CATALYTIC SYNTHESIS OF AROMATIC MONOISOCYANATES FROM NITRO COMPOUNDS AND CARBON MONOXIDE

B. K. Nefedov and V. I. Manov-Yuvenskii UDC 542.97:547.551.43:547.546:546.262.3-31

Aromatic monoisocyanates are valuable industrial raw materials for the production of pesticides. They are generally synthesized by phosgenation of amines. A new and potentially useful method of preparing aromatic isocyanates is the catalytic carbonylation of nitro compounds with carbon monoxide. The catalysts are palladium or rhodium compounds, which are active at CO pressures of 700-900 atm [1, 2]. However, under these conditions the yields of phenyl isocyanates do not exceed 30-40%. Attempts have been made to activate $PdCl_2$ [3] and $PdCl_3$ [4] with vanadium pentoxide. In this case nitrobenzene can be carbonylated under CO pressures of 70-120 atm, but the catalyst requires prolonged pretreatment with CO under pressure. We have shown [5] that the activity of $PdCl_2$ in the carbonylation of dinitro compounds is increased by activation with pyridine and with oxides of some transition metals. We have developed this work by making a detailed study of the conditions of the synthesis of aromatic monoisocyanates from nitro compounds and CO in the presence of $PdCl_2$ promoted with pyridine and transition-metal oxides.

Carbonylation of Nitrobenzene. The conversion of nitrobenzene on $PdCl_2$ with added pyridine (1 : 8) at 200°C and a CO pressure of 100 atm in chlorobenzene is 80% and the yield of phenyl isocyanate 60% (Table 1). Addition of the oxides V_2O_5 or MoO_3 to the reaction system increases the conversion of nitrobenzene to ∿100% and the yield of the isocyanate to 80%. Conversely, WO_3 reduces the conversion of nitrobenzene to 60% and the yield of phenyl isocyanate to 57%, while simultaneously increasing the selectivity to 95%; addition of Ta_2O_5 reduces the yield of the isocyanate to 66% but does not affect the selectivity of carbonylation. Thus the most active catalyst for the carbonylation of nitrobenzene to phenyl isocyanate is $PdCl_2$ promoted with pyridine and V_2O_5 or MoO_3 (molar ratio 1 : 8 : 1), in the presence of which the reaction gives a high yield of the desired product (∿ 70%) even under a pressure of 50 atm (Fig. 1). Without the addition of a transition-metal oxide the activity of the $PdCl_2$ + pyridine catalyst under a CO pressure of less than 100 atm is two to three times lower. The $PdCl_2$ + pyridine + transition-metal oxide catalyst does not require pretreatment with CO.

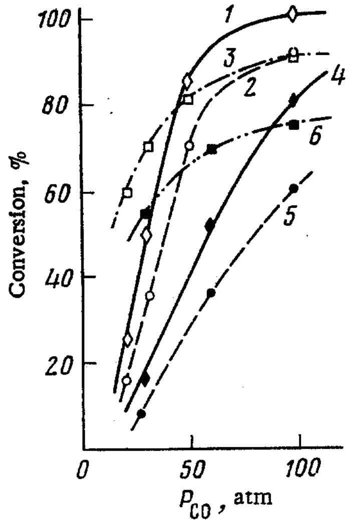

Fig. 1. Effect of pressure on 1, 4) the conversion of nitrobenzene, 2, 5) the yield of phenyl isocyanate, and 3, 6) selectivity of its formation on 1, 2, 3) $PdCl_2$ + pyridine + MoO_3 and 4, 5, 6) $PdCl_2$ + pyridine at 200°C.

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TABLE 1. Carbonylation of Aromatic Mononitro Compounds [200°C, P_{CO} 100 atm, reaction time 2 h, catalyst $PdCl_2$ + pyridine + transition-metal oxide (1 : 8 : 1), $PdCl_2$: nitro compound = 1 : 40]

Reaction indices, %	Metal oxide					
	—	V_2O_5	Nb_2O_5	Ta_2O_5	MoO_3	WO_3
	Nitrobenzene					
Conversion of nitro compound	80	100	75	66	100	60
Yield of isocyanate	60	80	73	50	80	57
Selectivity	75	80	97	76	80	95
	p-Nitrotoluene					
Conversion of nitro compound	51	100	47	69	100	66
Yield of isocyanate	20	82	45	37	90	55
Selectivity	40	82	95	54	90	83
	p-Chloronitrobenzene					
Conversion of nitro compound	72	100	65	56	100	60
Yield of isocyanate	27	90	43	50	73	57
Selectivity	38	90	67	90	73	95

Carbonylation of Nitrotoluenes. Table 1 shows that on $PdCl_2$ promoted only by pyridine the conversion of p-nitrotoluene is only 51% and the yield of p-methylphenyl isocyanate is 20% at 200°C and a CO pressure of 100 atm. Addition of oxides of V, Mo, Nb, W, or Ta to the reaction system increases the yield of the isocyanate to 37-90% and the selectivity of its formation from 40 to 54-90%. The best catalyst for the carbonylation of nitrotoluenes is $PdCl_2$ + pyridine + MoO_3 (or V_2O_5), over which at 200-210°C and a CO pressure of 50-100 atm the yields of o-, m-, and p-methylphenyl isocyanates are 78-84, 85-89, and 80-90%, respectively, and the conversion of the nitro compound is 100% (Table 2). Reduction in the reaction temperature to 205°C at a pressure of 50 atm cuts the nitrotoluene conversion to 66-86% while scarcely affecting the selectivity.

