Synthetic Methods and Reactions; 47.[1] $AlCl_3$/Pd-Catalyzed Reduction of Aryl Substituted Alcohols and Olefins by Hydrogen Transfer from Cyclohexene

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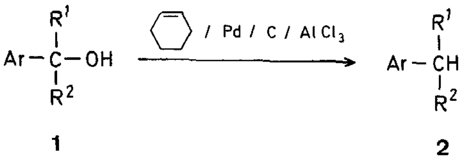
Brieger and Fu[2] reported the iron(III) chloride/Pd-promoted transfer hydrogenolysis of aryl carbonyl compounds with olefins. In related work, we reported the Pd/asbestos-catalyzed reductive cleavage of azo- and hydrazoarenes giving aminoarenes[3].

In continuation of our studies on transfer hydrogenation[3], we wish to report the convenient and facile reduction of arylmethanols and olefins. The reduction of alcohols goes to completion in 36 h in refluxing cyclohexene/Pd/C/$AlCl_3$. The results of the reduction of aryl substituted alcohols are listed in Table 1.



R^1, R^2 = aryl, alkyl, H

Scheme A

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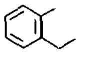
Table 1. Reduction of Alcohols (Scheme **A**)

Ar	R[1]	R[2]	Yield[a,b] [%]	m.p. or b.p./torr	Lit.[8] m.p. or b.p./torr
C_6H_5	CH_3	C_6H_5—CH(CH_3)—	94	123.0°	126°[e]
C_6H_5	C_6H_5	C_6H_5	90	94.0°	94.0°
C_6H_5	CH_3	CH_3	84	152–153°	152–153°
C_6H_5	—(CH_2)$_5$—		87	126.0°/30	127–128°/30
C_6H_5	C_6H_5	CH_3	84	148°/15	150°/16
C_6H_5	C_2H_5	*cyclo*-C_3H_5	81[c]	51°/0.5	103°/25
C_6H_5	norbornyl[d]		90	102°/0.5	102°/3[9]
C_6H_5	C_6H_5	H	92	126.0°/10	120°/10
C_6H_5	H	H	74	111.0°	110.0

[a] Products confirmed by comparison of I.R., N.M.R., and physical constant data with that reported.

[b] Yield of isolated product. [c] Product is 3-phenylhexane. [d] *exo* and *endo*. [e] *meso*.

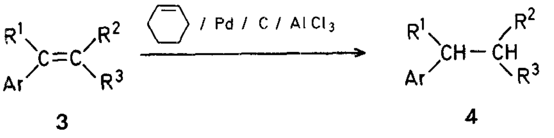
Table 2. Reduction of Aryl Substituted Alkenes (Scheme **B**)

Ar	R[1]	R[2]	R[3]	Yield[a,b] [%]	m.p. or b.p./torr	Lit.[8] m.p. or b.p./torr
C_6H_5	C_6H_5	C_6H_5	C_6H_5	93	211–212°	211°
C_6H_5	H	C_6H_5	H	90	51–52°	52°
H			H	77	176.0°/760	177°/760
C_6H_5	—(CH_2)$_4$—		H	86	126.0°/30	127–128°/30

[a] Products confirmed by comparison of I.R., N.M.R., and physical constant data with that reported.

[b] Yield of isolated products.

The observed reduction of the cyclopropyl to *n*-propyl group in the case of phenyl-ethyl-cyclopropylmethanol leads to the realization that aryl substituted olefins should also be reduced under the reaction conditions. In following studies aryl substituted olefins were reduced in good yields when they were refluxed in cyclohexene with Pd/C/$AlCl_3$ for 48 h. The results are listed in Table 2.



R^1, R^2, R^3 = H, alkyl, aryl

Scheme **B**

The reaction necessitates the presence of at least one aryl group and did not proceed with purely alkyl substituted alcohols or olefins. The exact mechanism of the reduction is not yet established. The most probable mechanism is similar to the one suggested in our earlier work[3] on azobenzene reduction, wherein the hydrogen donor cyclohexene and the substrate are coordinated to the palladium metal and the reaction is initiated by hydride transfer from an allylic position. The role of Lewis acid is to activate the substrate and initiate the acid-catalyzed hydrogen transfer. Other hydrogen donors, such as limonene or tetralin, also work well. Our choice of cyclohexene is based on its cheapness, good results, and convenient work-up of the reaction, in spite of the formation of benzene as by-product.

The present transfer hydrogenation offers distinct advantages over other reduction methods[4,5,6]. The reductions are carried out at atmospheric pressure without the use of hydrogen gas, inexpensive cyclohexene being the source of hydrogen. Product isolation is simple and yields are generally high. The method thus can serve as an alternative to catalytic hydrogenation[7].

General Procedure for Reduction of Aryl Substituted Alcohols and Olefins:

The respective alcohol or olefin (10 mmol), along with 10 % palladium on carbon (20 % of substrate's weight) and aluminum chloride (20 mg) are mixed with cyclohexene (15 ml) and the mixture is refluxed. In general, the reduction of alcohols is complete in 36 h and of olefins in 46 h. The product is isolated by diluting the mixture with diethyl ether, filtering, evaporating the solvent, and subsequently distilling or recrystallizing. The course the reaction is further easily followed by T.L.C.

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