BRIEF COMMUNICATIONS

CATALYTIC SYSTEMS FOR REDUCTION OF NITRO COMPOUNDS INVOLVING CERIUM COMPLEXES WITH ORGANIC LIGANDS

A. D. Shebaldova, T. A. Bol'shinskova,
V. N. Kravtsova, M. L. Khidelkel',
V. P. Khramov, T. V. Zakharova,
A. V. Lapitskaya, and S. B. Pirkes

UDC 542.941.7:547.546

Catalytic systems, composed of a catalyst and a compound that respectively function as an H_2 activator and an electron-transfer agent, increase both the rate and specificity of reducing nitrobenzene [1-3]. As the electron-transfer agent it is expedient to use Ce complexes [4, 5] with organic ligands. In [6] it was shown that Pd/C and Pt/C, containing 1% of the metal, are most effective as the H_2 activator for the reduction of NO_2 groups.

The hydrogenation of aromatic nitro compounds on 1% Pd/C in the presence of Ce complexes with organic ligands was studied in the present paper (Table 1); Ce complexes were not used previously in similar processes.

As a rule, the addition of Ce complexes to a catalytic system increases the rate of hydrogenating $C_6H_5NO_2$ when compared with 1% Pd/C (Fig. 1). The complexes with nitrilotrimethylphosphonic acid (III) and (IV) exhibit the highest activity, in whose presence the initial hydrogenation rate increases threefold.

An increase in the temperature affects the rate of H_2 absorption. Thus, for 1% Pd/C + (III) a change in the temperature from 25 to 50°C doubles the reduction rate during the absorption of the first mole of H_2.

In a neutral or weakly acid medium the NO_2 group is usually reduced in the following sequence:

$$C_6H_5NO_2 \xrightarrow{H_2} C_6H_5NO \xrightarrow{H_2} C_6H_5NHOH \xrightarrow{H_2} C_6H_5NH_2$$

In the hydrogenation $C_6H_5NO_2$ on heterogeneous Pt and Pd catalysts the nitrosobenzene (NSB) and phenylhydroxylamine (PHA) do not accumulate, and instead they are reduced to aniline as fast as they are formed.

In the presence of complexes (II), (VI), and (VII) the amount of PHA after the absorption of 2 moles of H_2 is 36-40%; with further hydrogenation the PHA is converted to aniline. The coordination of Ce with the oxygen of the OH group is characteristic for the enumerated complexes. In the case of phosphonates (III)-(V) the formation of PHA after the absorption of 2 moles of H_2 is not observed, and the hydrogenation proceeds to aniline.

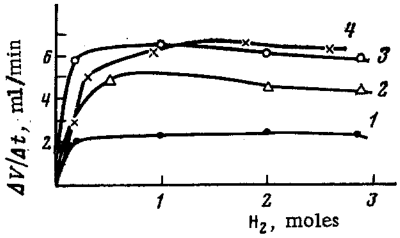
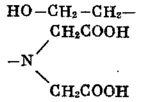
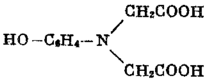
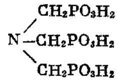
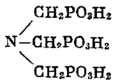
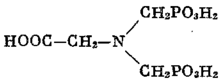
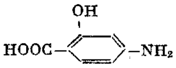
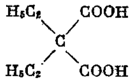
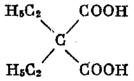
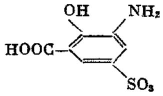


Fig. 1. Hydrogenation of nitrobenzene in presence of catalytic systems: 1) 1% Pd/C; 2) 1% Pd/C + (II); 3) 1% Pd/C + (III); 4) 1% Pd/C + (IV).

Branch of Institute of Chemical Physics, Academy of Sciences of the USSR, Chernogolovka. N. G. Chernyshevskii Saratov State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1104-1107, May, 1979. Original article submitted May 26, 1978.

