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HYDROFORMYLATION OF CYCLIC DIENES CATALYSED BY ACETATOCARBONYLBIS(TRIPHENYLPHOSPHINE)RHODIUM(I)

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Summary

The hydroformylation of cyclic dienes in benzene using $Rh(CO_2Me)(CO)(PPh_3)_2$ as catalyst was studied The formation of mono- or di-aldehydes was critically dependent on ring size, the smaller cyclic dienes favouring dihydroformylation. Intermediate alkene-aldehydes could be isolated under appropriate conditions, indicating that initial attack on the diene was by hydroformylation Under hydroformylation conditions, these intermediates underwent either hydroformylation or hydrogenation, depending on the ring size Linear dienes gave complex mixtures of products.

Introduction

Although numerous studies of the hydroformylation of linear dienes have been made [1], many of which appear in the patent literature, the hydroformylation of cyclic dienes has been little investigated. Adkins et al. [1a] and Matsubura [2], have reported the cobalt catalysed hydroformylation of 1,3-cyclopentadiene, the major product being cyclopentane carboxaldehyde. The hydroformylation of 1,5-cyclooctadiene has also been studied and pressures far above those normally used were required to achieve dihydroformylation [3,4] At more conventional pressures, monohydroformylation occured. Polycyclic dienes and higher alkenes have also been studied [5,6]

Results

The hydroformylation of 1,3- and 1,4-cyclohexadiene, 1,3- and 1,5-cyclooctadiene; 1,3-cycloheptadiene, 1,3-cyclopentadiene, and bicyclo-(2,2,1)-hepta-2,5-diene was investigated. The complex $Rh(CO_2Me)(CO)(PPh_3)_2$ was used as catalyst in benzene solution. Reactions were carried out at 100°C and at a pressure of 100 at. H_2/CO (1 : 1), unless otherwise stated

Substrate/catalyst ratios of 1000 and 200 were in general used. The former ratio led to the presence of appreciable amounts of alkene-aldehydes in the final reaction mixtures, whereas at a ratio of 200, almost complete conversion to dialdehyde or saturated monoaldehyde occured

The results of the hydroformylation of 1,3- and 1,4-cyclohexadiene are given in Table 1. The 1,3-diene gave up to five hydroformylation products, three of which were identified as cyclohexane dicarboxaldehyde, subsequently shown to be the 1,4-isomer (below), tetrahydrobenzaldehyde, and cyclohexane carboxaldehyde Comparison of the NMR spectrum of the tetrahydrobenzaldehyde formed with that of an authentic sample indicated it to be the 1,2,3,6-isomer The two remaining (minor) products were not studied in detail Their NMR spectra suggested that they were unsaturated monoaldehydes, and they may be other isomers of tetrahydrobenzaldehyde

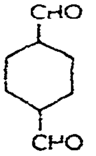
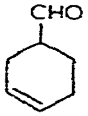
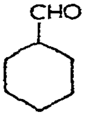
From 1,4-cyclohexadiene at a substrate/catalyst ratio of 1000 only dialdehyde and 1,2,3,6-tetrahydrobenzaldehyde were formed, together with a trace of cyclohexane carboxaldehyde The NMR and IR spectra of the dialdehyde were identical with those of the product from 1,3-cyclohexadiene Increasing the catalyst concentration to give a ratio of 200 produced a yield of 73% of the 1,4-dialdehyde. No trace of the 1,3-isomer could be detected

From Table 1, it can be seen that with 1,4-cyclohexadiene, at substrate/catalyst ratios of 1000 or 200, the total yield of unsaturated monoaldehyde plus dialdehyde is high (> 80%). This requires that the initial attack on the diene be predominantly hydroformylation, rather than hydrogenation

Since 1,2,3,6-tetrahydrobenzaldehyde occurs as an intermediate in the reaction, its hydroformylation was investigated (Table 1). The NMR and IR spectra of the dialdehyde product were again identical with those of the products from 1,3- and 1,4-cyclohexadiene. The extremely high preference for hydroformylation of this species suggests that in the diene hydroformylations where it is the major intermediate, it is converted almost exclusively to dialdehyde Thus the

