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Reaction of Diazonium Salts with Transition Metals. II. Palladium-catalyzed Arylation of Ethylene with Arenediazonium Salts

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Arylation of ethylene (7 atm) was carried out with various arenediazonium tetrafluoroborates (25 mmol) in the presence of bis(dibenzylideneacetone)palladium (0.5 mmol) and sodium acetate (75 mmol). Substituted styrenes were obtained in good yields (61—78%) under mild reaction conditions (1 h, room temperature) in a 1:1 mixture of acetone and dichloromethane, with some exceptions. Phenylbutenes, main by-products in dichloromethane, were presumed to form by the reaction of styrene with ethylene under catalysis of hydridopalladium species.

Previous work[1] has shown that arenediazonium salts are good arylating reagents of olefins in the presence of palladium(0) catalyst. The reaction not only proceeds under much milder conditions than those for the related palladium-catalyzed arylations,[2-4] but also was found to be applicable to unactivated olefins as compared to the copper salt catalyzed arylation (Meerwein arylation[5]). The direct synthesis of 4′-vinylbenzocrown[6] from ethylene and 4′-aminobenzocrown is an example to show synthetic utility of the present arylation, especially to one or more substituted aryl olefins. This paper describes a continuation of our studies on the arylation of ethylene with a variety of monosubstituted benzenediazonium salts to improve yield and to gain a scope of the reaction (reaction 1). A related arylation of ethylene using bromobenzene derivatives has been recently reported.[7]

$$\text{X-C}_6\text{H}_4\text{-N}_2{}^+\text{BF}_4{}^- \xrightarrow[\text{Pd(dba)}_2,\ \text{NaOAc}]{\text{CH}_2\text{=CH}_2} \text{X-C}_6\text{H}_4\text{-CH=CH}_2 + \text{N}_2 \qquad (1)$$

$\text{X} = \text{CH}_3$, CH_3O, CO_2Et, Cl, Br, and NO_2

Results and Discussion

TABLE 1. EFFECTS OF CONDITIONS IN THE REACTION OF BENZENEDIAZONIUM SALT

Temp	Time	Solvent/ml		Yield/%[a)]	
°C	min	$(\text{CH}_3)_2\text{CO}$	CH_2Cl_2	Styrene	By-product
0	120	0	100	20	15
0	120	100	0	20	0
r. t.	60	0	100	40	17
r. t.	60	100	0	40	0
r. t.	60	50	50	51	0

a) Analyzed by GLC for the product solution being passed through a silica-gel column. Internal standard; decane. The yield of the by-product was calculated as phenylbutene.

TABLE 2. YIELDS OF SUBSTITUTED STYRENES[a)]

Substituent	Yield/%	Substituent	Yield/%
o-CH_3	75	2,4,6-(CH_3)	3[b)]
m-CH_3	30	*p*-OCH_3	62
p-CH_3	61	*p*-CO_2CH_3	62
o-Cl	75	*p*-Br	14[c)]
m-Cl	78	*p*-NO_2	3[d)]
p-Cl	63	*o*-NO_2	—[d)]

a) See experimental section for the reaction conditions. b) Mesitylene was produced (18%). c) Ten mg of 4,4′-dibromostilbene was isolated. d) The main product was nitrobenzene (28—32%).

Reaction of Ethylene with Monosubstituted Benzenediazonium Salts. Although the reaction can be conducted either in aqueous or in non-aqueous media, this study was carried out in the latter system (acetone, dichloromethane or their mixture) by considering increased solubility of ethylene, and tetrafluoroborates (25 mmol) were reacted in the presence of bis(dibenzylideneacetone)palladium(0) [Pd(dba)$_2$] as the catalyst (0.5 mmol). Preliminary experiments with benzenediazonium salt revealed that the formation of stilbene, one of the possible by-products,[7] was very little (below 1%) under the pressure of ethylene of 6—8 atm in both solvents. However, in dichloromethane a considerable amount (30—40% of the product) of higher boiling product was produced (*vide infra*). The by-product did not form in acetone, but the total yield rather decreased (Table 1). Use of a mixture of the solvents(1:1 v/v) was found to give good yield, preventing the formation of the higher boiling product. The amount of the solvent influenced the formation of tarry material which had to be removed from the reaction mixture by chromatography on silica gel, and 150 ml of the solvent to 25 mmol of the diazonium salt was found enough to eliminate the treatment. Thus, the product (styrene and substituted styrenes) could be isolated by simple distillation of the reaction mixture in the presence of a small amount of *t*-butylcatechol. The results were summarized in Table 2. In most cases, substituted styrenes were obtained in good yields in 1 h and at room temperature (20—25 °C). The low yield of vinylmesitylene can be explained by steric effect of the two ortho substituents to suppress the formation of an arenepalladium species, a plausible active intermediate[1], in view of a good result obtained with *o*-methyl counterpart. Nitrobenzenediazonium salts are known to be good substrates in Meerwein arylation, which is generally considered to proceed by a radical process, but in the present reaction reduction to nitrobenzene was the principal course, though 11% of substitution product had been obtained in the reaction with cyclopentene.[1] Purity or stability of a diazonium salt seems to be one of the factors influencing the product yield in this procedure. Thus, *m*-methylbenzenediazonium tetrafluoroborate, which is much more sensitive to decomposition than the other isomers, gave a lower yield. Under the similar conditions naphthalene-2-diazonium salt gave 72% yield of 2-vinylnaphthalene, mp 64—66 °C (lit,[8] mp 65—66 °C).