0568-5230/79/2805-1032$07.50

TABLE 1. Hydrogenation of $C_6H_5NO_2$ in Presence of Catalytic Systems That Contain Ce Complexes (1% Pd/C, H_2 = 1 atm, and solvent = 2:1 ethanol–water)

Compound	Ce complexes	Ligand	v_{init}, ml/min	PHA,* %
(I)	Hydroxyethyliminodiacetate $[Ce(HA)_2]NO_3 \cdot 4H_2O$†		2,8	10
(II)	o-Hydroxyphenyliminodiacetate $[Ce(C_{10}H_8O_4N)_2]NO_3 \cdot 2H_2O$ ‡		5,0	40
(III)	Nitrilotrimethylphosphonate (polynuclear) $[Ce_2(HA)]NO_3 \cdot 5H_2O$		6,0	–
(IV)	Nitrilotrimethylphosphonate (mononuclear) $Ce(H_3A) \cdot 5H_2O$		6,5	16
(V)	Glycinebismethylphosphonate $Ce(H_2A) \cdot 4H_2O$		4,6	–
(VI)	p-Aminosalicylate $CeA_3 \cdot H_2O$		3,8	37,6
(VII)	p-Aminobenzoate $CeA_3 \cdot H_2O$		2,2	37,6
(VIII)	Diethylmalonate $Ce_2A_3 \cdot 4H_2O$		1,9	30
(IX)	Diethylmalonate (acid) $CeHA_2 \cdot H_2O$		3,5	16
(X)	3-Amino-5-sulfosalicylate $Ce_2A_3 \cdot 13H_2O$		4,0	–

---

*PHA = phenylhydroxylamine. The other product is aniline. The composition of the products is given after the absorption of 2 moles of H_2.

†H_nA is the acid moiety of the ligand; the structure of the complexes is discussed in [7].

‡The ligand retains the betaine ring in the complex.

To ascertain the effect of the nature and position of the substituents in the benzene ring on the hydrogenation rate a study was made of the reduction of the isomeric nitrotoluenes, dinitrobenzenes, nitrophenol, nitroaniline, and nitrobenzoic acid (Table 2).

The insertion of a substituent in the nitrobenzene molecule has practically no effect on the reduction rate in the presence of 1% Pd/C (Fig. 2, curve 1). On the catalytic system 1% Pd/C + (III) the nitrobenzene derivatives with electron-acceptor substituents are reduced at a faster rate than nitrobenzene. The presence of electron-donor groups leads to a decrease in the reduction rate: p-NO_2, p-COOH, p-OH > H > o-CH_3, m-CH_3, p-NH_2, p-Cl. A linear relation exists between the absorption rates of H_2 during the hydrogenation of nitrocompounds and the corresponding Hammett constants [8] (see Fig. 2).

EXPERIMENTAL

The synthesis of complexes (I)-(V), (VII), (VIII), and (IX) was described in [7, 9-11]. Complexes (VI) and (X) were obtained by pouring together water solutions of equivalent amounts of the ammonium (sodium) salt of the appropriate acid and soluble Ce salt at pH 5-6. The complexes crystallized on standing for several days. Their structure was confirmed by the elemental analysis and IR spectroscopy data.

Ce p-Aminosalicylate (VI). Found: C 41.09; H 3.26; N 6.69; Ce 22.61%. $C_{21}H_{18}N_3O_9Ce$. Calculated: C 41.04; H 3.25; N 6.84; Ce 22.81%. Infrared spectrum (ν, cm^{-1}): 3480, 3380 (NH_2), 1510, 1420 (COO^-).