TABLE 1

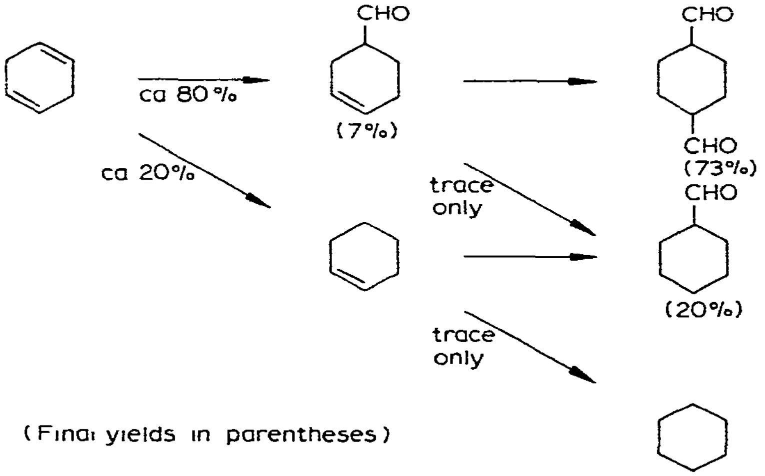
HYDROFORMYLATION OF CYCLOHEXADIENES AND TETRAHYDROBENZALDEHYDE IN BENZENE BY $Rh(CO_2Me)(CO)(PPh_3)_2$ [a]

Substrate [b]	Substrate/ catalyst	Main products  	 	
1 4-CHD	1000	44	54	
1 4-CHD	200	73	7	20
1,3-CHD	1000	18	13	17
1 3-CHD	200	29	5	25
THB	1000	91	4	5
THB	200	94	4	2

[a] Substrate, 1 M benzene, 50 ml, 100°C, 100 at. 1 : 1 H_2/CO 6 h. [b] CHD, cyclohexadiene THB, 1,2,3,6-tetrahydrobenzaldehyde.

cyclohexane carboxaldehyde observed must be formed by the alternative route via cyclohexene. The absence of other than traces of cyclohexane can be attributed to the very rapid hydroformylation of cyclohexene under the reaction conditions, as confirmed in a separate experiment. In the case of 1,4-cyclohexadiene, then, the attack on the diene favours initial hydroformylation in the ratio of ca 4 : 1 as indicated in Scheme 1.

SCHEME 1



(Final yields in parentheses)

At 60° C and 60 at. total pressure, 1,3- and 1,4-cyclohexadiene gave very low conversions to hydroformylation products, but in both cases, the 1,4-dialdehyde was formed.

The structure of the dialdehydes obtained above was established by oxidising them to the diacids with alkaline permanganate and comparing their NMR and IR spectra with those of the authentic 1,2-, 1,3, and 1,4-cyclohexane dicarboxylic acids. This indicates that all three substrates led to the 1,4-isomer. By careful gas chromatography, the dialdehydes could be partly separated into the *cis* and *trans* isomers. A complete separation was not achieved.

The *cis* : *trans* ratio was 35 : 65% (± 5%) regardless of the substrate used. The major isomer was established as *trans*-form by isolation of a sample by preparative gas chromatography (90% major isomer). This was oxidised to the diacid and recrystallised. Its melting point (301—302° C, sublimes) indicated that it was the *trans*-1,4-isomer [7].

Table 2 gives the results of the hydroformylation of 1,3- and 1,5-cyclooctadiene. In both cases the product was cyclooctane carboxaldehyde in high yield. At a substrate catalyst ratio of 200, small amounts of higher boiling species were present, but no dialdehyde was detected. At a ratio of 1000, the only other products observed in addition to cyclooctane carboxaldehyde were cyclooctene, and, from 1,5-cyclooctadiene, the 1,3-isomer. Hydroformylation of 1,5-cyclooctadiene at 60°C and 60 at. H_2/CO pressure gave a 71% yield of cyclooctene carboxaldehydes. The NMR spectrum showed the product to be a 1 : 1

TABLE 2

HYDROFORMYLATION OF CYCLOOCTADIENES AND CYCLOOCTENE CARBOXYALDEHYDE IN BENZENE BY $Rh(CO_2Me)(CO)(PPh_3)_2$ [a]

