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CATALYTIC ASYMMETRIC HYDROFORMYLATION WITH A CHIRAL PHOSPHINE-RHODIUM COMPLEX[1)]

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Styrene, α-ethylstyrene and phenyl vinyl ether are hydroformylated asymmetrically in the presence of chlorocarbonylbis(diphenylneomenthylphosphine)rhodium(I) as catalyst.

Rhodium complexes have been known to be very active as catalysts in hydroformylation and hydrogenation of olefins.[2)] A few examples of catalytic asymmetric hydrogenation of olefins in the presence of chiral phosphine-rhodium complexes have been reported.[3)] We now report the first example of catalytic asymmetric hydroformylation of a few olefins with a chiral phosphine-rhodium complex.

Chlorocarbonylbis(diphenylneomenthylphosphine)rhodium(I) was prepared according to the usual method[4)] from rhodium chloride dihydrate, diphenylneomenthylphosphine[5)] and formaldehyde in ethanol, m.p. 182.8-183.6°, $[\alpha]_D^{22}$ + 172° (benzene, c = 4.9).[6)]

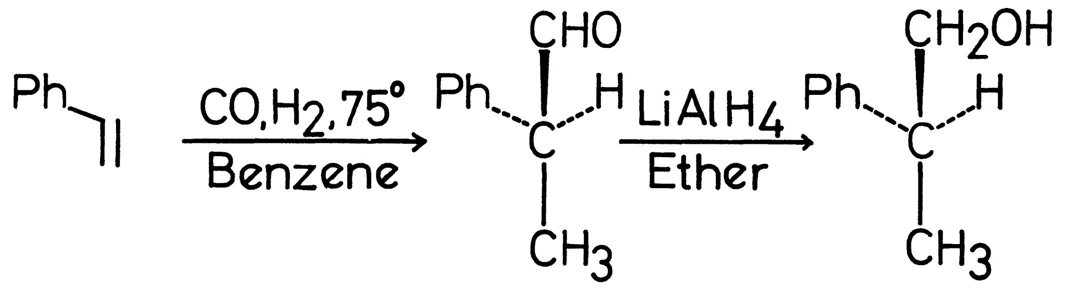
Hydroformylation reactions were carried out employing olefins 15 ml and benzene 15 ml as solvent in a 100 ml autoclave. The catalyst concentration was 8.7×10^{-7} M. In all cases, optical active aldehydes were isolated by distillation. The products were identified by ir and nmr spectroscopy.

Hydroformylation of styrene was carried out at an initial pressure 100 atm (CO/H_2 = 1) and temperature 75° over a period 13 hr. The reaction mixture was distilled to give hydratropaaldehyde (29.0 %), $[\alpha]_D^{23}$ + 2.04° (neat), which was then reduced by lithium aluminium hydride to (-)-(S)-2-phenyl-1-propanol (**1**), $[\alpha]_D^{23}$ - 0.182° (neat). This optical rotation corresponds to 1.2 % optical purity.7)

α-Ethylstyrene was hydroformylated at 140 atm, 90° over a period 5 hr to yield 3-phenylvaleraldehyde (61.4 %), $[\alpha]_D^{19}$ + 0.070° (neat), which was reduced to (-)-(R)-3-phenylpentanol (2), $[\alpha]_D^{23}$ - 0.145° (neat); 1.0 % optical purity.8)

Similarly, phenyl vinyl ether was hydroformylated under the analogous conditions to yield 2-phenoxypropionaldehyde (57.1 %), $[\alpha]_D^{18}$ - 0.051° (neat), which was oxidized by silver oxide to (+)-(R)-2-phenoxypropionic acid (3), $[\alpha]_D^{16}$ + 0.132° (ethanol, c = 9.2); 0.3 % optical purity.9)

We are now investigating the hydroformylation reaction of other prochiral olefins with various chiral phosphine-transition metal (Rh or Co) complexes. These results and discussions will be reported in the near future.



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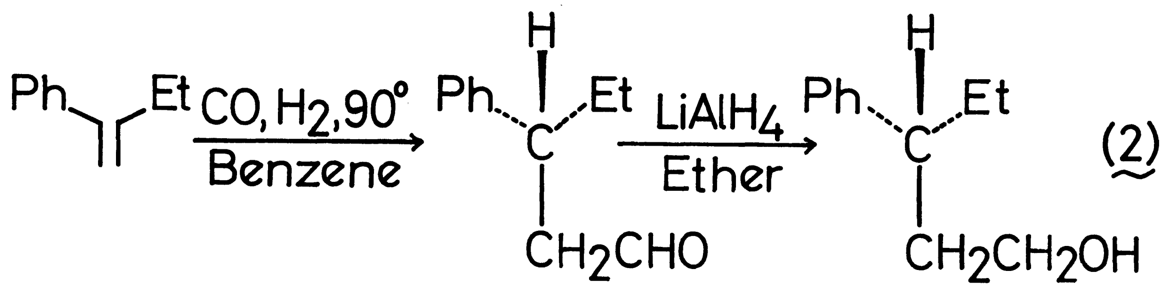

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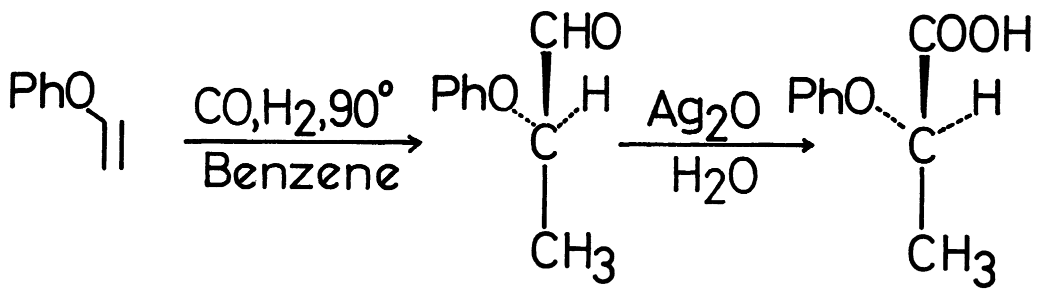

(3)

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