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CLEAVAGE OF ARALKYL- AND ARYL-OXYGEN AND -NITROGEN BONDS BY THE HYDROGEN TRANSFER FROM ORGANIC COMPOUNDS CATALYZED BY NOBLE METAL SALTS

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Aralkyl- and aryl-oxygen bonds of ethers, esters, and alcohols, and aralkyl- and aryl-nitrogen bonds of amines, an imide and an amide were hydrogenolyzed by the hydrogen transfer from organic compounds such as indoline in the presence of some noble metal salts. In these reactions, not only benzyl group but phenethyl and phenyl group were removed.

Organic compounds such as benzylic esters, benzylic amines, and phenethylamine, have been reported to be hydrogenolyzed by the catalytic hydrogen transfer from organic hydrogen donors.$^{1)}$ However, so far as we know, homogeneous catalytic transfer hydrogenolysis of C-O and C-N bonds in organic compounds seems to have not yet been reported except for the disproportionation of benzylic alcohols.$^{2)}$ We found that these bonds are cleaved by the hydrogen transfer from organic compounds in the presence of some transition metal salts. The hydrogenolysis of several ethers, esters, amines, and some other compounds was carried out by heating indoline (0.5 M), a substrate (0.5 M), and a catalyst (0.08 M) in cumene at 180°C for 5 hr. As catalysts, palladium chloride, palladium acetate, and rhodium trichloride were used. The identification and the evaluation of yield of products were performed by glc analysis and the results are summarized in Table. The fact that the amount of indole formed from the dehydrogenation of indoline harmonizes with the value calculated from the amount of products in all the cases examined suggests that these transfer hydrogenolyses proceed without remarkable side reactions. The substrates having benzyl group were cleaved exclusively at benzyl position to give toluene and realized higher conversion than those having phenethyl or phenyl group instead of benzyl group. The yields of toluene in the reaction of benzyl p-tolyl ether, benzyl phenyl ether, and acetophenyl benzyl ether were 79, 48, and 5%, respectively. This fact shows that the electronegative nature of aryl groups depresses the reactivity of aryl benzyl ethers. Benzyl esters were more reactive than benzyl ethers, the yield of toluene in the reaction of the former being 100%. Phenethyl acetate, phenethylamine, and phenethyl alcohol gave ethylbenzene in 90, 39, and 5% yield, respectively. Amines having benzyl groups also underwent hydrogenolysis effectively. It may be noteworthy that when palladium chloride was used as a catalyst, one mole of dibenzylamine and tribenzylamine gave one and two moles of toluene, respectively, while benzylamine hardly reacted. Rhodium trichloride did not show such selectivity. In the reaction of triphenylamine, diphenylamine, aniline, and phenyl acetate, benzene was obtained in the yield of 19, 10, 5, and 5%, respectively.

When indoline and benzyl acetate were used as a hydrogen donor and a substrate, Table. Transfer hydrogenolysis of aralkyl- and aryl-oxygen and -nitrogen bonds by indoline[a)]

Substrate	Catalyst	Products, Yield (%)
Benzyl methyl ether	$PdCl_2$	Toluene, 68; methanol, 66
Benzyl ethyl ether	$PdCl_2$	Toluene, 83; ethanol
Benzyl propyl ether	$PdCl_2$	Toluene, 65; propanol
Benzyl p-tolyl ether	$PdCl_2$	Toluene, 79; p-cresol
Benzyl phenyl ether	$PdCl_2$	Toluene, 41; phenol, 40
p-Acetophenyl benzyl ether	$PdCl_2$	Toluene, 5; p-acetophenol
Benzyl alcohol	$PdCl_2$	Toluene, 73
Phenethyl alcohol	$PdCl_2$	Ethylbenzene, 5
Benzyl acetate	$Pd(OAc)_2$	Toluene, 100; acetic acid, 98
Benzyl butyrate	$Pd(OAc)_2$	Toluene, 100; butyric acid
Benzyl benzoate	$Pd(OAc)_2$	Toluene, 100; benzoic acid
Phenethyl acetate	$Pd(OAc)_2$	Ethylbenzene, 90; acetic acid
Tribenzylamine[b)]	$PdCl_2$	Toluene, 200;[c)] benzylamine
Tribenzylamine[b)]	$RhCl_3.3H_2O$	Toluene, 126;[c)] dibenzylamine; benzylamine
Dibenzylamine[d)]	$PdCl_2$	Toluene, 100;[c)] benzylamine
Dibenzylamine[d)]	$RhCl_3.3H_2O$	Toluene, 175;[c)] benzylamine
Benzylamine	$PdCl_2$	Toluene, trace
Benzylamine	$RhCl_3.3H_2O$	Toluene, 59
Phenethylamine	$RhCl_3.3H_2O$	Ethylbenzene, 39
Triphenylamine	$RhCl_3.3H_2O$	Benzene, 19; diphenylamine
Diphenylamine	$RhCl_3.3H_2O$	Benzene, 10; aniline
Aniline	$RhCl_3.3H_2O$	Benzene, 5
N-Benzylphthalimide	$RhCl_3.3H_2O$	Toluene, 54; phthalimide
N-Benzylacetamide	$RhCl_3.3H_2O$	Toluene,26; acetamide

a) Indoline (0.5 M), a substrate (0.5 M), and a catalyst (0.08 M) were heated in cumene at 180° C for 5 hr.

b) The concentration of the indoline added was 1.5 M.

c) $[\text{Toluene}]_{\text{formed}} / [\text{Substrate}]_{\text{added}} \times 100$.

d) The concentration of the indoline added was 1.0 M.

the catalytic activity of noble metal salts, as shown in the yield of toluene, decreased in the order; $Pd(OAc)_2$ (100%), $PdCl_2$ (79%), $(NH_4)_2PdCl_4$ (69%), $RhCl_3.3H_2O$ (60%), K_2PtCl_4 (33%), $IrCl_3$ (18%), and $RuCl_3.xH_2O$ (11%). In the hydrogenolysis of benzyl acetate catalyzed by palladium acetate, the hydrogen-donating ability decreased in the order; indoline (100%), 1,2-dihydronaphthalene (80%), formic acid (79%), 3-pentanol (75%), dioxane (61%), cyclohexene (53%), tetralin (48%), 1,4-dihydronaphthalene (22%), and 1-pentanol (14%).

References

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