LITERATURE CITED

1. N. I. Ershov, Huang Ch'ong Yem, and Ya. T. Éidus, Izv. Akad. Nauk SSSR, Ser. Khim., 894 (1974).
2. Ya. T. Éidus, N. I. Ershov, and Huang Ch'ong Yem, Izv. Akad. Nauk SSSR, Ser. Khim., 1876 (1974).
3. Ya. T. Éidus, A. L. Lapidus, and V. I. Mashinskii, Izv. Akad. Nauk SSSR, Ser. Khim., 1307 (1976).
4. N. M. Popova, L. V. Babenkova, and G. A. Savenkova, The Adsorption and Interaction of Gases on Group VIII Metals [in Russian], Nauka, Alma-Ata (1979), p. 218.

SYNTHESIS OF ISOCYANATES BY THE CARBONYLATION OF AROMATIC NITRO COMPOUNDS, AZOBENZENE, AND AZOXYBENZENE ON PALLADIUM CATALYSTS CONTAINING MOLYBDENUM AND VANADIUM

A. L. Lapidus, V. I. Manov-Yuvenskii,
and K. B. Petrovskii

UDC 542.97:547.546:547.556.3

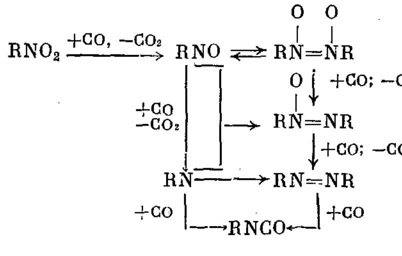
Aryl isocyanates are important intermediates in the industrial production of polyurethanes and pesticides and may be obtained by the catalytic carbonylation of aromatic nitro compounds by carbon monoxide [1].

In the presence of catalytic amounts of $Fe(CO)_5$, mono- and polynitro derivatives of benzene are reduced by carbon monoxide to azo compounds [2]. Nitroso complexes $[Fe(CO)_3RNO]_2$ and $Fe(CO)_3RNO$ [3, 4] are separated during the reduction of nitro compounds by stoichiometric amounts of iron carbonyl upon UV and gamma irradiation, while nitrene complexes $(RN)_2Fe_2(CO)_6$, $(RN)_2Fe_2(CO)_7$, and $(RN)_2Fe_3(CO)_9$ are formed in this case upon heating [5, 6].

Nitrenes not bound in complexes formed upon the decomposition of azides react with CO under pressure to yield azo compounds and isocyanates [7-9]. Azo compounds are capable of reacting with CO to form isocyanates either without catalyst or with typical catalysts for the carbonylation of nitro and nitroso compounds as Pd, Rh, Ru on Al_2O_3, C, $BaSO_4$, $CaCO_3$, palladium black, $PdCl_2$, and $Co_2(CO)_8$ [10-14].

We might expect that isocyanates are obtained either upon the reduction of nitro compounds to nitrenes and its subsequent carbonylation or by the carbonylation of azo compounds which may form by two pathways (see Scheme 1): by recombination of nitrenes or reduction of azoxy compounds. The aim of the present work was determination of which of these two pathways is realized under CO carbonylation conditions. Since azo compounds under the carbonylation conditions are extremely reactive and readily undergo carbonylation into isocyanate and other nitrogen-containing products, the mechanism may be clarified by using catalyst additives which slow the conversion of azo compounds and permit their isolation and identification.

Scheme 1



The basis of most of the known catalysts for the synthesis of isocyanates by the carbonylation of nitro compounds is the $PdCl_2$–pyridine (Py) system. In the presence of this system, isocyanates are readily formed both from azobenzene (AB) and nitrobenzene (NB) (Tables 1 and 2). We have found that the addition of $Ca(VO_3)_2$

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2743-2746, December, 1981. Original article submitted April 23, 1981.