Structure and Its Possible Route of Formation of the Higher-boiling Product. As mentioned above, a considerable amount of higher-boiling product consisted of at least three components was produced in the arylation with benzenediazonium salt in dichloromethane. Hydrogenation of the fraction over Raney nickel gave a mixture containing *s*-butylbenzene and *n*-butylbenzene in a ratio of 11 to 1. The main component of the by-product by preparative GLC was proved to be *trans*-2-phenylbut-2-ene by comparison with an authentic sample (GLC and NMR), but the remainders, probably a combination of 1-phenylbutenes and the other 2-phenylbutenes, could not be isolated in pure form to allow their structural confirmations. In order to obtain some informations suggesting a likely route to the phenylbutene, the reaction of ethylene was carried out in the presence of styrene (30 mmol) under the conditions used in the above reaction except for the use of a reduced amount of benzenediazonium salt (2 mmol). The amount of the salt is only two equivalents of the palladium catalyst (1 mmol), and was selected with the object of generating hydridopalladium species. No phenylbutenes was produced in acetone, while in dichloromethane there was obtained 32% yield of the higher-boiling product and neither stilbene nor any dimers of styrene were detected. The yield was based on styrene added and much over 100% based on the diazonium salt. On hydrogenation the product afforded an 8 : 1 mixture of *s*-butylbenzene and *n*-butylbenzene. The results show that the phenyl butenes produced by the reaction of styrene and ethylene under the catalysis of the hydridopalladium species. The difference between the behavior of the two solvents may be rationalized by the lability of the catalyst to collapse to palladium(0) under the present reaction conditions. In this connection, it is noted that 1-phenylbutenes were the principal products in the related palladium-catalyzed codimerization reported previously.[9,10]

Experimental

Materials. Pd(dba)$_2$ was prepared by the published method.[11] Substituted anilines were commercial origin and used as received. Most of the arylamines were diazotized in aqueous 1:1 mixture of HBF$_4$ (42%) with aq NaNO$_2$ at 0 °C. White crystals precipitated were washed with cold 5% HBF$_4$, cold methanol, and cold ether. The tetrafluoroborate was dried under vacuum and stored in a refrigerator until to be used. Diazotization of those with nitro and ethoxycarbonyl groups was performed in aq H$_2$SO$_4$, and the precipitates obtained by addition of HBF$_4$ (42%) to the mixture at 0 °C were treated as above. Authentic 1-phenylbut-1-ene and *trans*-2-phenylbut-2-ene were prepared by dehydration of 1-phenylbutan-1-ol and 2-phenylbutan-2-ol, respectively. The solvents were distilled and used without further purification.

General Procedure for the Arylation of Ethylene. A mixture of Pd(dba)$_2$ (0.29 g, 0.05 mmol), NaOAc(6.15 g, 75 mmol), and 150 ml of a mixed solvent (acetone and dichloromethane, 1:1) in a glass autoclave(300 ml) was cooled in a Dry Ice–acetone bath, and arenediazonium tetrafluoroborare (25 mmol) was added (addition at a higher temperature caused a reaction of the diazonium salt with the catalyst). After the air in the vessel was displaced with ethylene, the mixture was allowed to warm to room temperature. Ethylene was introduced to a pressure of 6—8 atm and the mixture was stirred for 1 h at room temperature. The reaction mixture was neutralized with aq sat NaHCO$_3$ soln and washed with aq sat NaCl soln, and dried (MgSO$_4$). The solution was placed in a distilling flask containing a small amount of *t*-butylcatechol and the solvent was removed. The residue was distilled under vacuum to give the product. After purity of the distillate was checked by GLC, its structure was confirmed by IR and NMR analyses ($\nu_{C=C}$; 1620—1640 cm^{-1}, δ_{C-H}; 900—910 cm^{-1}, and ABX pattern due to $-CH=CH_2$). Formation of stilbene was examined for the distillation residue by recrystallization or column chromatography (silica gel).

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