Substrate	Substrate/catalyst	Temp (°C)	Pressure (at)	Product (%)
1 5-COD [b]	1000	100	100	COA (78) [b]
1 5-COD	200	100	100	COA (75)
1 3-COD	1000 or 200	100	100	COA (74)
1 5-COD	1000	60	60	COE (71) [b]
COE	1000	100	100	COA (75)
COE	200	100	100	COA (75)

[a] Substrate 1 M benzene 50 ml 6 h [b] COD cyclooctadiene COA cyclooctane carboxaldehyde COE cyclooctene carboxaldehyde (mixture of two species see text)

mixture of two isomers, and further indicated that the conjugated isomer was not present

The production of cyclooctene carboxaldehydes in such high yield under these conditions indicates that initial attack on the diene is again by hydroformylation If cyclooctene carboxaldehydes are really intermediates in the hydroformylation at 100°C and 100 at , then the mixture obtained above should undergo hydrogenation under these conditions This was found to be so, the yield of cyclooctane carboxaldehyde being the same as that obtained from the dienes (Table 2)

Hence, whereas the cyclic C_6-dienes give mainly dialdehydes in yields of ca 73%, the cyclic C_8-dienes give similar yields of saturated monoaldehydes The occurence of tetrahydrobenzaldehyde and cyclooctene carboxaldehydes as intermediates in the reactions rules out the possibility of a concerted process in which for example, hydroformylation or hydrogenation of the second double bond might occur in a chelated acyl—alkyl species This rules out the possibility of the effect of ring size on product formation being due to chelation From the study of models of the possible intermediates, such an effect seems in any case unlikely, since chelation of alkyl or acyl species appears equally possible for both rings, principally because of the increased flexibility of the C_8-ring. The observed difference in the second stage of the reactions must therefore stem from electronic and steric differences in the alkyl and acyl species formed.

Falbe et al. hydroformylated 1,2,3,6-tetrahydrobenzaldehyde using cobalt and rhodium based catalysts [8] With rhodium catalysts, mixtures of 55—65% 1,3-dialdehyde and 45—40% 1,4-dialdehyde were obtained The catalyst was derived from Rh_2O_3, and in the absence of bulky phosphine ligands, steric hindrance would have been relatively mild. Since formation of the 1,4-dialdehyde should be sterically most favourable, the occurence of the 1,3-isomer as the major product must be due to electronic effects out-weighing steric ones in this case The presence of two triphenylphosphine ligands in the catalyst used in this work would increase the importance of steric effects considerably, thus favouring formation of the 1,4-isomer, as observed. However, since it is possible to predict neither the outcome of electronic effects on the addition of tetrahydrobenzaldehyde to the Rh—H bond, nor the electronic effects in the alkyl and acyl species leading to the 1,3- and 1,4-dialdehydes [9], it is not known whether the observed formation of the 1,4-isomer is solely due to steric factors

In view of the behaviour of the above dienes, 1,3-cycloheptadiene and 1,3-cyclopentadiene were studied briefly From the former was obtained in 35% yield cycloheptane carboxaldehyde, and a highly involatile, probably polymeric material (ca. 50%). No dialdehyde was detected, 1,3-cyclopentadiene gave yields of 43—50% of a species which from elemental analyses and its NMR spectrum was a dialdehyde The analyses of samples which were pure by gas chromatography did not correspond satisfactorily to that required for cyclopentane dicarboxaldehyde, and the NMR spectrum showed the aldehyde signal as a triplet, suggesting the group —CH_2CHO was present This product was not investigated further. Attempted hydroformylation of bicyclo-(2,2,1)-hepta-2,5-diene at 100°C and 100 at pressure produced only a clear resinous solid, presumed to be a diene polymer At 50°C and 100 at pressure, a 40% yield of dialdehyde was obtained It is therefore clear that with this catalyst, dihydroformylation is favoured by small ring size, those rings above C_6 giving only monoaldehydes

The cyclic dienes studied here gave, in general, high yields of individual products Linear dienes are reported to give mixed products [1] and this we have confirmed with the catalyst used here with 1,3-butadiene, 1,4-pentadiene, and 1,5-hexadiene. Two explanations suggest themselves for this Firstly, the dialdehydes produced from linear dienes are thermally less stable than their cyclic counterparts, and are therefore more susceptible to decomposition under the reaction conditions Secondly, it has been pointed out that both intra- [10] and inter-molecular [11] decomposition of metal alkyl and acyl species may occur Because of reduced flexibility in the former case and greater steric hinderance in the latter, both of these processes would be more difficult with intermediates stemming from cyclic dienes, than with those from linear species

