

Catalytic Transfer Reduction of Carbonyl Compounds

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Summary Aromatic aldehydes and ketones can be reduced to the corresponding hydrocarbons in good yield by catalytic transfer reduction using cyclohexene or limonene as donor, palladium-carbon as catalyst, and a Lewis acid promotor such as ferric chloride.

THE reduction of carbonyl compounds to hydrocarbons can be accomplished by a variety of methods including Clemmensen and Wolff-Kishner reductions. Ordinary catalytic hydrogenation can also be used to accomplish complete reduction of aromatic aldehydes and ketones.¹ Catalytic transfer hydrogenation on the other hand has not been utilized to any extent² perhaps because of the early observations of Braude *et al.*³ that disproportionation and hydro-

donor, and the acceptor carbonyl compound for a period of 3–5 h. The results are given in the Table.

The donor, cyclohexene, is converted into benzene and, in the case of limonene, most of it is converted into *p*-cymene, although some disproportionation to *p*-menthane also takes place. Limonene reacts more rapidly than cyclohexene with aryl ketones, presumably because of its higher boiling point. The method is convenient and totally dispenses with the use of elaborate equipment or potentially explosive hydrogen.

Concerning the mechanism of the reduction, we have found that alcohols are produced as intermediates, but the reaction cannot be profitably stopped at the alcohol stage. However in the cases of *o*-carboxybenzaldehyde and *o*-car-

TABLE. Catalytic transfer reduction of aromatic aldehydes and ketones.

Compound	Donor	Catalyst (Promoter) ^b	Hydrocarbon (%)
PhCHO	Cyclohexene	10% Pd-C (FeCl ₃)	PhMe (80)
<i>p</i> -MeOC ₆ H ₄ CHO	"	"	<i>p</i> -MeOC ₆ H ₄ Me (80)
<i>p</i> -Me ₂ NC ₆ H ₄ CHO	"	"	<i>p</i> -Me ₂ NC ₆ H ₄ Me (75)
<i>o</i> -HO ₂ CC ₆ H ₄ CHO	"	"	<i>o</i> -HO ₂ CC ₆ H ₄ Me (35), Lactone (45)
<i>m</i> -MeO- <i>p</i> -HOC ₆ H ₃ CHO	"	"	<i>m</i> -MeO- <i>p</i> -HOC ₆ H ₃ Me (70)
PhCOMe	(+)-Limonene	"	PhEt (100)
<i>p</i> -HOC ₆ H ₄ COMe	"	"	<i>p</i> -HOC ₆ H ₄ Et (90)
<i>p</i> -MeOC ₆ H ₄ COMe	"	"	<i>p</i> -MeOC ₆ H ₄ Et (90)
<i>o</i> -HO ₂ CC ₆ H ₄ COMe	"	"	<i>o</i> -HO ₂ CC ₆ H ₄ Et (0), Lactone (80)
Ph ₂ CO	"	"	Ph ₂ CH ₂ (100)

^a Donor-acceptor ratio 15/20/1. ^b Catalyst 40% and promotor 4% of acceptor weight. ^c Yields were determined by g.l.c.

gen transfer from cyclohexene, in the presence of palladium black, is specifically inhibited by the presence of carbonyl compounds, such as benzaldehyde.

We report that catalytic hydrogen transfer to carbonyl compounds can occur and that aromatic aldehydes and ketones can be reduced to the corresponding hydrocarbons by this method.

In the presence of catalytic amounts of Lewis acids such as ferric chloride, aluminium chloride, or indeed even water, aromatic aldehydes and ketones can be reduced in good yield by catalytic hydrogen transfer from such donors as cyclohexene or limonene. The major competing reaction in the case of aldehydes is decarbonylation.⁴ Otherwise the reaction is clean and straightforward, involving essentially nothing more than heating to reflux the catalyst, the

boxyaceto-phenone appreciable amounts of the intermediate alcohols are trapped as the lactones, which are less readily reduced. It is interesting to note that Clemmensen reduction, which we used for comparison with the same compounds, lead to the formation of the same lactones. This is direct evidence of the intermediacy of alcohols in the Clemmensen reduction, a point still in question in the mechanism of this reaction.⁵ The formation of lactones suggested the possibility that intermediate alcohols might be trapped by a suitable reagent such as acetic anhydride. Reduction of benzaldehyde in the presence of acetic anhydride lead to the formation of benzyl acetate (72%).

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⁴ J. O. Hawthorne and M. H. Wilt, *J. Org. Chem.*, 1960, **25**, 2215.

⁵ H. O. House, 'Modern Synthetic Reactions,' Benjamin, California, 1972, pp. 166 ff.