Enantioselective Telomerization of Butadiene with Formaldehyde yielding Divinyltetrahydropyrans

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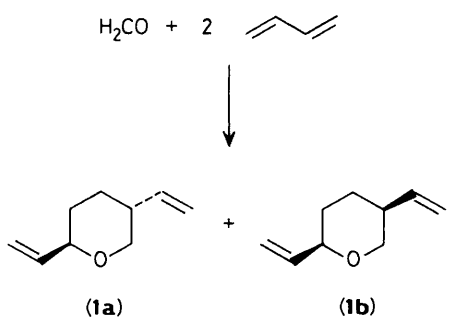
The enantioselective telomerization of butadiene with formaldehyde, catalysed by $Pd(OAc)_2$ plus bidentate phosphine ligands, yielding 2,5-divinyltetrahydropyran in optical purity up to 36% is described; a fused-silica capillary with a chiral stationary phase of cyclodextrin has been prepared and successfully applied in product analysis for the first time.

Telomerization reactions of dienes with nucleophiles are useful in the synthesis of a variety of valuable compounds. For example, terpenols, jasmonates, pheromones, and other fine chemicals are accessible by this reaction route,[1] and the introduction of chiral centres during such syntheses is of substantial interest.[2] However, there is only one example of an enantioselective telomerization, reported by Hidai,[3] who successfully converted isoprene and methanol into 1-methoxy-2,6-dimethylocta-2,7-diene. Using various monodentate menthylphosphorus derivatives co-ordinated as chiral ligands to allylic complexes of palladium he obtained a maximum enantiomeric excess (e.e.) value of 35% for menthyldi-isopropylphosphine. Chelates such as diphosphines proved inactive.

We have accomplished the enantioselective telomerization of butadiene and formaldehyde using chiral diphosphines, according to Scheme 1. This reaction was reported previously,[4] without introduction of chirality.

Typically, a propan-2-ol solution of paraformaldehyde (0.05 mol) and butadiene (0.097 mol) was allowed to react at room temperature in the presence of palladium acetate (0.1 mmol)



(1a) (1b)

Scheme 1. Telomerization of butadiene with formaldehyde. *Reagents and conditions*: $Pd(OAc)_2$, PP*, Pr^iOH, 20 °C, 40 h.

Table 1. Enantioselective telomerization of formaldehyde with butadiene catalysed by palladium acetate and diphosphine ligands.

Run	Chiral ligand	Chemical yield (%)	Diastereoisomeric ratio (**1a**) : (**1b**)[g]	% E.e. of (**1b**)	% E.e. of (**1a**)
1	(+)-DIOP[a]	65	5.0 : 0	26	18
2	(−)-DIOP	64	5.5 : 1	25	17
3	BPPM[b]	45	2.6 : 1	5	2
4	CIRA[c]	30	3.6 : 1	20	15
5	NORPHOS[d]	55	5.6 : 1	36	3
6	NMDPP[e]	25	3.9 : 1	30	13
7	PHEN[f]	45	3.9 : 1	24	5

[a] DIOP = 2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane. [b] BPPM = (2*S*,4*S*)-*N*-t-butoxycarbonyl-2,4-bis(diphenylphosphino)methylpyrrolidine. [c] CIRA = (2*R*,3*R*)-2,3-bis(diphenylphosphinobutane). [d] NORPHOS = (2*R*,3*R*)-2,3-bis(diphenylphosphino)bicyclo[2.2.1]hept-5-ene. [e] NMDPP = (1*R*,2*R*,5*S*)-neomenthyldiphenylphosphine. [f] PHEN = (*R*)-1,2-bis(diphenylphosphino)-3-phenylpropane. [g] (**1a**) has the (2*R*,5*R*)/(2*S*,5*S*) configuration, (**1b**) has the (2*S*,5*R*)/(2*R*,5*S*) configuration. The absolute configuration of the excess isomer was not determined.

and a chiral diphosphine ligand (0.15 mmol) for 40 h. The results obtained using various chiral phosphines are listed in Table 1.

The diastereoisomeric products were separated by column liquid chromatography and assigned structures (**1a**) and (**1b**) on the basis of ^{1}H n.m.r. analysis, which showed that in the excess diastereoisomer both vinylic groups are equatorial.

As the optical rotations of (**1a**) and (**1b**) were unknown, we determined the enantiomeric excess by capillary gas chromatography.† In this way, a rapid and quantitative separation of all four stereoisomers was achieved.

This is the second example of a catalytic asymmetric telomerization, the application of a diphosphine chelate being essential.

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† Heptakis[2,3,6-tri(*O*-methyl)]-β-cyclodextrin in OV-1701 was used as the chiral stationary phase.[5] A fused-silica capillary was coated with a cyclodextrin phase for the first time {25 m × 0.25 mm fused-silica capillary, coated with 10% heptakis[2,3,6-tri(*O*-methyl)]-β-cyclodextrin in OV-1701; 50 °C, carrier gas: 1.5 bar H_2}.