TABLE 2. Effect of Nature and Position of Substituent on Catalytic Reduction Rate of Nitro Group [1% Pd/C + (III), 25°, H_2 = 1 atm, and solvent = 2 : 1 ethanol–water]

Nitro compound	v_{init}, ml/min	Hydrogenation products
Nitrobenzene	6.0	Aniline
p-Nitrotoluene	6.0	p-Toluidine
o-Nitrotoluene	4.5	o-Toluidine
m-Nitrotoluene	5.0	m-Toluidine
p-Dinitrobenzene	7.0	m-Tolylhydroxylamine p-Phenylenediamine
m-Dinitrobenzene	6.5	m-Phenylenediamine
p-Nitroaniline	3.0	p-Phenylenediamine
p-Chloronitrobenzene	2.6	Aniline, p-chloroaniline
p-Nitrophenol	7.0	p-Aminophenol
p-Nitrobenzoic acid	7.0	p-Aminobenzoic acid

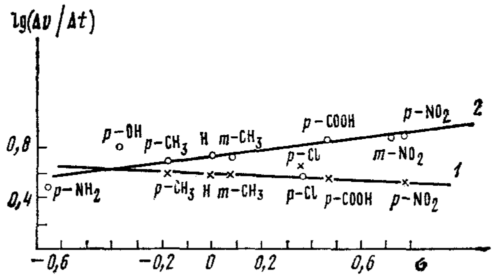


Fig. 2. Relation between logarithm of reduction rate of nitro compounds and corresponding Hammett constants: 1) 1% Pd/C; 2) 1% Pd/C + (III).

Ce-3-Amino-5-sulfosalicylate (X). Found: C 21.27; H 3.70; S 7.64; Ce 22.80%. $C_{21}H_{15}N_3O_{18}S_3Ce_2$. Calculated: C 20.88; H 3.40; S 7.95; Ce 23.20%. Infrared spectrum (ν, cm^{-1}): 3460, 3400 (NH_2), 1522, 1540 (COO^-), 1160, 1050 (SO_3).

The hydrogenation was run in a thermostated "duck" (hydrogenation vessel) with vigorous stirring. Due to the low solubility of the Ce complexes in aqueous alcohol (2:1) we used saturated solutions that contained $0.15 \cdot 10^{-4} - 0.5 \cdot 10^{-5}$ mole of the complex. In each experiment we used $0.2 \cdot 10^{-4} - 0.8 \cdot 10^{-5}$ g-atom of palladium (1% Pd/C), $0.2 \cdot 10^{-2}$ mole of nitro compound, and 30 ml of solvent.

The products were identified by TLC (using Silufol plates and the following mixtures as eluants: benzene–cyclohexane–ether; benzene–ethanol; heptane–acetone). The amount of PHA was determined by potentiometric titration as described in [6].

CONCLUSIONS

Effective catalytic systems were developed for the reduction of aromatic nitro compounds, which consist of a heterogeneous palladium catalyst and cerium complexes with organic ligands.

LITERATURE CITED

1. S. N. Zelenin and M. L. Khidekel, Usp. Khim., 39, 209 (1970).
2. R. B. Ivanova and M. L. Khidekel, Zh. Obshch. Khim., 39, 2394 (1969).
3. E. N. Sal'nikova, S. N. Zelenin, and M. L. Khidekel, Zh. Obshch. Khim., 39, 2368 (1969).
4. A. P. Tomilov and S. G. Mairanovskii, Electrochemistry of Organic Compounds [in Russian], Khimiya, Leningrad (1968), p. 591.
5. T. T. Bakumenko, Catalytic Properties of Rare and Rare-Earth Elements [in Russian], Izd. AN Ukr. SSR, Kiev (1963).
6. A. D. Shebaldova, V. N. Kravtsova, T. A. Bol'shinskova, E. V. Selyaeva, and M. L. Khidekel, Izv. Akad. Nauk SSSR, Ser. Khim., 1975, 1665.
7. V. P. Khramov, Complexonates of Rare-Earth Elements [in Russian], Izd. Saratovsk. Univ. (1974).