0568-5230/81/3012-2282$07.50

TABLE 1. The Effect of $Ca(VO_3)_2$ Added to the $PdCl_2$–Py Catalyst on the Conversion of Nitrobenzene, Azobenzene, and Azoxybenzene over 1 h at 453°K with 10 MPa Initial CO Pressure

Starting compound*	Additive†	Conversion, %			Yield, %		
		nitrobenzene	azobenzene	azoxybenzene	phenylisocyanate	aniline	azobenzene
NB	+	57	–	–	36	0	0
NB	+	83	–	–	62	3	0
AB	–	–	84	–	47	4	–
AB	+	–	10	–	6	3	–
NB+AB	–	30	30	–	39	9	–
NB+AB	+	99	0	–	71	5	–
AOB	–	–	–	99	27	3	45
AOB	+	–	–	99	21	2	58
NB+AOB	–	19	–	98	37	5	42
NB+AOB	+	58	–	92	43	4	65

*AOB) azoxybenzene.

†The "+" sign indicates "with additive," while the "–" sign indicates "without additive."

TABLE 2. Effect of Additives on the Conversions of Azobenzene, Nitrobenzene, and Nitrotoluenes (10 MPa initial CO pressure, 453°K)

Reaction time, min	Starting compound*	Additive	Conversion, %				Yield, %		
			4-nitrotoluene	3-nitrotoluene	nitrobenzene	azobenzene	4-methylphenyl isocyanate	3-methylphenyl isocyanate	phenyl isocyanate
60	NB	–	–	–	57	–	–	–	36
60	»	$CdMoO_4$	–	–	94	–	–	–	21
60	»	$(NH_4)_2MoO_4$	–	–	97	–	–	–	27
30	»	H_2MoO_4	–	–	99	–	–	–	59
60	»	H_2MoO_4	–	–	100	–	–	–	25
60	»	$Pd(VO_3)_2$	–	–	100	–	–	–	42
60	»	$Al(VO_3)_3$	–	–	81	–	–	–	61
60	»	$Ca(VO_3)_2$	–	–	83	–	–	–	62
30	4-MNT+AB	–	25	–	–	42	13	–	15
30	»	MoO_3	79	–	–	8	45	–	5
30	»	H_2MoO_4	100	–	–	17	48	–	9
30	»	$(NH_4)_2MoO_4$	98	–	–	31	36	–	9
30	»	$CdMoO_4$	57	–	–	0	18	–	0
30	3-MNT+AB	–	–	30	–	39	–	13	14
30	»	V_2O_5	–	48	–	18	–	35	8
30	»	$Pb(VO_3)_2$	–	58	–	2	–	32	1
30	»	$Ca(VO_3)_2$	–	53	–	10	–	34	3

*4-MNT) 4-mononitrotoluene; 3-MNT) 3-mononitrotoluene.

to the $PdCl_2$–Py system leads to an increase in the conversion of NB from 57 to 83% and of the yield of phenyl isocyanate (PI) from 36 to 62% but to a decrease in the conversion of AB by a factor of 8 relative to the experiment without additive. In the carbonylation of a 2:1 mixture of NB and AB in the presence of added $Ca(VO_3)_2$, the conversion of NB increases from 30 to 99%, while the conversion of AB is reduced from 30 to 0% (see Table 1). The addition of $Ca(VO_3)_2$ does not affect the extent of reduction of azoxybenzene but blocks the subsequent conversions of AB. We also studied the effect of addition of V_2O_5, $Al(VO_3)_3$, $Pb(VO_3)_2$, MoO_3, H_2MoO_4, $(NH_4)_2MoO_4$, and $CdMoO_4$, which are inactive in the absence of palladium compounds on the carbonylation of nitro compounds and AB. These additives lead to an increase in the conversion of NB from 57 to 81-100% (see Table 2). The addition of MoO_3, H_2MoO_4, $(NH_4)_2MoO_4$, and $CdMoO_4$ produce an increase in the conversion of 4-nitrotoluene from 25 to 57-100% and concurrent decrease in the AB conversion from 42 to 0-31%. Additives of V_2O_5 and $Pb(VO_3)_2$ increase the conversion of 3-nitrotoluene from 30 to 48-58% and decrease in the conversion of AB from 39 to 2-18%. Thus, vanadium and molybdenum compounds increase the carbonylation of nitro compounds and hinder the carbonylation of AB on palladium catalysts to a different extent.