Experimental

IR and ^1H NMR spectra were recorded on Perkin—Elmer 21 and Varian HA-60 instruments respectively An F and M Series 810 Gas Chromatograph, using carbowax 20M and oxydipropionitrile columns was used for chromatographic work Dienes were from Fluka or Aldrich, and were purified as previously described [12] 1,2,3,6-Tetrahydrobenzaldehyde (Fluka) and the cyclooctene carboxaldehyde mixture were redistilled under reduced pressure before use Rhodium trichloride trihydrate was obtained from Johnson Matthey. Elemental analyses were performed by the ETH Microlabor, Zurich

Acetatocarbonylbis(triphenylphosphine)rhodium (I)

This wes prepared by a modification of the literature method [13] To benzene (10 ml) which was stirred with a moderate stream of carbon monoxide passing, was added $Rh(CO_2Me)(PPh_3)_3$ (1 g) [12] After 30 min, ether (25 ml) saturated with carbon monoxide was added to produce a bright yellow precipitate. This was collected, washed with carbon monoxide saturated ether (10 ml) and dried in vacuo. Yield 0 48 g (64%).

Hydroformylation

A 0.3 l steel autoclave, equipped with a stirrer, was used for all hydroformyl-

TABLE 3

ELEMENTAL ANALYSES

Compound	Found				Calculated			
	C	H	N	M.wt.	C	H	N	M.wt.
$C_6H_{10}(CHO)_2$ (from 1,3-Cyclohexadiene)	68.18	8.50		148	68.52	8.64		140
$C_6H_{10}(CHO)_2$ (from 1,4-Cyclohexadiene)	68.70	8.59		159				
$C_{20}H_{20}N_8O_6$ [a]	48.55	4.29	21.79	495	47.98	4.03	22.39	500
$C_8H_{15}CHO$	76.61	11.27		157	77.09	11.49		140
$C_{15}H_{20}N_4O_4$ [a]	56.19	6.21	17.67	330	56.22	6.30	17.49	320
$C_8H_{13}CHO$	77.81	10.36		144	78.20	10.21		138
$C_7H_{13}CHO$	75.24	10.74		128	76.13	11.18		126
$C_7H_{10}(CHO)_2$	70.63	7.83		158	71.01	7.96		152
$C_6H_{10}(CO_2H)_2$	55.28	7.00			55.78	7.03		

[a] 2,4-dinitrophenylhydrazones of preceeding aldehydes.

ations. Benzene (50 ml) was used as solvent. Substrates were added to give a concentration of one molar, and catalyst, as required for the desired substrate/catalyst ratio, was added sealed in a glass bulb under argon. The autoclave was then sealed, stirred 1 min under 50 at. 1 : 1 H_2/CO mixture, evacuated, and then filled to the required pressure. It was then heated to the required temperature and stirred for 6 h. After removal of a sample for GC analysis, (0.5 ml), the reaction mixture was fractionally distilled under reduced pressure. Where necessary, products were further purified by gas chromatography, and characterised by elemental analyses and NMR and IR spectroscopy.

Aldehyde oxidation

The cyclohexane dicarboxaldehyde was oxidised by alkaline permanganate ion according to the standard procedure [14] and recrystallised from water. For comparison, cyclohexane-1,2-dicarboxylic acid was obtained as a commercial product (Fluka), the 1,3-isomer was prepared from isophthalic acid by esterification, ring hydrogenation (Raney nickel) and saponification, and the 1,4-isomer by oxidation of 1,4-bis(hydroxymethyl) cyclohexane, again with permanganate. The elemental analyses were satisfactory. The IR and NMR spectra indicated that the 1,4-isomer was obtained in the hydroformylation process.

In order to determine whether the major isomer of the 1,4-dialdehyde was *cis* or *trans*, a sample obtained 90% pure by gas chromatography was oxidised as above and recrystallised. The melting-point of the product was 301–302°C (sublimes) indicating the *trans*-1,4-diacid [7]. Elemental analyses are given in Table 3.

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