 113.

5 M. Catellani, G. P. Chiusoli, and S. Concari, *Tetrahedron*, 1989, **45**, 5263.

6 B. Crociani, F. Di Bianca, A. Giovenco, and T. Boschi, *Inorg. Chim. Acta*, 1987, **127**, 169; B. Crociani, F. Di Bianca, L. Canovese, and P. Uguagliati, *J. Organomet. Chem.*, 1990, **381**, 17.