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Use of Aromatic Acid Anhydrides as Arylation Agents in the Heck Reaction

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Abstract—The use of bromide or chloride additives in styrene phenylation by benzoic acid anhydride results in an increase in catalytic activity and the yield of arylation products. The best results are obtained when LiCl is used. In this case, the yield of stilbene increases from 14 to 85%. Kinetics and regioselectivity of the reaction suggest that the reason for the activating effect of halides is the formation of benzoyl palladium halide complexes that readily eliminate CO in the form of an acidoligand.

INTRODUCTION

Recently, a method was proposed for the arylation of alkenes by anhydrides of aromatic acids (I), which does not require the use of bases in contrast to the Heck reaction (II). Reaction (I) has several advantages over other methods: the availability of reagents, the absence of bases in a reaction medium, and the possible reuse of acid formed in the reaction for anhydride synthesis. Note that the application of aromatic acid halides (III) is known [2], but this reaction also requires the presence of a base. That is, reaction (III) has the same limitation as the Heck reaction (II).

$$\begin{gathered}(\mathrm{ArCO})_2\mathrm{O} + \mathrm{H_2C{=}CHPh}\\ \xrightarrow[160\text{–}190^\circ\mathrm{C}]{\mathrm{Pd}^{2+}} \mathrm{ArCH{=}CHPh} + \mathrm{Ar(Ph)C{=}CH_2}\\ + \mathrm{ArCOOH} + \mathrm{CO}\uparrow,\end{gathered} \tag{I}$$

$$\begin{gathered}\mathrm{ArX} + \mathrm{H_2C{=}CHPh}\\ \xrightarrow[60\text{–}80^\circ\mathrm{C}]{\mathrm{Pd}^{2+},\ \mathrm{base}} \mathrm{ArCH{=}CHPh} + \mathrm{Ar(Ph)C{=}CH_2} + \mathrm{HX},\end{gathered} \tag{II}$$

$$\begin{gathered}\mathrm{ArCOX} + \mathrm{H_2C{=}CHPh}\\ \xrightarrow[100^\circ\mathrm{C}]{\mathrm{Pd}^{2+},\ \mathrm{base}} \mathrm{ArCH{=}CHPh} + \mathrm{Ar(Ph)C{=}CH_2}\\ + \mathrm{HX} + \mathrm{CO}\uparrow.\end{gathered} \tag{III}$$

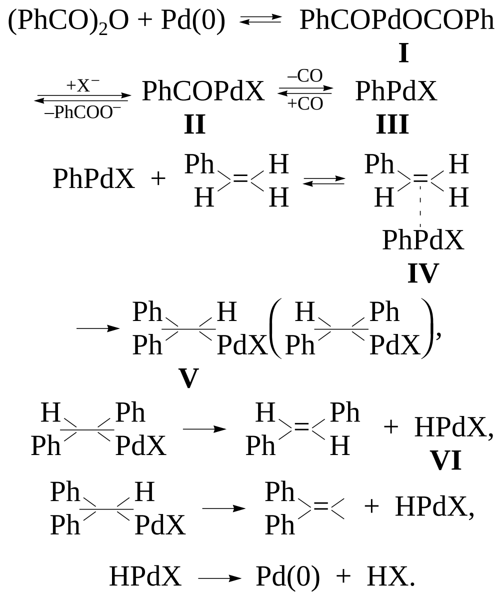
Although the new arylation method has advantages over the conventional Heck reaction (II) and reaction (III), the catalyst activity in reaction (I) is substantially lower. To reach acceptable yields of arylation products, it was necessary to increase the temperature to 160–190°C [1]. The goal of this study was to elucidate the mechanism of reaction (I) and develop a more efficient catalytic system.

EXPERIMENTAL

Styrene (10 mmol) and benzoic acid anhydride (10 mmol) were dissolved in 10 ml of *N*-methylpyrrolidone. The solution was added to a flask purged with argon, heated to a constant temperature of 140°C, and, equipped with a magnetic stirrer. Before adding the solution, the flask contained $\mathrm{PdCl_2}$ (0.16 mmol) and halides (1.6 mmol). The reaction was carried out until stilbene (the β-isomer) and 1,1-diphenylethylene (the α-isomer) stopped being formed. Analyses were carried out using GLC (with a HP-4890 chromatograph and 15-m columns packed with 15% polyphenylsilicon; 100–200°C; flame-ionization detector; and the internal standard was naphthalene). Reagents were purified according to standard procedures.

