Journal of Organometallic Chemistry, 93 (1975) 253—257

SYNTHESIS OF ARYL- AND VINYL-SUBSTITUTED ACETYLENE DERIVATIVES BY THE USE OF NICKEL AND PALLADIUM COMPLEXES

L. CASSAR

Research Center, Montedison, Novara (Italy)

(Received January 17th, 1975)

Summary

Acetylene or monosubstituted acetylenes are converted into aryl- and vinyl-substituted acetylene derivatives by reaction with aryl and vinyl halides in the presence of a nickel or palladium triarylphosphine complex along with a base. With the palladium triphenylphosphine complexes the conversion can be carried out catalytically under mild conditions.

Aryl iodides are known to react with cuprous acetylides in refluxing pyridine [1] to give arylacetylenic compounds according to eqn. 1. This reaction

$$ArI + CuC{\equiv}CR \rightarrow ArC{\equiv}CR + CuI \quad (1)$$

occurs with aromatic iodides or activated bromides and requires a stoichiometric quantity of cuprous acetylide [2].

We describe here our studies directed towards finding a catalytic system which would allow the formation of arylacetylenes from aryl halides under mild conditions.

Results and discussion

We have found a new acetylenic substitution reaction of aromatic and vinylic halides based on the use of nickel(0) or palladium(0) triphenylphosphine complexes under mild conditions. With triphenylphosphinepalladium complexes the reaction proceeds catalytically.

The acetylenic substitution of aryl and vinyl halides by triphenylphosphinenickel(0) complexes involves two steps (eqns. 2 and 3). The first step

$$ArX + Ni[P(C_6H_5)_3]_3 \rightarrow Ni(Ar)X[P(C_6H_5)_3]_2 + P(C_6H_5)_3 \quad (2)$$

$$Ni(Ar)X[P(C_6H_5)_3]_2 + C_6H_5C{\equiv}CH + NaOCH_3 \rightarrow ArC(Ni[P(C_6H_5)_3]_2){\equiv}CC_6H_5 + NaX + CH_3OH \quad (3)$$

was described in previous papers [3]. The second step proceeds almost quan-

(continued on p. 256)

TABLE 1

PALLADIUM-CATALYZED SYNTHESIS OF ACETYLENIC COMPOUNDS IN DIMETHYLFORMAMIDE[a]

Organic halides (mmol)	Acetylenic reagent (mmol)	Catalyst (mmol)	Base (mmol)	Reaction temp. (°C)	Reaction time (h)	Products (% yield)
Iodobenzene (10)	phenylacetylene (10)	$Pd[P(C_6H_5)_3]_4$ (0.2)	CH_3ONa (11)	50	3	diphenylacetylene (95)
Iodobenzene (10)	phenylacetylene (10)	$C_6H_5Pd[P(C_6H_5)_3]_2I$[b] (0.3)	CH_3ONa (11)	50	3	diphenylacetylene (90)
Iodobenzene (10)	phenylacetylene (10)	$Pd[P(C_6H_5)_3]_4$ (0.2)	C_6H_5ONa (11)	50	3	diphenylacetylene (90)
Iodobenzene (5.0)	1-pentyne (5.0)	$Pd[P(C_6H_5)_3]_4$ (0.2)	CH_3ONa (6.0)	50	3	1-phenyl-1-pentyne (97)
Iodobenzene (10)	acetylene	$Pd[P(C_6H_5)_3]_4$ (0.5)	CH_3ONa (11)	50	6	phenylacetylene (50) diphenylacetylene (34)
Iodobenzene (5)	propargylic alcohol (5)	$Pd[P(C_6H_5)_3]_4$ (0.5)	CH_3ONa	50	3	3-phenylpropargyl alcohol (55)
Bromobenzene (5.0)	phenylacetylene (5.0)	$Pd[P(C_6H_5)_3]_4$ (0.3)	CH_3ONa (6.0)	80	4	diphenylacetylene (88)

