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Preliminary communication

OPTICALLY ACTIVE ALDEHYDES VIA HYDROFORMYLATION OF 1,3-DIENES WITH CHIRAL DIPHOSPHINERHODIUM COMPLEXES

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Summary

Optically active aldehydes have been obtained by hydroformylation of simple aliphatic conjugated dienes under standard oxo conditions (90 atm ($CO/H_2 = 1/1$) and 95°C), using $HRh(CO)(PPh_3)_3$/(−)DIOP as catalyst. The highest optical yield (32%) was achieved in the preparation of 3-methylpentanal from isoprene.

While much work has been done in recent years on the hydroformylation of conjugated dienes [1—5] and on asymmetric hydroformylation of olefins catalysed by chiral transition metal complexes [6—8], 1,3-dienes have not previously been determined as possible prochiral substrates for this process.

As part of our studies on the influence of the structure of the olefinic substrate on the type and extent of the asymmetric induction in the asymmetric hydroformylation [7], we have investigated this reaction using 1,3-butadiene, 2-methyl-1,3-butadiene (isoprene) and 2,3-dimethyl-1,3-butadiene as substrates and $HRh(CO)(PPh_3)_3$/(−)DIOP [6] (1-to-2 molar ratio) as a catalytic system. 2-Methyl-1-butene was also hydroformylated under the same conditions. Thus, 0.07—0.08 mol of the diolefin in 25 ml benzene were hydroformylated at 90 atm of an equimolecular mixture of CO and H_2 and at 95°C in the presence of 0.25 mmol of $HRh(CO)(PPh_3)_3$ and 0.5 mmol of (−)DIOP [6]. The results obtained are listed in Table 1.

As expected [3], complex mixtures of products were obtained, in which mono-saturated and unsaturated aldehydes and di-aldehydes were identified. For comparison with the asymmetric hydroformylation of mono-olefins, we looked only at the mono-saturated aldehyde, which represents the main reaction product under the conditions used, and was separated from the high boiling

TABLE 1

RESULTS OF ASYMMETRIC HYDROFORMYLATIONS

Substrate	Reaction time (h)	Overall hydroformylation yield (%)[a]	Saturated mono-aldehyde yield (%)	Isolated optically active compound			
				Name	$[\alpha]^{25}_{D}$	o.p. (%)	Configuration
1,3-Butadiene	60	82	41[b]	2-methylbutanal	+0.01	<1[c]	(*S*)
2-Methyl-1,3-butadiene (isoprene)	160	52	25[d]	3-methylpentanoic acid	+2.86	32.3[e]	(*S*)
2,3-Dimethyl-1,3-butadiene	160	40	18[d]	3,4-dimethylpentanoic acid	+0.70	5.7[f]	(*R*)
2-Methyl-1-butene	24	50	40[d]	3-methylpentanoic acid	−0.02	<1[e]	(*R*)

[a] Determined on the mixture of the acids obtained by Ag_2O-oxidation of the hydroformylation products. [b] n-Pentanal + 2-methylbutanal determined by gas-chromatographic analysis (normal/iso ratio 75/25). [c] Calculated using $[\alpha]^{25}_{D}$ + 36.5 [9] for optically pure (+)(*S*)-2-methylbutanal. [d] Determined on the corresponding purified mono-carboxylic acid. [e] Calculated using $[\alpha]^{25}_{D}$ + 8.83 [10] for optically pure (+)(*S*)-3-methylpentanoic acid. [f] Calculated using $[\alpha]^{25}_{D}$ −12.33 [11] for optically pure (−)(*S*)-3,4-dimethylpentanoic acid.

material by fractional distillation. Optical activities were measured on the corresponding saturated acids obtained by Ag_2O-oxidation followed by treatment with Br_2 at −30°C in order to eliminate any residual unsaturated compound, and further fractional distillation of the bromination mixture.

From the results listed in Table 1 some interesting observations can be made: (i) the regioselectivity of the hydroformylation for formation of the branched mono-aldehyde in the case of butadiene is rather low, not exceeding 25%; (ii) the hydroformylation of isoprene to 3-methylpentanal takes place with rather high optical yield (32%) compared with that in the formation of the same aldehyde from 2-methyl-1-butene (the latter compound represents an intermediate step in isoprene hydrogenation); (iii) the predominant configuration (*S*) of the 3-methylpentanal obtained from isoprene is the opposite of that of this aldehyde formed from the mono-olefin; (iv) the optical purity of the 3,4-dimethylpentanal produced from 2,3-dimethyl-1,3-butadiene was much lower than that of 3-methylpentanal from isoprene, and the configurations of the two aldehydes were opposite.

These results confirm beyond any doubt that the mechanism of the formation of the mono-saturated aldehydes from the 1,3-dienes is substantially different from that for their formation from simple olefins [3]. It should be noted that in the hydroformylation of these substrates it is possible to follow the course of the reaction by gas-chromatography [2,3], and thus, at relatively low diene conversion, to obtain evidence for the presence of isomeric unsaturated aldehydes in the reaction mixture. These compounds, which were rapidly formed in the first stage of the reaction, were slowly hydrogenated to saturated aldehydes or further hydroformylated to di-aldehydes under the reaction conditions [3].

It is clear that in the case of isoprene and 2,3-dimethyl-1,3-butadiene the observed asymmetric induction does not arise from an enantioface-discriminating hydroformylation of an intermediate mono-olefin as in the case of 2-methyl-1-butene, but from an enantioface-discriminating hydrogenation of a mixture of stereomeric α,β-unsaturated aldehydes which cannot undergo the hydroformylation [12]. It is known that these compounds can be produced in the reaction medium even by a thermally induced double bond shift from β,γ-unsaturated aldehydes [3] directly formed by 1,4-addition of the intermediate rhodium hydride complex to the conjugated system [13].

The low optical purity of (*S*)-2-methylbutanal obtained by hydroformylation of 1,3-butadiene must result substantially from the enantioface-discrimination in the hydrogenation of a mixture of *trans*- and *cis*-2-methyl-2-butenal formed by the much less favoured Markownikoff 1,2-addition of the catalytically active rhodium hydride complex to the diene [2]. Asymmetric hydrogenation of preformed tiglic aldehyde (*trans*-2-methyl-2-butenal) under analogous oxo-conditions has been reported [14] to give 2-methylbutanal with very low optical yield (0.6%) and the same (*S*) configuration.

Experiments are currently in progress to obtain more information on the mechanism of the asymmetric hydroformylation of substrates with conjugated double bonds.

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