8. K. Johnson, Hammett Equations [Russian translation], Mir (1977).
9. G. I. Efremova, R. T. Buchkova, A. V. Lapitskaya, and S. B. Pirkes, Zh. Neorg. Khim., 22, 948 (1977).
10. T. V. Zakharova, A. V. Lapitskaya, and S. B. Pirkes, Zh. Neorg. Khim., 19, 362 (1974).
11. T. V. Zakharova, A. V. Lapitskaya, and S. B. Pirkes, Zh. Neorg. Khim., 20, 1765 (1975).

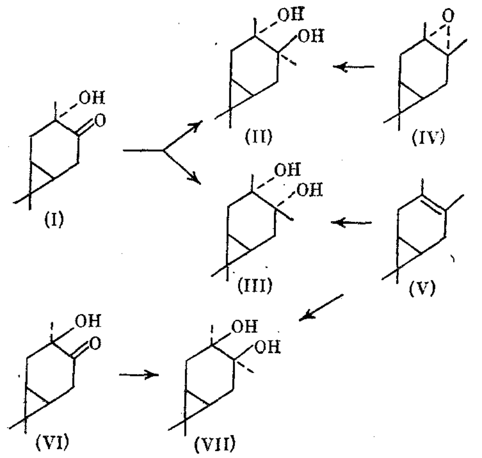
4-METHYL-3,4-CARANEDIOLS

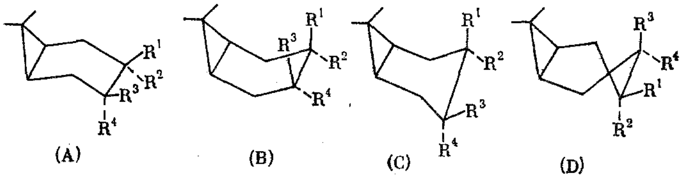
Z. G. Isaeva, G. Sh. Bikbulatova,
O. B. Skripnik, and I. P. Povodyreva

UDC 542.91:547.597

The nucleophilic addition of Grignard reagent (CH_3MgI) to the cis- and trans-4-caranones proceeds at the C=O group predominantly in the trans position relative to the cyclopropane ring (CPR) and is determined by the shielding effect of the 8-CH_3 group, which hinders approach of the nucleophile from the β-side [1]. In cis-4-caranone both steric factors (8- and 10β-CH_3 groups) act in one direction, while in trans-4-caranone (8- and 10α-CH_3 groups) they act in opposite directions. As a continuation of these studies it seemed of interest to study the reaction of CH_3MgI with hydroxy-substituted 4-caranones in order to ascertain the effect of the additional steric factor (OH or OMgI) on the stereochemistry of the nucleophilic addition.

3α-Hydroxy-4-caranone (I) reacts with CH_3MgI to give a mixture of isomeric diols, which are liquid and crystalline (mp 85-86°C), in a 1:3.5 ratio, while 3β-hydroxy-4-caranone (VI) reacts to give one diol (mp 60.5-62°). The structures 4-methyl-3α,4β-caranediol (II) and 4-methyl-3α,4α-caranediol (III) are possible for the diols from the reaction of ketol (I); the structure of either 4-methyl-3β,4β-caranediol (VII) or (II) is possible for the diol from ketol (VI). The obtained stereoisomers of 4-methyl-3,4-caranediol were identified by comparing with authentic specimens, which were obtained employing the stereospecific reactions: the α-cis-hydroxylation of 4-methyl-3-carene (V) with OsO_4 [2], the β-cis-hydroxylation of (V) by the Woodward method [3], and the hydration of α-3,4-epoxy-4-methylcarane (IV) in acid medium [2].





$R^1 = R^4 = CH_3$, $R^2 = R^3 = OH$ (II): $R^1 = R^3 = CH_3$,
$R^2 = R^4 = OH$ (III): $R^2 = R^4 = CH_3$, $R^1 = R^3 = OH$ (VII)

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch of the Academy of Sciences of the USSR. A. N. Tupolev Kazan Aviation Institute. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1107-1110, May, 1979. Original article submitted June 27, 1978.

0568-5230/79/2805-1035$07.50