Azo compounds were not found in the reaction products of any of the carbonylation reactions of NB and 2-, 3-, and 4-mononitrotoluenes in the presence of the $PdCl_2$–Py system either with or without the vanadium and molybdenum compounds studied.

Hence, nitro compounds are converted to isocyanates on palladium catalysts containing vanadium and molybdenum compounds bypassing the formation and carbonylation of azo compounds, apparently as a result of the direct carbonylation of nitrenes. The carbonylation of azoxybenzene is accompanied by its reduction to AB.

EXPERIMENTAL

The carbonylation was carried out in a 0.15-liter steel autoclave, in which 2 ml ($19.5 \cdot 10^{-3}$ mole) nitrobenzene and/or an equivalent amount of nitrotoluene, azobenzene, and azoxybenzene (see Tables 1 and 2), 10 ml chlorobenzene, 50 mg $PdCl_2$ ($2.8 \cdot 10^{-4}$ mole), 200 mg ($2.5 \cdot 10^{-3}$ mole) pyridine, and an additive containing $4.7 \cdot 10^{-4}$ g-atom molybdenum or vanadium were charged. CO was bubbled into the autoclave and heated up to 453°K and 10 MPa CO pressure over 0.5-1.0 h, then cooled, and the solution was analyzed by gas–liquid chromatography using our previous procedure [1].

CONCLUSIONS

1. Nitro compounds are converted by the action of CO into isocyanates on palladium catalysts containing vanadium and molybdenum compounds bypassing the formation and carbonylation azo compounds, apparently as a result of the direct carbonylation of nitrenes.

2. The addition of $Ca(VO_3)_2$, $Al(VO_3)_3$, $Pb(VO_3)_2$, H_2MoO_4, $(NH_4)_2MoO_4$, and $CdMoO_4$ to the $PdCl_2$–pyridine catalytic system promote the carbonylation of nitro compounds and inhibit the conversions of azo compounds by the action of CO.

LITERATURE CITED

1. V. I. Manov-Yuvenskii, B. A. Redoshkin, B. K. Nefedov, and G. P. Belyaeva, Izv. Akad. Nauk SSSR, Ser. Khim., 133 (1980).
2. J. E. Kmiecik, J. Org. Chem., 30, No. 6, 2014 (1965).
3. E. K. Gustorf and M.-J. Jun, Z. Naturforsch., 20b, 521 (1965).
4. E. K. Gustorf, M. C. Henry, R. E. Sacher, and C. Z. DiPietro, Z. Naturforsch., 20b, 1152 (1966).
5. H. Alper, Inorg. Chem., 11, 976 (1972).
6. J. M. Landesberg, L. Katz, and C. Olsen, J. Org. Chem., 37, 930 (1972).
7. R. P. Bennett and W. B. Hardy, J. Am. Chem. Soc., 90, 3295 (1968).
8. W. J. Chambers, C. W. Tulloch, and D. D. Coffman, J. Am. Chem. Soc., 84, 2337 (1962).
9. F. J. Z. Weigart, J. Org. Chem., 38, 1316 (1973).
10. W. B. Hardy, R. P. Bennett, and S. M. Davis, French Patent No. 92,664 (1968); Chem. Abstr., 71, 321 (101603v) (1969).
11. S. I. Trotz, T. J. Hurley, Jr., and E. H. Kober, US Patent No. 3,660,458 (1972): Chem. Abstr., 77, 465 (61537s) (1972).
12. Netherlands Patent No. 6,410,490 (1964): Chem. Abstr., 62, 384 (14571) (1965).
13. T. Yamahara, T. Deguchi, M. Usui, H. Yoshihara, and K. Hirose, West German Declaration No. 2,334,532 (1974); Chem. Abstr., 80, 371 (95469y) (1974).
14. T. Yamahara and M. Usui, Japanese Patent No. 74,139,943 (1974); Chem. Abstr., 82, 557 (155776z) (1975).