CHEMISTRY LETTERS, pp. 159-162, 1977. Published by the Chemical Society of Japan

REACTION OF DIAZONIUM SALTS WITH TRANSITION METALS. I. ARYLATION OF OLEFINS WITH ARENEDIAZONIUM SALTS CATALYZED BY ZERO VALENT PALLADIUM

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Various olefins, especially those bearing electron donating groups, were successfully arylated by arenediazonium salts in the presence of a catalytic amount of palladium(0) complexes. An arylpalladium species was supposed to be an intermediate in this reaction.

Arenediazonium salts are known to react with various kinds of transition metal complexes giving arylazo- or arylmetal complexes1). The resulting complexes, however, have not yet found any useful synthetic utility in organic chemistry.

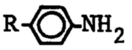
Now we have observed that various olefins are successfully arylated by arenediazonium salts in the presence of palladium(0) complexes in an aqueous acetonitrile solution buffered at about pH 4.5 by the addition of sodium acetate(eq. 1).

$$\mathrm{ArN_2X} + \mathrm{Pd(0)} \longrightarrow [\mathrm{Ar{-}Pd{-}X}] \xrightarrow{\mathrm{-CH{=}C-}} \mathrm{Ar{-}C{=}C{-}} + \mathrm{Pd(0)} + \mathrm{HX} \qquad (1)$$

As is implicated in eq. 1, the reaction is essentially catalytic with respect to palladium. Utility of the precedure is shown in Table I. The reaction of benzenediazonium salt with allyl alcohol produced the same products as those of arylmercury compounds-palladium acetate2) or aryl halides-palladium salts3b,c). The formation of phenylacetaldehyde and acetophenone from n-butyl vinyl ether instead of an expected product, butyl styryl ether, could be explained by hydrolysis of the latter under the reaction condition. The zero valent palladium catalyst was conveniently introduced into the system via in situ reduction of palladium chloride by sodium formate. The use of zero valent palladium complex, bis(dibenzylideneacetone)palladium4), gave better results. Bivalent palladium, however, was found ineffective or resulted a long induction period. This implies the importance of zero valent palladium in the initiation of this catalytic reaction.

The arylation of olefins by arenediazonium salts catalyzed by copper salts have been well known as the Meerwein arylation reaction5)(eq. 2). Although the mechanism of the reaction has not yet been well elucidated, the intermediacy of aryl radical has been assumed. The reaction has been favorably used for olefins activated with electron attracting group such as styrene, cinnamic acid or acrylic acid, but only poor

Table I. Arylation of olefins with arenediazonium salts catalyzed by palladium[a]

Olefin	Catalyst[b]	R in 	$\frac{\mathrm{ArNH_2}}{\mathrm{Pd}}$	Product[c]	Yield, % based on $ArNH_2$
Styrene	A	H	50	trans-Stilbene	8
"	"	CH_3	10	trans-p-Me-stilbene	57
"	"	"	100	"	5.1
Cyclopentene	B	H	50	1- and 3-Ph-CP(41:59)	70
"	C	"	"	" (58:42)	60
"	A	CH_3	"	1- and 3-Tol-CP(54:46)	30
"	B	"	"	" (70:30)	41
"	C	"	"	" (50:50)	53
"	B	NO_2	"	3-Nitrocyclopentene	11
"	C	Cl	"	1- and 3-Cl-CP(10:90)	10
Allyl alcohol	B	H	"	2- and 3-Ph-Pra(10:90)[e]	41
"	A	CH_3	"	2- and 3-Tol-Pra(20:80)[e]	17
"	B	"	10	" (")[e]	39
"	"	CH_3O	50	2- and 3-An-Pra(30:70)[e]	20
"	"	NO_2	"	-[d]	trace
2-Methylallyl alcohol	"	H	"	2-Benzylpropionaldehyde[f]	52
"	"	H	10	" [f]	64
Ethyl acrylate	A	CH_3	50	Ethyl p-Me-cinnamate	10
n-Butyl vinyl ether	B	H	"	Acetophenone and phenylacetaldehyde(85:15)[g]	15

a) General procedure described for the catalyst condition "B" in the 2nd column is as follows. Aniline or substituted aniline(0.10mol) was diazotized by the conventional procedure in aqueous hydrochloric acid(concd. HCl, 30ml; H_2O, 20ml) with sodium nitrite(7.0g) at 0~5°C. To the diazotized solution(total ~ 150ml) was added 25g of sodium acetate, and the solution was filtered. The cold filtrate was added dropwise to a mixture of 0.2mol of olefin, 0.002mol of $LiPdCl_3$ in 30ml of acetonitrile and 2g of sodium formate in 20ml of water. After evolution of nitrogen gas ceased, the mixture was warmed to 40 ~50°C and stirred for one hour.

b) Three methods were employed for the introduction of catalyst. A: To a mixture of $LiPdCl_3$ and olefin in acetonitrile were added the cold mixture of aqueous diazonium salt and sodium formate. B: described in a) C: Bis(dibenzylideneacetone)palladium(0)[4] was used instead of the combination of $PdCl_2$-HCOONa.

