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HYDROFORMYLATION OF PHENYL-SUBSTITUTED OLEFINS WITH COBALT CATALYSTS

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Summary

A study of the hydroformylation of styrene, α-methylstyrene, allylbenzene and *trans*-propenylbenzene catalysed by octacarbonyldicobalt has shown that use of pyridine as a catalyst activator has a marked influence on the selectivity of the reaction and that the isomeric composition of the aldehydes is strongly dependent upon the temperature. Deuterium scrambling was observed in the hydrogenation and hydroformylation products concurrently formed from 2-phenylpropene-1d_2-3d_3 even at $p(\text{CO}) = 100$ atm.

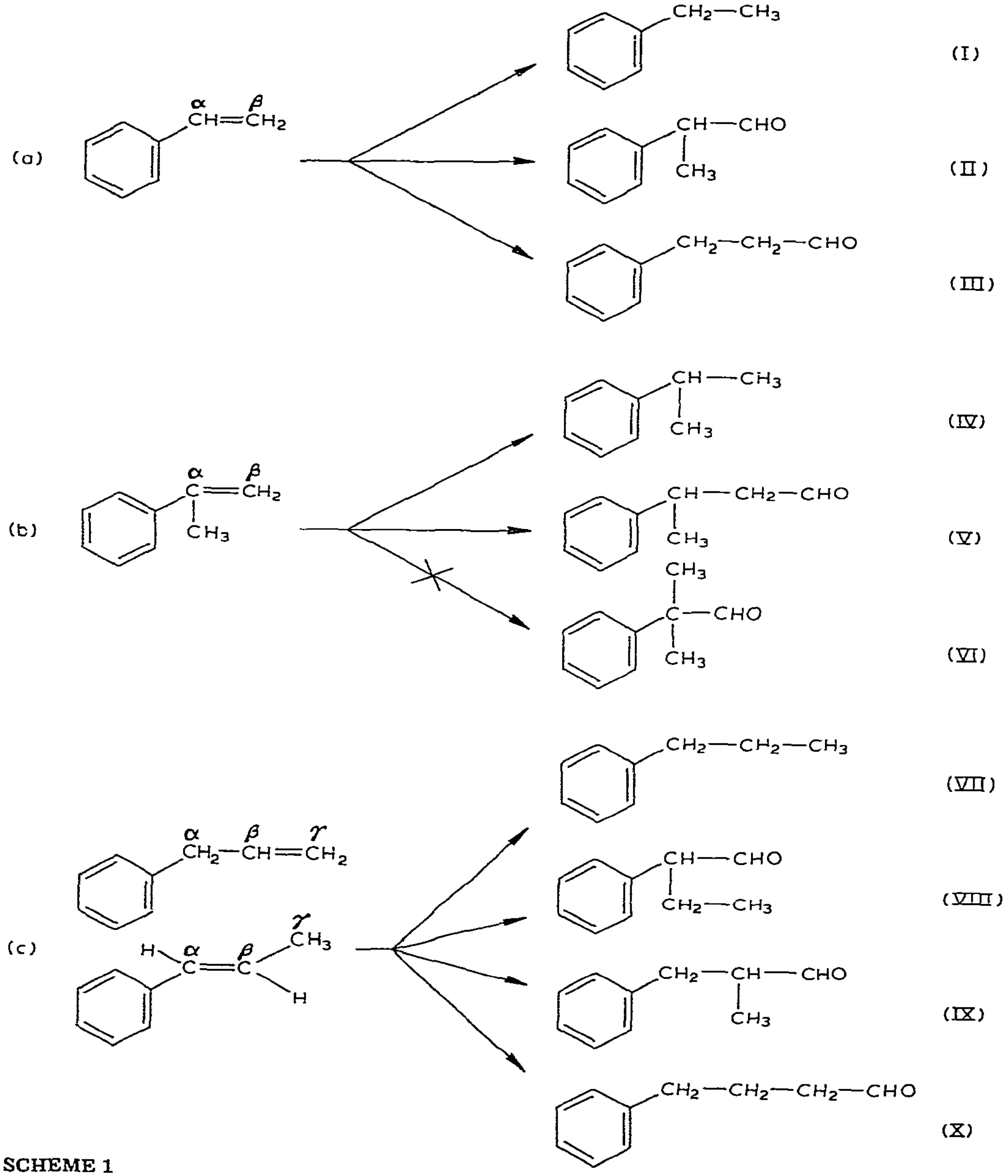
Introduction

Hydroformylation of olefins containing phenyl substituents has been relatively little studied in the last decade [1,2]. In reactions involving cobalt catalysts the selectivity is markedly lower than that in reactions of wholly aliphatic substrates, and in most cases hydrogenation of the double bond is the main reaction. Moreover, when the olefinic double bond is conjugated with the aromatic ring, the addition of the formyl group occurs with high regioselectivity at the carbon atom α to the phenyl ring (Markownikoff addition).

