EFFECT OF METHYL IODIDE IN SYNTHESIS OF PHENYL ISOCYANATE BY CARBONYLATION OF NITROBENZENE IN PRESENCE OF $PdCl_2$ – PYRIDINE CATALYST

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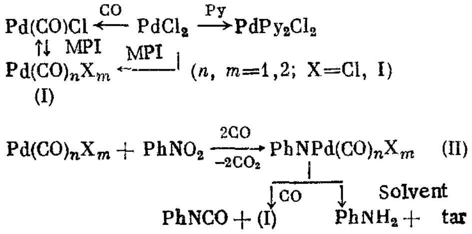
Phenyl isocyanate (PI) and its derivatives are intermediates in the production of herbicides. They are obtained by the catalytic carbonylation of nitro compounds in the presence of $PdCl_2$ under comparatively drastic conditions (190-220°C and a CO pressure of 700-900 atm) [1]. We found that the activation of $PdCl_2$ by pyridine (Py), which leads to the formation of homogeneous palladium complexes, makes it possible to lower the pressure to 50-100 atm [2]. In the present paper it was shown that activation of the $PdCl_2-Py$ catalyst by methyl iodide makes it possible to lower the temperature in the synthesis of PI to 160°. This opens up the possibility of developing low-temperature metal complexes, which are grafted on the support, as catalysts for the synthesis of phenyl isocyanates.

As can be seen from Fig. 1, in the presence of the $PdCl_2-Py$ (1 : 4) catalyst the maximum PI yield of 60% was obtained at 200°. When the temperature is lowered both the PI yield and the nitrobenzene (NB) conversion, respectively, decrease to 9 and 15% at 160°. Marked tarring occurs above 200°. The addition of MeI to the $PdCl_2-Py$ catalyst permits lowering the optimum synthesis temperature to 160° and enhances the dependence of the reaction on the temperature. Here the NB conversion increases from 0 to 100%, and the PI yield increases from 0 to 55%, when the temperature is raised from 145 to 160°.

In order to optimize the composition of the $PdCl_2-Py-MeI$ catalyst and ascertain the nature of the effect of MeI we studied the effect of the MeI : Py mole ratio. The reaction does not go at 160° without the Py and MeI, or in the presence of MeI alone (Table 1). With increase in the amount of MeI up to 75% both the NB conversion and the PI yield, respectively, increase to 100 and 90%. However, the selectivity of the reaction decreases with further increase in the amount of MeI. When the MeI and Py are mixed, N-methylpyridinium iodide (MPI) is formed in the solvent even before the start of reaction, which apparently activates the $PdCl_2$ by forming complexes (I) with it that are more active than $Pd(Py)_2Cl_2$, which is usually formed from $PdCl_2$ and Py in the absence of MeI [3].



$$\begin{tikzcd}
Pd(CO)Cl \arrow[d, shift left, "MPI"] & PdCl_2 \arrow[l, "CO"'] \arrow[r, "Py"] \arrow[dl, "MPI"] & PdPy_2Cl_2 \\
\underset{(I)}{Pd(CO)_nX_m} \arrow[u, shift left] & (n,\ m=1,2;\ X=Cl,\ I) &
\end{tikzcd}$$

$$\begin{tikzcd}
Pd(CO)_nX_m + PhNO_2 \arrow[r, "2CO", "-2CO_2"'] & PhNPd(CO)_nX_m\ (II) \arrow[d, "CO"'] \arrow[dr, "Solvent"] & \\
& PhNCO + (I) & PhNH_2 + tar
\end{tikzcd}$$

From the data in Table 1 it can be seen that both the PI yield and NB conversion remain practically constant when the $MeI-Py$ mixture is replaced by an equimolar amount of freshly prepared MPI, and decrease when the amount of MeI + Py is decreased. MPI also activates the $Pd(Py)_2Cl_2$ complex, which is completely inactive at 160°. When a fourfold weight excess of MPI is added to the $Pd(Py)_2Cl_2$ catalyst the PI yield increases to 33%, while the NB conversion increases to 45%. MeI does not activate $Pd(Py)_2Cl_2$, apparently because the coordination displacement of Py under the influence of the MeI and the formation of MPI in the reaction system fails to occur under the reaction conditions.

When the CO pressure is reduced from 100 to 25 atm the PI yield decreases from 55 to 7% at 160°, and to 0% at 200°, but aniline is formed in the latter case in 21% yield. A decrease in the selectivity of synthesizing PI and the formation of aniline when the CO pressure is decreased are understandable if it is assumed that the reduction of NB in the presence of a Pd catalyst proceeds via the step of forming the nitrene (II) complex [4] with the catalyst. When the CO pressure is reduced its concentration in the liquid phase decreases,

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TABLE 1. Effect of Catalyst Composition on Synthesis of PI by Carbonylation of NB [160°, 100 atm, amount of $PdCl_2$ 0.05 g, $Pd(Py)_2Cl_2$ 0.1 g]

Amount of MeI + Py, g	Amt. of MeI in mixture, mole %	Conversion of NB, %	Yield of PI, %
$PdCl_2$+Py+MeI			
0	0	0	0
0,4	0	15	9
0,4	40	100	50
0,4	50	100	59
0,4	75	100	80
0,4	80	95	76
0,4	90	98	40
0,4	95	11	5
0,4	100	0	0
0,4	*	100	56
0,2	50	30	12
$Pd(Py)_2Cl_2$+MeI			
0	0	0	0
0,3	100	0	0
0,4	*	45	33

*MPI salt.

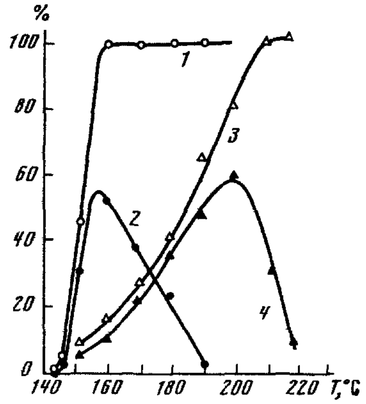

Fig. 1. Effect of temperature on conversion of NB (1, 3) and yield of PI (2, 4) in presence of catalysts: $PdCl_2$ + Py + MeI (1, 2) and $PdCl_2$ + Py (3, 4).

and consequently the nitrene that is adsorbed on the catalyst does not react with CO, but instead with the solvent to give aniline and tarry products.

EXPERIMENTAL

The experiments were run in a rotated 0.15-liter steel autoclave, into which were charged 10 ml of chlorobenzene (solvent), 2 ml of NB, 0.05 g of $PdCl_2$ or 0.1 g of $Pd(Py)_2Cl_2$, and 0-0.4 g of Py + MeI mixture. The autoclave was purged with CO, and CO pressure was raised to 100 atm, and the mixture was heated for 2 h. The reaction products were analyzed on an LKhM-8MD chromatograph (1-m long column packed with 5% XE-60 deposited on Chromaton W-AW-DMCS, 30-60 mesh, helium as the carrier gas, and a flow rate of 40 ml/min), with increase in the thermostat temperature in the range 50-250° at a rate of 12 deg/min. The quantitative composition of the reaction products was determined relative to chlorobenzene as the internal standard. The N-methylpyridinium iodide, isolated from the reaction mixture, was identified by comparing with the product obtained by counter synthesis.

CONCLUSIONS

When the $PdCl_2$–pyridine catalyst is activated by methyl iodide the optimum temperature for the synthesis of phenyl isocyanate by the carbonylation of nitrobenzene drops from 200 to 160°. The effect of the MeI consists in its reaction with the pyridine to give N-methylpyridinium iodide.

LITERATURE CITED

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