p-Bromotoluene (5.0)	phenylacetylene (5.0)	$PdCl_2[P(C_6H_5)_3]_2$ [b] (0.3)	CH_3ONa (6.0)	100	4	*p*-methyldiphenyl acetylene (75)
p-Bromoanisole (5.0)	phenylacetylene (5.0)	$PdCl_2[P(C_6H_5)_3]_4$ [b] (0.3)	CH_3ONa (6.0)	100	4	*p*-methoxydiphenyl-acetylene (77)
o-Bromobenzo-nitrile (5.0)	phenylacetylene (5.0)	$Pd[P(C_6H_5)_3]_4$ (0.3)	CH_3ONa (6.0)	80	4	*o*-cyanodiphenyl-acetylene (93)
p-Chlorobenzo-nitrile (5.0)	phenylacetylene (5.0)	$Pd[P(C_6H_5)_3]_4$ (0.3)	CH_3ONa (6.0)	80	8	*p*-cyanodiphenyl-acetylene (64)
Vinyl bromide (5.0)	phenylacetylene (5.0)	$PdCl_2[P(C_6H_5)_3]_2$ (0.3)	CH_3ONa (6.0)	40	3	4-phenyl-1-but-3-yne (52)
2-Bromostyrene (5.0)	phenylacetylene (5.0)	$Pd[P(C_6H_5)_3]_4$ (0.3)	CH_3ONa (6.0)	40	2,5	1,4-diphenyl-1-buten-3-yne (89)
Bromobenzene (5.0)	phenylacetylene (5.0)	$Pd[P(p\text{-}C_6H_4CH_3)_3]_4$ (0.3)	CH_3ONa (6.0)	80	4	diphenylacetylene (80)
Bromobenzene (5.0)	phenylacetylene (5.0)	$Pd[P(C_4H_9)_3]_4$ (0.3)	CH_3ONa (6.0)	80	4	diphenylacetylene (<5)

[a] Dimethylformamide 20 ml in each experiment. [b] $P(C_6H_5)_3$ (0.6 mmol) was added. [c] Yield determined by VPC.

titatively at room temperature. The acetylenic nickel complex is easily decomposed with aqueous hydrochloric acid to give the free acetylenic compound and nickel(II) salt.

We were not able to base a catalytic process on these reactions probably because coordination of acetylenic compounds to nickel lowers its ability to undergo oxidative addition. However, use of tetrakis(triphenylphosphine)-palladium(0) does provide a catalytic process (eqn. 4):

$$ArX + RC{\equiv}CH + NaOCH_3 \xrightarrow{Pd[P(C_6H_5)_3]_4} ArC{\equiv}CR + NaX + CH_3OH \qquad (4)$$

A variety of aromatic and vinylic halides were treated with acetylenic compounds in the presence of catalytic amounts of $Pd[P(C_6H_5)_3]_4$ in dimethylformamide. Some palladium(II) compounds can also be used, but are probably reduced to Pd^0 complexes under the reaction conditions.

A base, such as sodium methoxide or sodium phenoxide, is necessary for the reaction (Table 1). Triarylphosphines are much more effective than trialkylphosphines, as observed in the catalytic cyanation of aryl halides [4]. Both alkyl- and aryl-acetylenic compounds can be used.

The rate of formation of acetylenic compounds is influenced by the nature of the substituents on the aryl halides and by the identity of the halide leaving group.

We have measured relative rates of formation of the acetylenic compounds by carrying out competitive reactions with pairs of aryl halides. We found that *p*-bromobenzonitrile was 100 times and *p*-bromoanisole 0.29 times as reactive as bromobenzene. Moreover iodobenzene was 700-800 times as reactive as bromobenzene and *p*-bromobenzonitrile 400 times as reactive as *p*-chlorobenzonitrile. The influence of substituents and of the halide leaving group is qualitatively similar to that found in the oxidative addition of $Pd[P(C_6H_5)_3]_4$ to aryl halides [5]. Heck reported similar results in the case of palladium-catalyzed carbalkoxylation of aryl halides [6].

