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CONCLUSIVE EVIDENCE FOR DIRECT HYDROFORMYLATION OF THE TRIPLE BOND CATALYZED BY CHIRAL RHODIUM-COMPLEXES

C. Botteghi and Ch. Salomon

Swiss Federal Institute of Technology
Department of Industrial and Engineering Chemistry
Universitätstrasse 6, 8006 Zurich, Switzerland

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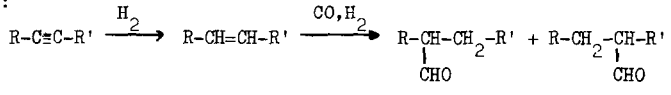
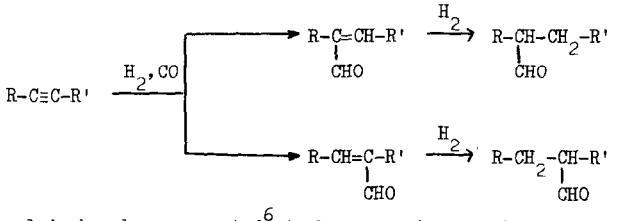
Only a few reports on hydroformylation of alkynes with rhodium catalysts have appeared in the literature in recent years [1,2,3]. Normally, more vigorous reaction conditions are used than in the case of the corresponding olefins and only saturated aldehydes are formed in lower yields. To explain the lower reactivity of the alkynes in comparison with the olefins with respect to the rhodium catalyzed hydroformylation, the formation of rather stable complexes by interaction of the alkyne with the catalyst was taken into account[2]. However, no information is available about the reaction mechanism up to date.

The hydroformylation of an alkyne may proceed via the following paths:[4]

1.) Addition of hydrogen to the triple bond followed by hydroformylation of the intermediate olefin formed:



2.) Hydroformylation of the acetylenic substrate with the formation of an α,β-unsaturated aldehyde, which cannot be further hydroformylated[5], and hydrogenation to the saturated aldehyde:



Indeed, acrolein has been reported[6] to be present among the products obtained by hydroformylation of acetylene at 1-10 at of total pressure at 140-150°C using metallic cobalt as cata-

lyst, but experimental details are lacking. However, no further mention has been made about the formation of unsaturated aldehydes during the cobalt- or rhodium-catalyzed hydroformylation of acetylenic hydrocarbons until now.

Our first attempts to demonstrate the intermediary presence of unsaturated aldehydes in the hydroformylation mixtures of terminal alkynes as phenylacetylene and 1-octyne failed. Even at very low conversion under typical oxo-conditions we obtained only a mixture of saturated aldehydes (Table 1). Furthermore, acetylenic substrates were not hydroformylated under mild conditions[2].

The presence of α,β-unsaturated aldehyde as reaction intermediate was finally substantiated by partial hydroformylation of 2-butyne with rhodium catalysts (Table 1, runs 1 and 2).

Table 1: Hydroformylation of Alkynes in the Presence of $HRh(CO)(PPh_3)_3$ and (-)-DIOP [a]

Run	Alkyne[b]	Reaction conditions[c] t, °C	p, at CO/H_2=1	Time, hrs.	conversion %	Reaction Products	
1	2-Butyne	80	100	24	20	(S)-2-methylbutanal, (E)-2-methyl-2-butenal,	68% 32%
2	2-Butyne	80	d)	115	10	(S)-2-methylbutanal, (E)-2-methyl-2-butenal,	80% 20%
3	Phenyl-acetylene	95	85	28	99	3-phenylpropanal, (R)-2-phenylpropanal,	62% 38%
4	1-Octyne	95	80	24	78	n-nonanal (S)-2-methyloctanal	73.5% 26.5%

a) $1.25 \cdot 10^{-4}$ mole $HRh(CO)(PPh_3)_3$ and $5.0 \cdot 10^{-4}$ mole (-)-DIOP[(-)-2,3-O-Isopropyliden--2,3-dihydroxy-1,4-bis(diphenylphosphino)butane)[7]].

b) 0.036 mole phenylacetylene or 1-octyne in 50 ml benzene; 0.2 mole 1-butyne without solvent.

c) all experiments in a 0.150-liter rocking autoclave heated with a thermostated oil bath.

d) 25 at H_2 and 75 at CO.

