Tetrahedron Letters,Vol.24,No.8,pp 813-816,1983
Printed in Great Britain

0040-4039/83/080813-04$03.00/0

A NEW CATALYTIC PROCESS BASED ON SEQUENTIAL INSERTION OF STRAINED OLEFINS AND CARBON MONOXIDE INTO Pd-C BONDS.

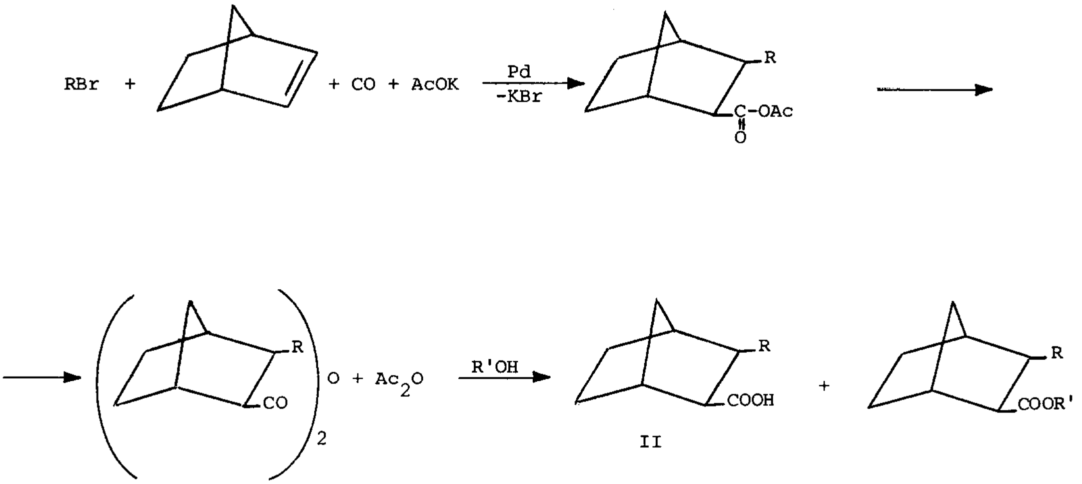
Marta Catellani, Gian Paolo Chiusoli and Cesare Peloso.
Istituto di Chimica Organica dell'Universita',
Via M. D'Azeglio 85, 43100 Parma, Italy.

Summary A palladium-catalyzed synthesis of carboxylic acids, esters and anhydrides by sequential alkylation, vinylation or arylation and carbonylation of strained olefins is reported.

Catalytic sequential insertion of olefins and carbon monoxide into transition metal-carbon bonds has been previously described in the case of allylnickel complexes.[1] Allylpalladium bonds are rather reluctant to insert simple olefins and carbon monoxide, although they react with butadiene and carbon monoxide.[2] Nickel-bonded aromatic and vinylic groups insert carbon monoxide instead of the olefin.[3]

Palladium complexes, easily formed by oxidative addition of aromatic and vinylic halides to Pd(O)[4], also are known to react with carbon monoxide,[5] but to our knowledge no report has appeared on the insertion of olefins and carbon monoxide in sequence. We recently described the sequential insertion of strained olefins and alkynes into Pd-C bonds.[6] We thus decided to use strained olefins, in particular bicyclo[2.2.1]hept-2-ene, together with carbon monoxide, at temperatures ranging from 20° to 90°C and at atmospheric pressure, in presence of a Pd(O) complex with triarylphosphines and of potassium acetate, required to promote insertion,[7] in anisole or alcohols as solvent. The source of the Pd-bonded organic group R (vinyl, aryl, benzyl or alkyl, the latter with electronwithdrawing substituents in α) was the corresponding bromide and in some cases (aromatic compounds with electronwithdrawing substituents) the chloride.

When the reactions were carried out between room temperature and 50-60°C, depending on the nature of R, the predominant product was the one deriving from direct attack of R on carbon monoxide. In anisole the product was present as the anhydride, whereas in alcohols R'OH a mixture of the carboxylic acid and its ester was formed. At temperatures around 80°C, however, the main product originated from the sequential insertion of olefin and carbon monoxide according to the following Scheme:



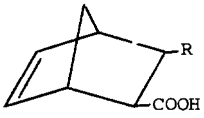
I

II

The reaction was completely stereoselective, the cis,exo compound only being obtained.

Bicyclo[2.2.1]hept-2-ene with E-β-bromostyrene in anisole at 80°C gave the anhydride I(R=E-PhCH=CH-), m.p. 120-121°C, in a 65% yield. 130 Mol of product were obtained per mol of palladium complex, but no optimization work was carried out. M^+ 466; IR (KBr): 1735, 1805 cm^{-1}. Hydrolysis with water gave acid II (R=E-PhCH=CH-), m.p. 109-110°C; M^+ 242; IR (KBr):980, 1700 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ : 28.6, 28.7 (t,C-5,C-6), 35.4 (t,C-7),39.5, 42.1 (d,C-1,C-4), 50.1, 52.3 (d,C-3,C-2), 125.9, 126.7, 128.1, 129.7, 130.7, 137.2 (aromatic and vinylic C), 179.5 (s,COOH). Reaction of bromobenzene with bicyclo[2.2.1]hept-2-ene followed by hydrolysis gave a 46% yield of II (R=Ph) m.p. 127°C.[8] 1-Bromooct-1-ene, benzyl bromide and methyl bromoacetate behaved analogously.