Carbonylation of Halogen-Substituted Nitrobenzenes. In the presence of $PdCl_2$ with added pyridine (200°C and P_{CO} 100 atm) the conversion of p-chloronitrobenzene is 72% and the yield of p-chlorophenyl isocyanate 27% (Table 1). Promotion of the $PdCl_2$ + pyridine catalyst with V_2O_5 or MoO_3 increases the yield of the isocyanate to 73-90%. Addition of Nb, Ta, or W oxides reduces the conversion of chloronitrobenzene to 56-65% while increasing the selectivity of formation of the isocyanate by a factor of 1.8-2.5. The best catalyst for the carbonylation of chlorine-substituted nitrobenzenes is $PdCl_2$ + pyridine + V_2O_5 (or V_2O_4) (molar ratio 1 : 8 : 1), on which the conversion of o-, m-, p-chloro-, and 3,4-dichloronitrobenzene is 80-100% and the yield of the isocyanate is 70-90% at 200°C and a CO pressure of 100 atm (Table 3). Comparison of the reactivity of p-chloro-, p-bromo-, and o-iodonitrobenzenes reveals that the yield of the isocyanate diminishes in the same order as the strength of the C—Hal bond, $Cl > Br \gg I$. Increase in the CO pressure to 150 atm raises the yield of p-bromophenyl isocyanate by only 8%.

We have thus synthesized aromatic monoisocyanates by carbonylation of nitro compounds with CO under comparatively mild conditions in the presence of $PdCl_2$ + pyridine + vanadium or molybdenum oxide. Nitrobenzene and chlorine-substituted nitrobenzenes form the isocyanates at 200°C and a CO pressure of 100 atm in 70-90% yield with a selectivity of 80-90%. Nitrotoluenes are carbonylated to methylphenyl isocyanates in high yield (78-85%) even under a CO pressure of 50 atm. The position of the CH_3 group or chlorine atom in the phenyl ring only slightly affects the reactivity of the nitro compound.

Two consecutive reactions are apparently involved in the carbonylation of nitro compounds to isocyanates: reduction of the NO_2 group to a nitrene adsorbed on the catalyst ($PdCl_2$) and reaction of this nitrene with CO. However, without promoters $PdCl_2$ is relatively inactive under low pressures of CO. The organic promoter, pyridine, increases the activity of $PdCl_2$ but carbonylation is then insufficiently selective. The third component of the catalyst, vanadium or molybdenum oxide, increases not only the rate of reduction of the nitro group but also that of formation of the isocyanate and may have a stabilizing effect by inhibiting decomposition and polymerization of the isocyanate under the reaction conditions.

TABLE 2. Carbonylation of Nitrotoluenes [catalyst $PdCl_2$ + pyridine + MoO_3 (1 : 8 : 1), reaction time 2 h, $PdCl_2$: nitro compound = 1 : 40]*

Nitro compound	200°, 100 atm			205°, 50 atm			210°, 50 atm		
	C	Y	S	C	Y	S	C	Y	S
o-Nitrotoluene	100	84	84	76	62	81	100	78	78
m-Nitrotoluene	100	89	89	66	61	93	100	85	85
p-Nitrotoluene	100	90	90	86	76	89	100	80	80

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*C is the conversion of the nitro compound, %; Y, the yield of the isocyanate, %; and S, the selectivity, %.

TABLE 3. Carbonylation of Halogen-Substituted Nitrobenzenes [200°C, P_{CO} 100 atm, catalyst $PdCl_2$ + pyridine + oxide (1 : 8 : 1), reaction time 2 h, $PdCl_2$: nitro compound = 1 : 40]

Nitro compound	Catalyst					
	$PdCl_2$ + pyridine + V_2O_5			$PdCl_2$ + pyridine + V_2O_4		
	C	Y	S	C	Y	S
o-Chloronitrobenzene	88	78	89	100	90	90
m-Chloronitrobenzene	100	70	70	100	85	85
p-Chloronitrobenzene	100	90	90	100	92	92
p-Bromonitrobenzene	75	32	43	–	–	–
o-Iodonitrobenzene	100	Trace	–	–	–	–
3,4-Dichloronitrobenzene	–	–	–	99	83	94