Gas chromatographic analysis of the 2-butyne hydroformylation mixture at ∿20% conversion (Table 1, run 1) showed the presence of only two reaction products which were separated by preparative gas chromatography (20% polypropylenglycol on Chromosorb A, 4.5 m, 140°C). These compounds were identified as 2-methylbutanal and 2-methyl-2-butenal by comparison with reference samples synthetized by us[8,9].

The stereochemistry about the double bond of the unsaturated aldehyde was unequivocally determined to be (E), based on comparison of its NMR spectrum with that of our configurationally defined sample[9]. The presence of the (Z) isomer was excluded owing to the absence in the NMR-spectrum of aldehyde proton signal at $\delta>10$ ppm[11]. The (E) configuration of the α,β-unsaturated aldehyde is in agreement with the recent sterochemical findings on the addition of rhodiumhydride-complexes to the triple bond[12].

To obtain further information about the actual reaction mechanism, and particularly to confirm the Path 2 represents the only reaction course, we have performed all hydroformylations of the acetylenic hydrocarbons using $HRh(CO)(PPh_3)_3$ and (-)-DIOP as catalytic system and the same reaction conditions used for the corresponding olefins (Table 1).

In Table 2 the hydroformylation products obtained from alkynes are compared with those from the corresponding olefins.

Table 2: Comparison of optical purity and configuration of the chiral aldehydes obtained by asymmetric hydroformylation of alkynes and of the corresponding olefins.

Substrate	Optically active aldehyde				Ref.
	Name	$[\alpha]_D^{25}$(neat)	Optical purity, %	Configuration of prevailing enantiomer	
Styrene	2-phenylpropanal	-29.0	12.2[a]	(R)	14
Phenylacetylene		- 2.17[b]	0.9[a]	(R)	
1-Octene	2-methyloctanal	- 0.75[c]	2.5[d]	(R)	15
1-Octyne		+ 0.07[c](R)	0.2[d]	(S)	
cis-Butene	2-methylbutanal	+ 2.85[g]	8.1[f]	(S)	15
2-Butyne		+ 0.07[g]	0.2[f]	(S)	

a) Taking for the optically pure (R)-2-phenylpropanal, $[\alpha]_D^{25}$ -238(neat)[13].
b) Extrapolated value from a mixture of distilled products containing 56.3%-phenylbutanal.
c) α_D^{25} (ℓ=1).
d) Taking for the optically pure (S)-2-methyloctanal, α_D^{25} +29.9° (ℓ=1, neat)[15].
e) Extrapolated value from a mixture of distilled products contaning 66% n-nonanal.
f) Taking for the optically pure (S)-2-methylbutanal, $[\alpha]_D^{25}$+35.1(neat)[8].
g) In the run 2 (Table 1) (+)(S)-2-methylbutanal was obtained, which had $[\alpha]_D^{25}$ +0.102.

It is interesting to observe that i) consistently the optical yields obtained by asymmetric hydroformylation of the alkynes are much lower than those for the corresponding olefins ii) the configuration of the prevailing enantiomer is the same for phenylacetylene and styrene, and 2-butyne and cis-butene respectively, but is opposite for 1-octyne and 1-octene.

From these results no definitive conclusion can be drawn, excluding olefins (Path 1) as reaction intermediates; however, the different configurations obtained for 2-methyloctanal derived from 1-octyne and 2-octene would tend to support such a hypothesis.

The most important indication that Path 2 is practically the only reaction way is obtained with asymmetric hydrogenation a sample of (E)-2-methyl-2-butenal: this unsaturated aldehyde in pentane solution was kept in the presence of the same catalytic system used for asymmetric hydroformylations under identical reaction conditions. The saturated aldehyde, 2-methylbutanal, obtained after 30 hr. with 60% yield had $[\alpha]_D^{25}$ +0.210, corresponding to 0.6% optical purity, but to the identical (S) configuration as for the same aldehyde obtained by asymmetric hydroformylation of 2-butyne (Table 2).

It is noteworthy that hydroformylation of acetylenic hydrocarbons with an internal double bond, when optimized, can represent a valuable method for obtaining α,β-unsaturated aldehydes having definite stereochemistry about the double bond.

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