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DIALDEHYDES BY HYDROFORMYLATION OF CONJUGATED DIENES

Bernhard Fell and Wolfgang Rupilius

Institut für Technische Chemie und Petrolchemie, Technische Hochschule Aachen

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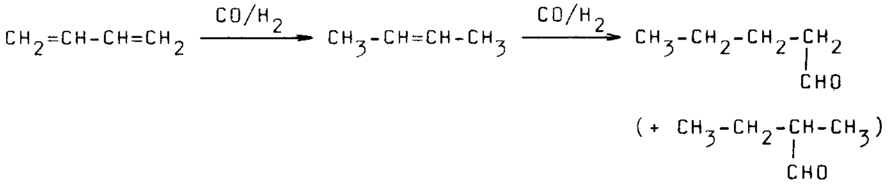
As is well known the hydroformylation of conjugated diolefins yields only mono-aldehydes or alcohols, e.g. a mixture of n- and iso-Valeraldehyde, results from butadiene (1, 2). The second double bond is hydrogenated. All atempts to prepare dialdehydes by hydroformylation of conjugated diolefins were unsuccessful. Dienes with isolated double bonds also yield primarily monoaldehydes, since a positional isomerisation of the isolated double bonds to the more stable conjugated system takes place under the normal oxo reaction conditions. The hydroformylation of a conjugated diolefin may proceed via following paths (3):

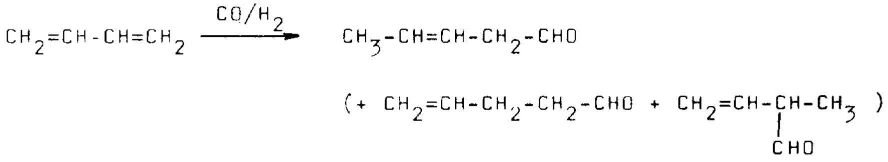
1.) 1,4-(or 1,2-) addition of hydrogen to the conjugated double bonds followed by hydroformylation of the mono-olefin formed:



$$CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{CO/H_2} CH_3{-}CH{=}CH{-}CH_3 \xrightarrow{CO/H_2} CH_3{-}CH_2{-}CH_2{-}\underset{|\atop CHO}{CH_2}$$

$$(+\ CH_3{-}CH_2{-}\underset{|\atop CHO}{CH}{-}CH_3)$$

2.) 1,4-(or 1,2-) hydroformylation of the diolefin with the formation of a β,γ-unsaturated aldehyde:



$$CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{CO/H_2} CH_3{-}CH{=}CH{-}CH_2{-}CHO$$

$$(+\ CH_2{=}CH{-}CH_2{-}CH_2{-}CHO\ +\ CH_2{=}CH{-}\underset{|\atop CHO}{CH}{-}CH_3\ )$$

The β,γ-unsaturated compound isomerizes immediately to the thermodynamically more stable α,β-unsaturated aldehyde, which cannot be hydroformylated and is instead hydrogenated to the saturated aldehyde (4).

As has already been found by us (5), it is possible to carry out the hydroformylation of an olefin without isomerization when a rhodium-trialkyl phosphine-complex, with a definite ratio of phosphine to rhodium, is used as catalyst. It should, therefore, be also possible to hydroformylate a conjugated diene to the corresponding dialdehyde with this catalyst, assuming the reaction to proceed via the unsaturated monoaldehydes.

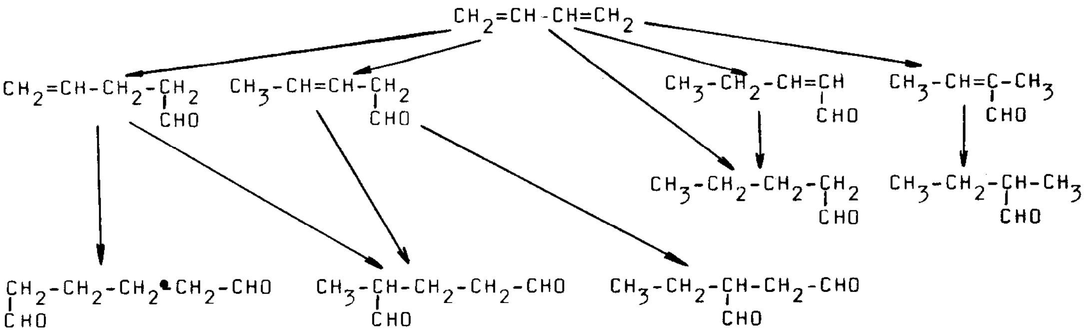
Thus on hydroformylation of butadien-(1,3) and pentadien-(1,3) we obtained 80-90 % yields of hydroformylation products, which contained 40-45 % C_6- and C_7-dialdehydes respectively.

The hydroformylation of butadiene was carried out at 125°C under 200 atm. (cold) CO/H_2-pressure (1:2) using diethyl ether as solvent. 0,02 mol-% Rh_2O_3 and 1,7 mol-% tri-n-butyl phosphine were employed as catalyst. The active catalyst was pre-formed in the autoclave by heating to 150°C for 30 min. Rh_2O_3 and tri-n-butyl phosphine in diethyl ether. After allowing to cool down to 125°C, butadien was fed into the autoclave by means of a pressure resistant dropping funnel at such a rate that this temperature was not exceeded. After a total reaction period of 3 hours 80-90 % yields of a hydroformylation product was obtained, which consisted 58 mol-% C_5-monoaldehydes and 42 mol-% C_6-dialdehydes.

The C_5-monoaldehyde fraction contained surprisingly more than 96 % of n-valeraldehyde besides 4 % only of iso-valeraldehyde. The composition of the C_6-dialdehyde fraction, determined by gaschromatographic analysis of the diacetates of the corresponding diols formed on hydrogenation of the dialdehydes with $LiAlH_4$, was as follows:

58 %	2-methylpentandial-(1,5)
29 %	2-ethylbutandial-(1,4)
9 %	hexandial-(1,6)
4 %	not identified

The intermediary presence of the different pentenals was substantiated by partial hydroformylation of butadiene and subsequent gaschromatographic analysis of the products. Most of them were identified by comparison with original samples synthesized by us. The following scheme demostrates the possible course of hydroformylation of butadiene in presence of rhodium-trialkyl phosphine catalysts, leading to the various end products via the pentenals:



The hydroformylation of pentadien-1,3 under the conditions employed in the case of butadien gave similarly 80-90 % yields of a mixture of approx. 55 % C_6-mono and 45 % C_7-dialdehydes. The composition of the C_6-monoaldehyde fraction was as follows:

92 %	2-methyl-n-pentanal-1
5 %	n-hexanal-1
3 %	not identified

The C_7-dialdehyde fraction contained:

39 %	2,4-dimethylpentandial-(1,5)
22 %	2-ethylpentandial-(1,5)
18 %	2-methylhexandial-(1,6)
15 %	2-ethyl-3-methylbutandial-(1,4)
3 %	2-propylbutandial-(1,4)
3 %	not identified

On hydroformylation of sorbic acid methyl ester in the presence of the above mentioned rhodium-phosphine catalyst we obtained, surprisingly, only the monohydroformylated product. The intermediate formation of cis- and trans-hexene-3- and cis- and trans-hexene-4-acid-1 methyl ester was confirmed by gaschromatographic analysis.

In continuation of the present work we shall report shortly on further applications of the "non-isomerizing" hydroformylation of olefinic compounds.

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