In connection with our studies of asymmetric hydroformylation of phenyl-substituted olefins catalysed by carbonyl cobalt complexes containing chiral ligands [3], we were interested in the influence of the temperature on the selectivity of the reaction and on the isomer distribution of the hydroformylation products. We report below the results obtained in hydroformylation of styrene, α-methylstyrene, allylbenzene and *trans*-propenylbenzene with octacarbonyldicobalt at various temperatures and in the presence of pyridine as activator [4]. For a mechanistic study the hydroformylation of 2-phenylpropene-1d_2-3d_3 was also performed.

Results

The hydroformylation of styrene, α-methylstyrene, allylbenzene and *trans*-propenylbenzene was carried out using crystalline octacarbonyldicobalt at 60—120°C and 80 atm total pressure ($CO/H_2 = 1$). Each experiment was repeated in the presence of pyridine (Co : pyridine molar ratio = 1) as activator The reaction products, in addition to the expected aldehydes (II), (III), (V), (VIII), (IX), (X), were alkylbenzenes (I), (IV), (VI), derived from the hydrogenation of the substrate (Scheme 1).



SCHEME 1

TABLE 1

INFLUENCE OF PYRIDINE ON THE RATE AND ON THE ALDEHYDE DISTRIBUTION IN THE COBALT CATALYZED HYDROFORMYLATION OF PHENYL SUBSTITUTED OLEFINS

Reaction pressure: 80 atm, CO/H_2 = 1.

Olefin	Catalytic system [a]	Reaction time, (h)	Reaction temperature (°C)	Conversion [b] (%)	Selectivity [c] (%)	Position of formylation [d]		
						α	β	γ
Styrene	A	20.5	60	8.4	90	83	17	—
	B	20.5	60	57.4	61	87	13	—
	A	3.5	120	n.d.	n.d.	63	37	—
	B	1.5	110	87.3	35	65	35	—
trans-Propenylbenzene	A	21	110	100	26	60	10	30
	B	12	110	100	7.3	59	8	33
α-Methylstyrene	A	26	60	1.1	n.d.	—	~100	—
	B	18.5	60	35.5	~0	—	—	—
	A	9	110	77.2	28	—	~100	—
	B	1.5	110	72.4	8	—	~100	—

[a] A = $Co_2(CO)_8$ (0.18 g/5.5 g olefin in 40 ml benzene); B = $Co_2(CO)_8$/pyridine = 0.5/1 (molar ratio). [b] Conversion (%) = 100 × moles of substrate transformed/moles of olefin charged. [c] Selectivity (%) = moles of aldehydes × 100 moles of reacted olefin. [d] 100 × moles of aldehyde/moles of total aldehydes.

The results reported in Table 1 clearly indicate, in agreement with previous observations [4] that pyridine has a marked influence on the reaction rate; and in its presence satisfactory reaction rates are attained even at 60°C (Table 1).

Particularly interesting is the effect of the base on selectivity of the reaction. For example, in the case of styrene the amount of ethylbenzene was increased from 10 to 39% by the presence of pyridine in hydroformylations carried out at 60°C. Under the same reaction conditions α-methylstyrene was not hydroformylated in the presence of pyridine and cumene was the only product.

The pyridine had little effect on the aldehyde distribution (Table 1). However, change of temperature does strongly affect the isomeric composition of the aldehydes. All the olefins showed similar behaviour: viz. the proportion of formylation at the α-carbon (Scheme 1) was increased as temperature was lowered (Table 2). Very high regioselectivity ($\geqslant$90%) for the α position was found in the hydroformylation of styrene and *trans*-propenylbenzene (Table 1): at 60°C, $p(CO) = 100$ atm and $p(H_2) = 40$ atm in the presence of pyridine 90% of hydratropaldehyde (II) was obtained. This aldehyde was practically the only reaction product from hydroformylation of styrene at room temperature and 80 atm total pressure ($CO/H_2 = 1$) : 2% overall yield of hydroformylation product was obtained, and only traces of ethylbenzene (I) and 3-phenylpropanal (III) were formed.