EXPERIMENTAL

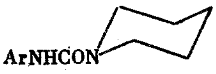
Carbonylation was carried out in a 0.15-liter steel rotary autoclave. In each run the autoclave was charged with $PdCl_2$ (0.05 g), the metal oxide (0.05 g), and a 20% solution (10 ml) of the nitro compound in chlorobenzene containing 2% pyridine. After purging of the autoclave with CO, the CO pressure was raised to 50-100 atm, and the reaction mixture was heated at a preset temperature for 2 h. The reaction products were separated from the catalyst and analyzed by GLC on an LKhM-8MD chromatograph (katharometer, 1 m × 3 mm column, 5% XE-60 on Chromaton N-AW-DMCS 0.16-0.2 mm, carrier gas helium, 40 ml/min) with temperature programming (from 60°C at a rate of 12°C/min). Reaction products were identified by comparison of retention times with those of authentic samples of the pure compounds. The quantitative composition of the reaction mixture was calculated relative to an internal standard, chlorobenzene. The starting nitro compounds were synthesized by published methods [6]. The synthetic isocyanates were isolated by rectification and characterized by their IR spectra, elemental analysis, and via their derivatives – the unsymmetrical N,N'-derivatives of urea, prepared by reaction with piperidine. The properties of the aryl isocyanates and N-aryl-N'-pentamethylene ureas are summarized in Table 4. The presence of the N=C=O and NCON groups in the synthetic aryl isocyanates and N-aryl-N'-pentamentyleneureas was confirmed by the bands at 2275-2280 (ν_{NCO}), 1600-1610, and 1640-1655 cm^{-1} (ν_{NCON}) in their IR Spectra.

CONCLUSIONS

1. We have synthesized aromatic monoisocyanates in 78-90% yield by carbonylation of nitro compounds with carbon monoxide in the presence of a $PdCl_2$ + pyridine + V_2O_5, V_2O_4, or MoO_3 catalyst at 200°C and a CO pressure of 50-100 atm.

2. The reactivity of methyl- and chlorine-substituted nitrobenzenes depends only slightly on the number and position of the substituents in the phenyl ring.

TABLE 4. Properties of Aryl Isocyanates and N-Aryl-N'-pentamethyleneureas,



Aryl isocyanate	bp, °C (p, mm Hg)	N-Aryl-N'-pentamethyleneurea					
		Ar	mp, °C	found/calculated, %			
				C	H	N	Hal
C_6H_5NCO	68 (30)	C_6H_5	167	70,58/70,01	7,84/8,24	13,72/14,13	–
o-$CH_3C_6H_4NCO$	91 (30)	o-$CH_3C_6H_4$	117–118	71,56/71,40	8,26/8,27	12,82/12,70	–
m-$CH_3C_6H_4NCO$	90 (30)	–	–	–	–	–	–
p-$CH_3C_6H_4NCO$	90 (29)	p-$CH_3C_6H_4$	149–150	71,56/71,88	8,26/8,26	12,84/13,00	–
o-ClC_6H_4NCO *	101 (25)	–	–	54,72/54,58	2,60/2,65	9,12/9,35	23,13/22,96
m-ClC_6H_4NCO	100 (25)	m-ClC_6H_4	152–153	60,50/60,60	6,30/6,26	11,76/11,69	14,71/14,81
p-ClC_6H_4NCO	103 (26)	p-ClC_6H_4	181–182	60,50/60,60	6,30/6,26	11,76/11,63	14,71/14,81
3,4-$Cl_2C_6H_3NCO$	–	3,4-$Cl_2C_6H_3$	173–174	52,75/52,73	5,13/5,20	10,26/10,50	26,00/26,20
p-BrC_6H_4NCO	–	p-BrC_6H_4	191–192	50,88/50,70	5,30/5,40	–/–	28,27/27,80

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*Results of elemental analysis for o-chlorophenyl isocyanate.

3. The reactivity of halogen-substituted nitrobenzenes diminishes in the order Cl > Br ≫ I.

LITERATURE CITED

1. W. W. Prichard, French Patent No. 1570333 (1969); Chem. Abs., 72, 100263 (1970).
2. Dutch Patent No. 6513844 (1966); Chem. Abs., 65, 20056 (1966).
3. E. Kober, W. Schnabel, and H. Hammond, French Patent No. 1558898 (1969); Chem. Abs., 72, 43191 (1970).
4. E. Kober, W. Schnabel, and T. Kraus, French Patent No. 155896 (1969); Chem. Abs., 72, 43190 (1970).
5. B. K. Nefedov, V. I. Manov-Yuvenskii, Kh. O. Khoshdurdyev, and S. S. Novikov, Dokl. Akad. Nauk SSSR, 232, 1088 (1977).
6. E. Yu. Orlova, Chemistry and Technology of Explosives [in Russian], Khimiya, Leningrad (1973), p. 310.