c) Abbreviation used in the Table: Me=methyl, Ph=phenyl, Tol=p-tolyl, An=p-methoxyphenyl, CP=cyclopentene, Pra=propionaldehyde.

d) IR spectrum revealed the presence of p-nitrophenyl and aldehyde groups.

e) Contaminated with a few percents of cinnamaldehyde derivatives.

f) Contaminated with a few percents of 2-Ph-2-Me-propionaldehyde.

g) Most of the phenylacetaldehyde had been changed to a self-condensation product (a resinous material).

yields have been reported for olefins with electron donating substituents. Sometimes the formation of the addition product, ArCHRC(R)ClZ, becomes a serious side reaction.

$$\mathrm{ArN_2Cl + RCH{=}CRZ \xrightarrow{copper\ salt} ArCR{=}CRZ + ArCHRC(R)ClZ} \qquad \mathrm{Z{=}Ar,\ C{=}O,\ CN,\ etc.,} \tag{2}$$

As compared to the Meerwein arylation, the substituent effect is a notable feature of the present reaction. As is seen in the Table, electron donating group on either olefins or benzenediazonium salts gives a better yield than those with electron attracting group. The complementarity between the two methods would afford the utility of the current process for organic synthesis. The catalytic efficiency was generally good and is seemed to be determined mainly by deactivation of the catalyst due to by-products formed by spontaneous reaction of the diazonium salt(e.g. phenols and/or coupling products).

Arylpalladium reagents utilized for olefin arylation have been obtained from several sources, which may be divided into two categories according to the valency state of the palladium(eq. 3 and 4).

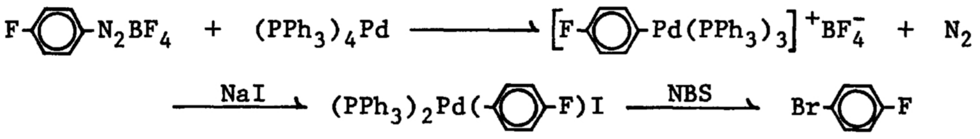
$$\mathrm{ArX + Pd(II)Y_2 \longrightarrow Ar\text{-}Pd\text{-}Y + XY} \qquad \mathrm{X{=}H^{6)},\ Hg(OAc)^{7)},\ PAr_2^{8)}\ ,\ etc.} \tag{3}$$

$$\mathrm{ArX + Pd(0) \longrightarrow Ar\text{-}Pd\text{-}X} \qquad \mathrm{X{=}Br\ or\ I^{3)}} \tag{4}$$

The present method of generating arylpalladium reagent and its usage would offer the following advantages over the previous methods. i) Only a catalytic amount of palladium is needed. ii) A wide variety of diazonium salts are readily available. iii) Special precautions may not be excercised in manipulation of the reactants, as compared with highly toxic arylmercury compounds. iv) The disposition of substituents on arylated products are determined unequivocally(eq. 3, X=H).

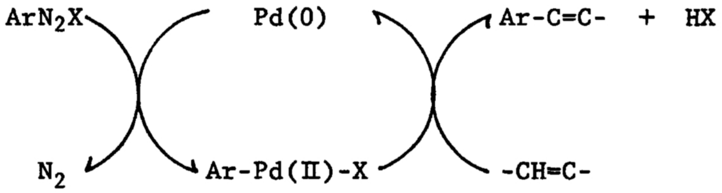
The method described in eq. 4, though seems to be quite general, also suffered from a very low reactivity of aromatic halides bearing electron donating groups[3a]. Moreover, the substituted aryl halides are generally derived from arenediazonium salts.

Preliminary study for the reaction intermediate was carried out stoichiometrically. The addition of an equimolar amount of benzenediazonium tetrafluoroborate to bis(dibenzylideneacetone)palladium(0) in acetonitrile generated nitrogen immediately even in Dry Ice-methanol bath. The amount of gas evolved corresponded to that of the diazonium salt utilized. The addition of cyclopentene to the reaction mixture and raising the temperature to 20°C produced phenylcyclopentenes in a moderate yield (17% based on Pd used). The intermediacy of arylpalladium complexes was also supported by the finding in the reaction of p-fluorobenzenediazonium tetrafluoroborate with tetrakis(triphenylphosphine)palladium(0) in ether. The resulting complex gave an arylpalladium complex on addition of sodium iodide, and following bromination with N-bromosuccinimide resulted in a formation of p-bromofluorobenzene[9] (eq. 5).



(5)

Though the detailed mechanism is not yet clear, the available data support the process shown in the following scheme.



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9) R. Yamashita, K. Kikukawa, and T. Matsuda, Unpublished data; The structure of bis(triphenylphosphine)-p-fluorophenylpalladium iodide (Found: C:58.87, H:4.14, Calcd. for $C_{42}H_{34}P_2FIPd$, C:59.14, H:4.02) was identified by comparison of the IR spectrum with that of the authentic sample prepared from p-fluoroiodobenzene and tetrakis(triphenylphosphine)palladium(0).

(Received December 7, 1976)