Hydroformylation of 2-phenylpropene-1d_2-3d_3 (isotopic purity ~83% by mass spectroscopy) was examined, the reaction products and the unreacted olefin being separated by preparative GLC. The deuterium content and distribution in the reaction products was determined by mass spectral analysis. At 60°C, and 80 atm total pressure ($CO/H_2 = 1$) in the presence of pyridine (Co/pyridine molar ratio = 1) cumene (IV) was, as expected, the only reaction product, and was found to contain an average of 4.15 deuterium atoms per molecule. However, this product was not uniformly deuterated: the mass spectrum showed the

TABLE 2

EFFECT OF TEMPERATURE VARIATION ON THE ALDEHYDE DISTRIBUTION IN THE COBALT CATALYZED HYDROFORMYLATION OF PHENYL SUBSTITUTED OLEFINS

Reaction pressure: 80 atm, $CO/H_2 = 1$.

Olefin [a]	Reaction temperature (°C)	Reaction time (h)	Yield (%)	Aldehyde distribution [b]		
				α	β	γ
Styrene	60	20.5	35	87	13	—
	80	14.0	37	78	22	—
	110	1.5	31	65	35	—
Allylbenzene	45	119.0	n.d.	42	8	50
	60	20.0	30	33	8	59
	110	1.5	30	12	13	75
trans-Propenylbenzene	60	24.0	7	95	1	4
	110	12.0	7.3	60	8	32

[a] Catalytic system: $Co_2(CO)_8$/pyridine = 0.5/1 (0.18 g of $Co_2(CO)_8$/5.5 g olefin in 40 ml benzene).
[b] 100 × moles of aldehyde/moles of total aldehydes.

presence of mono- and polydeuterated cumenes in almost statistical proportions.

This hydroformylation was repeated at 110°C and 80 atm ($CO/H_2 = 1$) without pyridine in order to test the role of the base in the deuterium-scrambling and to give the isotopic distribution in the hydroformylation product 3-phenylbutanal (V). In this case also no loss of deuterium was observed, but both the obtained cumene (IV) and 3-phenylpropanal (V) were mono- and polydeuterated according to the statistical pattern. It was impossible to determine the positions of the deuterium atoms in the hydrogenation and hydroformylation products by NMR analysis because of the complexity of the mixture of mono- up to hepta-deuterated compounds.

Similar deuterium scrambling was observed in the hydroformylation of the same substrate at 110°C with octacarbonyldicobalt and pyridine at $p(CO) =$ 40 atm and $p(H_2) = 40$ atm and even at $p(CO) = 90$ atm and $p(H_2) = 20$ atm (see Experimental). The mass spectra at 15 eV of the unreacted olefin revealed a temperature dependent loss of deuterium.

A mixture of the deuterated cumenes obtained from an hydroformylation experiment on 2-phenylpropene-1d_2-3d_3 carried out at 110°C and $p(CO) = p(H_2) = 40$ atm in the presence of pyridine was converted into benzoic acid by $KMnO_4$-oxidation; the acid was found to contain no deuterium atom (mass spectroscopy).

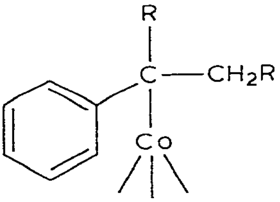
Discussion

Although the effect of nucleophilic reagents on the reaction rate of stoichiometric and catalytic hydroformylation with octacarbonyldicobalt has been much studied [1,4,5], the mechanism of its action had not been fully elucidated. The most accepted hypothesis is that the increase of the hydroformylation rate is due to a faster formation of catalytically active carbonylcobalt-hydride complexes in the reaction medium [4,5]. The results we have obtained show that the mechanism of reaction of the pyridine in the catalytic process is much more complicated, at least in the hydroformylation of the substrates we have used. It is difficult to explain the considerable selectivity variation, i.e. the increase of the substrate hydrogenation observed, only in terms of a base-assisted formation of active cobalt-hydride complexes. Moreover, since the aldehyde distribution is not affected by the pyridine, we suggest that there must be definite influence of the base in other steps of the catalytic process also, mainly in the oxidative addition of hydrogen to intermediate alkyl- and/or acyl-cobalt complexes and in the subsequent breakdown of the resulting intermediate complexes.

