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Pd(II) Catalyzed Arylation of Oximes

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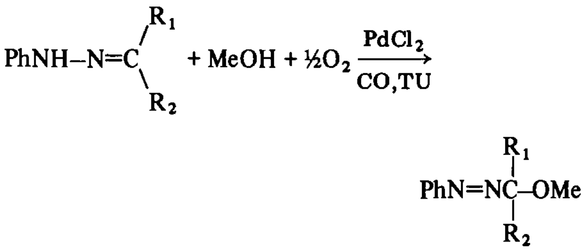
In spite of the large number of Pd(II) catalyzed oxidative reactions of olefins there are practically no corresponding reactions of –C=N– groups. In fact we are aware of only one, the oxidation of phenylhydrazones, which corresponds to an allylic oxidation of an olefin (TU = thiourea) [1]. In order



$$\mathrm{PhNH{-}N{=}C(R_1)(R_2)} + \mathrm{MeOH} + \tfrac{1}{2}\mathrm{O_2} \xrightarrow[\mathrm{CO,TU}]{\mathrm{PdCl_2}} \mathrm{PhN{=}NC(R_1)(R_2){-}OMe}$$

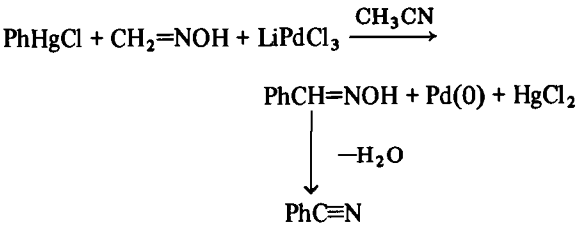
to see if –C=N– will undergo other Pd(II) catalyzed reactions we have studied the arylation of oximes, often called the 'Heck' reaction in olefin chemistry.

Formaldoxime did undergo the arylation reaction with phenylmercuric chloride but the isolated product was benzonitrile rather than benzaldehyde oxime. In addition, biphenyl formation was a serious side reaction. Results for several runs are given in Table I.

In the absence of reoxidant (Run 1) the yield of benzonitrile was slightly higher than biphenyl and in the absence of oxime (Run 2) the yield of biphenyl was almost quantitative, an expected result since th Pd(II) catalyzed coupling of aromatics is a known reaction [2].

Attempts to make the reaction catalytic in Pd(II) (Runs 3 and 4) were unsuccessful although the biphenyl formation did become catalytic. Probably the $CuCl_2$ complexes the formaldoxime thus making it less reactive. The low yield in Run 5 indicates the necessity of using LiOAc to form the oxime from its hydrochloride salt. Finally in Run 6 quinone was used as reoxidant in place of $CuCl_2$. The reaction was still not catalytic but the biphenyl formation was repressed.

The reaction must proceed by initial formation of benzaldehyde oxime which dehydrates under the reaction conditions to give benzonitrile. Pd(II) is reported to catalyze the dehydration of aldehyde oximes [3]. This dehydration must be quantitative



$$\mathrm{PhHgCl} + \mathrm{CH_2{=}NOH} + \mathrm{LiPdCl_3} \xrightarrow{\mathrm{CH_3CN}} \mathrm{PhCH{=}NOH} + \mathrm{Pd(0)} + \mathrm{HgCl_2}$$
$$\mathrm{PhCH{=}NOH} \xrightarrow{-\mathrm{H_2O}} \mathrm{PhC{\equiv}N}$$

under the reaction conditions since thin layer chromatography indicated no PhCH=NOH was present in the final reaction mixture.

Acetic acid and methanol were also tested as solvents. Acetic acid gave no PhC≡N but about a 35% yield of biphenyl while methanol gave 10% yields of both PhC≡N and Ph_2 with the remainder being methyl formate.

TABLE I. Arylation of Formaldoxime by PhHgCl in CH_3CN.

Run[a]	[$LiPdCl_3$]	[CH_2=NOH·HCl]	[$CuCl_2$]	Yield %[b]	
				PhCN	Ph_2
1	0.2	0.2	–	55	45
2	0.2	–	–	–	95
3	0.04	0.2	0.4	60	320
4	0.02	0.2	0.8	55	170
5	0.02	0.2	0.8	1.5	320
6	0.2	0.2	c	32	8

[a] All runs contain 0.4 *M* PhHgCl and all but Run 5 contain 0.4 *M* LiOAc. [b] Based on initial [Pd(II)] by VPC analysis. [c] Contains 0.2 *M* benzoquinone.

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Initial attempts to extend the reaction to other oximes were unsuccessful. Since substituted oximes would be even less reactive than formaldoxime coupling would be the main reaction with PhHgCl. Therefore CH_3HgCl, which has less tendency to couple, was tried with PhCH=NOH. A 55% yield of the oxime dehydration product, PhC≡N, was obtained. The reaction mixture was treated with thallic trinitrate to convert any oximes to carbonyl compounds [4]. VPC analysis of the treated reaction mixture indicated acetophenone was not present.

The present results indicate the –C=N– oxime bonds will react in a manner analogous to olefins but are less active so diphenyl formation becomes a serious side reaction. If the diphenyl formation could be repressed and the rates increased the palladium catalyzed reaction of –C=N– bonds could become a valuable synthetic reaction.

Experimental

Materials

The palladium(II) chloride and acetates were purchased from Engelhardt Inc. and the phenylmercuric chloride from BDH Chemicals. Formaldoxime and acetonitrile were obtained from Aldrich Chemical Co. The inorganic salts were of reagent grade.

Procedure

In a typical run, 10 ml of 0.2 *M* $LiPdCl_3$ solution was placed in a 25 ml erlenmeyer flask equipped with a magnetic stirring bar and to this was added 0.265 g (4.0 mmol) of lithium acetate, 0.163 g (2.0 mmol) of formaldoxime hydrochloride and 1.26 g (4.0 mmol) of phenylmercuric chloride. The reaction mixture was stirred at room temperature for 24 h then treated with zinc to precipitate the remaining palladium. The reaction mixture was analyzed by GLC on a Hewlett-Packard 5750 Research Chromatograph using a 6 ft × ¼ in. 20% Carbowax 20 M column on ABS (70–80 mesh) programmed from 100–225 °C at 10°/min. Helium flow rate was 60 ml/min. Initial identification of benzonitrile and biphenyl products was by comparative retention times while positive identification was by collection from the GLC stream and comparison of infrared spectra with authentic samples. Analysis was carried out by comparison of peak areas of products with those of standards run under the same conditions.

Acknowledgement

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