The reaction is probably a multi-step process, involving initial oxidative addition of the triarylphosphinepalladium to the aryl halide (eqn. 5):

$$ArX + Pd[P(C_6H_5)_3]_4 \rightarrow Ar\text{-}Pd(P(C_6H_5)_3)_2\text{-}X + 2\,P(C_6H_5)_3 \qquad (5)$$

The arylpalladium(II) complex then reacts with the acetylide anion produced by interaction of the acetylene with the base (methoxide, phenoxide):

$$RC{\equiv}CH + NaOCH_3 \overset{DMF}{\rightleftharpoons} RC{\equiv}C^-\,Na^+ + CH_3OH \qquad (6)$$

$$Ar\text{-}Pd(P(C_6H_5)_3)_2\text{-}X + RC{\equiv}C^- \rightarrow \left[Ar\text{-}Pd(P(C_6H_5)_3)_2(X)(C{\equiv}CR)\right]^- \rightarrow ArC{\equiv}CR + X^- + Pd[P(C_6H_5)_3]_2 \qquad (7)$$

$$ArC{\equiv}CR\,(Pd[P(C_6H_5)_3]_2) + P(C_6H_5)_3 \rightleftarrows ArC{\equiv}CR + Pd[P(C_6H_5)_3]_3 \qquad (8)$$

This mechanism is analogous to that proposed for the cyanation [4] of aryl halides, since $RC{\equiv}C^-$ is formally isoelectronic to CN^-.

A less likely alternative mechanism would involve insertion of the acetylene into the Pd—Ar bond, followed by base-catalyzed elimination of HX.

The difference in the behaviour of nickel and palladium complexes is of interest. Two main factors operate: (a) acetylenic compounds give stronger bonds with nickel(0) than with palladium(0) complexes [7], and the nickel complexes would be too stable to display catalytic activity; (b) palladium complexes with π-acceptor ligands generally dissociate more easily than the corresponding nickel complexes [8], to give rise to coordinatively-unsaturated species which may be more reactive.

Experimental

All reagents were commercially available and used without further purification. Palladium and nickel complexes were prepared by published procedures [3]. All reactions were carried out under nitrogen.

General procedure for the synthesis of acetylene compounds

The acetylenic reagent, organic halide, catalyst, base and dimethylformamide were placed under nitrogen in a 100 ml flask equipped with a magnetic stirrer. The mixture was stirred at the temperature indicated in Table 1, and then cooled, diluted with water (100 ml) and extracted with diethyl ether (30 ml × 3). The ethereal extract was washed with water, dried with sodium sulfate and evaporated under reduced pressure. Acetylenic compounds were purified by distillation or sublimation.

The identities of the products were confirmed spectroscopically, (IR, NMR, mass spectra) and where appropriate comparison was made with authentic samples. Yields reported in Table 1 were determined by VPC with an internal standard.

References

1 C.E. Castro, E.J. Gaughan and D.C. Owsley, J. Org. Chem., 31 (1966) 4071.
2 T.F. Rutledge, Acetylenic Compounds, Reinhold, New York, 1968, p. 84.
3 (a) M. Hidai, T. Kashiwagi, T. Ikeuchi and Y. Uchida, J. Organometal. Chem., 30 (1971) 279.
(b) D.R. Fahey, Organometal. Chem. Rev., 7 (1972) 245.
(c) M. Foa and L. Cassar, in press.
4 L. Cassar, S. Ferrara and M. Foa, Adv. Chem. Ser., 132 (1974) 252.
5 P. Fitton and E.A. Rick, J. Organometal. Chem., 28 (1971) 287.
6 A. Shoenberg, I. Bartoletti and R.F. Heck, J. Org. Chem., 39 (1974) 3318.
7 E.Q. Greaves, C.J.L. Lock and P.M. Maitlis, Can. J. Chem., 46 (1968) 3879.
8 C.A. Tolman, W.C. Seidel and D.H. Gerlach, J. Amer. Chem. Soc., 94 (1972) 2669.