DISCUSSION

We found that CO accumulated during reaction (I) results in a substantial decrease in the rate and the yields of arylation products. The presence of CO had a negative effect on reactions (II) and (III) as well. In all cases, the reason for an activity drop in the medium of CO may be the formation of stable palladium complexes PhCOPdX (complex **II** in the scheme):



Scheme.

Styrene phenylation by benzoic anhydride

No. of run	Halide added	$w \times 10^2$, mol l^{-1} min^{-1}	Stilbene yield, %	β/α[a]
1	–	1.0	14	21
2	NaBr	2.4	44	23
3	NaCl	0.7	6	30
4	NaI	0	0	–
5	$(NBu_4)I$	0.3	6	13
6[b]	–	29.0	65	13
7	$(NMe_4)Br$	0.4	10	25
8[c]	–	5.8	85	33
9[c]	NaI	2.9	46	13
10[d]	KBr	0.9	10	20
11	LiBr	2.1	53	25
12	LiCl	5.8	85	33
13[e]	LiCl	1.1	60	30

[a] The ratio of stilbene to 1,1-diphenylethylene.

[b] PhI is an arylation agent; NBu_3 (1.3×10^{-2} mol) is a base.

[c] RhCOCl is an arylation agent; NBu_3 (1.3×10^{-2} mol) is a base.

[d] KBr is poorly solvable in *N*-methylpyrrolidone.

[e] Reaction was carried out at 100°C for 3 h.

Halide additives changed the nature of catalytically active complexes. Thus, the regioselectivity of styrene phenylation (the β-to-α ratio) strictly depended on the nature of the halide anion added (see the table). The addition of NaCl or LiCl (see the table, rows 3 and 12) affected the regioselectivity in a similar way. About the same β-to-α ratio was observed if benzoyl chloride was used as an arylation agent (see the table, row 8), because $(HNBu_3)Cl$ is formed via a noncatalytic pathway in reaction (III) and reactive chlorine anions are formed. Regioselectivity was independent of the choice of bromides (see the table, rows 2, 7, and 11) with the exception of KBr (row 10) for which the value of regioselectivity was somewhat lower due to the low solubility of KBr in *N*-methylpyrrolidone. If NBu_4I was added to reaction (I) (row 5), regioselectivity was the same as in the conventional Heck arylation with iodobenzene as an arylation agent (row 6), in which case $(HNBu_3)I$ was formed as a product, and as in the case of arylation by benzoyl chloride with a NaI additive (row 9). The dependence of the regioselectivity in reaction (I) on halide anion points to the presence of the step of benzoate acidoligand substitution in complex **I** (see the scheme) for a halide anion. This complex is formed by the oxidative addition of benzoic anhydride to Pd(0) (complex **II**) as in [3]. Further elimination of CO results in the catalytically active σ-aryl palladium complexes (complex **III**) that transform via usual steps of the Heck reaction [4] (complexes **III**–**VI**). Thus, different resistances of palladium benzoyl complexes containing different acidoligands (complex **II** in the scheme) to CO elimination can determine the catalytic activity in reaction (I).

This conclusion agrees with the fact that the cation of a salt used substantially affected the catalyst activity (see the table). The nature of the cation in water-free *N*-methylpyrrolidone is very important for acidoligand substitution. Thus, the presence of potassium and tetraalkylammonium cations instead of sodium cations proposed in [1] was accompanied by a decrease in the activity (see the table, rows 5, 7, and 10). By contrast, lithium halides, which we used in reaction (I) for the first time (rows 11–13), resulted in a substantial increase in the reaction rate and arylation product yield. The use of LiCl as an activator allowed us to increase the reaction rate by a factor of 2–3 and increase the product yield from 14 to 85%. The use of LiCl also enables a decrease in the process temperature to 140°C. At 100°C, the reaction occurred with rather high yields as well (row 13).

CONCLUSION

Thus, we proposed a new catalytic system for the arylation of alkenes by the anhydrides of aromatic acids involving LiCl as an activator and enabling high yields of arylation products. Kinetics and regioselectivity of the reaction are suggestive of the effect of halides on the catalytic activity due to the substitution of the acidoligand by a halide anion in the intermediate complexes of the catalytic cycle. One of the reasons for the activating effect of LiCl is the lower stability of catalytically inactive palladium benzoyl complexes formed in the reaction.

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