The same reactions could also be carried out with bicyclo[2.2.1]hepta-2,5-diene. Acid III (R=Ph), m.p. 135°C,[8] obtained from bromobenzene in butanol together with its butyl ester, corresponds to the reaction of only one of the two double bonds.

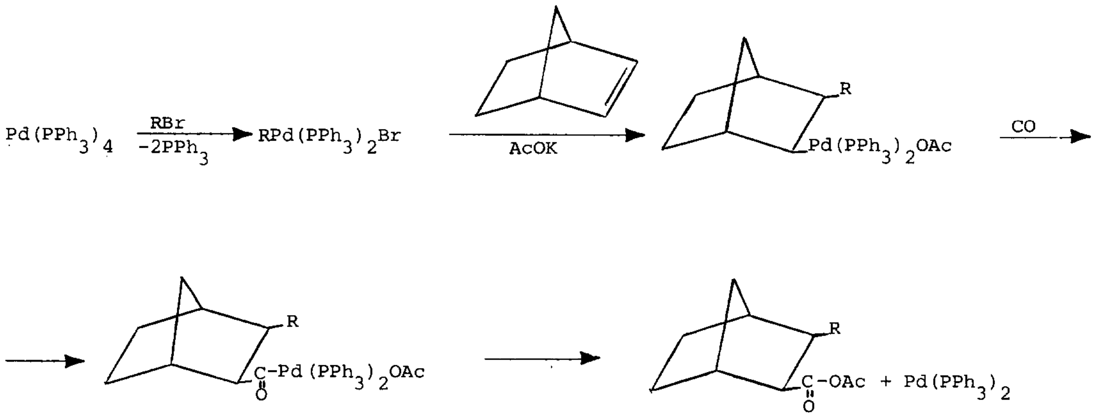


III

Hydrogenation of III on Pd/C gave II (R=Ph).

It should be observed that the use of butanol instead of anisole led to acids II or III and to their butyl esters in comparable amounts, showing that even in alcohols the reaction passes through the anhydride.

This points to the important role played by the carboxylate anion in blocking the acyl group and in providing a facile reductive elimination path that shifts the preceding reversible steps toward the final product. The following steps should be involved in the catalytic cycle:



Although the scope of this new reaction is still under examination it can be said that it offers a surprisingly mild method for the sequential insertion of strained olefins and of carbon monoxide.

General Procedure

A solution containing 5.2 mmol of the strained olefin and 5.2 mmol of the organic halide in 6 ml of solvent, e.g. anisole or butanol, is added to the palladium complex, e.g. $Pd(PPh_3)_4$, 0.026 mmol, together with an alkali salt of a carboxylic acid, e.g. potassium acetate, 5.2 mmol, with stirring under nitrogen.

The latter is displaced by carbon monoxide and the solution is heated at 80° C until the absorption of carbon monoxide is practically complete (generally a little less than 1 mol per mol of organic halide).

The solvent is removed by distillation. Conventional treatment and product separation on a SiO_2 column under pressure, using n-hexane-tetrahydrofuran mixtures as eluent, give the anhydride as the main product when anisole is used as solvent and the mixture of acid and ester when alcohols are used.

Acknowledgement

This work has been supported by the Italian National Research Council, Progetto Finalizzato Chimica Fine e Secondaria.

References

1. G.P. Chiusoli and L. Cassar in "Organic Syntheses via Metal Carbonyls", vol. 2, I. Wender and P. Pino Eds, Wiley, New York, 1977, p. 297.
2. D. Medema, R. Van Helden and C.F. Kohll, Inorg. Chim. Acta, 49, 856 (1969).
3. T.A. Weil, L. Cassar and M. Foa' in "Organic Syntheses via Metal Carbonyls" vol. 2, I. Wender and P. Pino Eds, Wiley, New York, 1977, p. 517.
4. P. Fitton and E.A. Rick, J.Organomet. Chem., 28, 287 (1971).
5. P.E. Garrou and R.F. Heck, J. Amer. Chem. Soc., 94, 4115 (1976).
6. M. Catellani and G.P. Chiusoli, Tetrahedron Lett., in press.
7. M.C. Gallazzi, L. Porri and G. Vitulli, J.Organomet. Chem., 97, 131 (1975).
8. K.Alder and W. Günzl, Chem. Ber., 93, 809 (1960).

(Received in UK 1 November 1982)