Hydroformylation experiments under standard-oxo conditions have been carried out using styrene and α-ethylstyrene as prochiral substrated and octacarbonyldicobalt as catalytic precursor in the presence of (+)(*S*)-3-s-butylpyridine [6]: both the hydratropaldehyde (II) and 2-phenylbutane obtained were optically inactive. These results seem to exclude a direct influence of the base on the first steps of the catalytic process, in which the asymmetric induction probably takes place [3].

The present data do not allow a detailed explanation of the influence of temperature on the regioselectivity of the CO and H_2 addition to the olefinic linkage.

A reasonable explanation of most of the experimental results can be given by assuming a temperature depending stabilization of the postulated intermediate σ-alkylcobalt complex.



This stabilization can arise from an interaction of the π-electron system of the aromatic ring with the empty *d*-orbitals of the metal, and seems to be more important at low temperature. From this complex the more branched aldehyde, corresponding to an α-formylation is formed. Another possible type of stabilization involving σ-electrons of the C—H bonds nearer to the metal seems to be not operative, as indicated by the results obtained in the hydroformylation of 2-phenylpropene-1d_2-3d_3, no deuterium being found in the phenyl ring of benzoic acid derived from the mixture of the deuterated cumenes. This result also, in our opinion, excludes the formation of an intermediate π-allyl complex involving a double bond of the phenyl substituent, previously postulated [7].

At higher temperatures isomerization of the olefinic double bond and of the postulated π-olefin complex would become more important and, of course, a higher straight-to-branched isomer ratio should be expected.

The behaviour of allylbenzene, the only non-conjugated olefin employed, is illustrative in this context: the results obtained in its hydroformylation (Table 2) indicate that at low temperature (45°C) a double bond shift toward conjugation with the aromatic system takes place (thermodynamic control), whereas at higher temperature (110°C) the π-olefin complex breaks down relatively rapidly to the products giving rise to a greater amount of straight chain aldehyde (kinetic control).

No significant information was provided by the hydroformylations of 2-phenylpropene-1d--3d_3 which were complicated by extensive deuterium scrambling, which was not expected under the conditions used. This result shows that the structure of the substrate plays a very important role in the mechanism of this catalytic process, as noted by other authors [8].

While no appreciable exchange between the deuterium atoms of the olefin and the cobalt-hydride complexes responsible for hydroformylation was observed at low temperature (see Experimental), nevertheless a nearly statistical distribution of mono- up to hepta-deuterated products was found, indicating that intermediate cobalt complexes involving additional olefin molecules must participate in the catalytic process [9]. This is supported by the results obtained for the deuterium distribution in the unreacted olefin. Because the substrate we used was not of very high isotopic purity (83%), we were able to observe definite deuterium redistribution also in the aliphatic chain of the olefin, but this does not reach the statistical value.

Further experiments are in progress to provide more understanding of the mechanism of this catalytic process.

Experimental

Gas-chromatographic analyses were performed with a F 30 Perkin-Elmer gas-chromatograph. Quantitative determinations were carried out using an internal standard: mesitylene in the hydroformylation of styrene, α-methylstyrene and α-ethylbenzene, and *m*-dimethoxybenzene for *trans*-propenylbenzene and allylbenzene. The 2-m column used was packed with 20% Silicone 550 on Chromosorb W at temperatures between 150—200°C.

Preparative gas-chromatographic separations were accomplished with a Perkin-Elmer F 21 gas-chromatograph using a 3-m column at 130°C packed with Silicone OV-17 10% on Chromosorb A (60—80 mesh). Mass spectra were determined with an Hitachi Perkin-Elmer RMU-6L mass spectrometer. Direct linkage of a gas-chromatograph (Perkin-Elmer 990) with the mass spectrometer was used to analyse the components of the mixtures.

Optical rotations were measured on a Perkin-Elmer model 241 polarimeter in 1 dm tube and on pure liquids.

Materials

Styrene, allylbenzene, α-methylstyrene and *trans*-propenylbenzene were commercial products (Fluka AG) and were distilled before use. Benzene was used after refluxing and distillation over metallic sodium under nitrogen. Pyridine was distilled over potassium hydroxyde pellets under nitrogen. Octacarbonyldicobalt (m.p. 52°C) was prepared as described by Natta and Ercoli [10] and purified by crystallization from light petroleum. α-Ethylstyrene was prepared from propiophenone and methylidenephosphorane iodide [11]. 2-Phenylpropene-1d_2-3d_3 was obtained in 70% overall yield by dehydration with acetic anhydride of 2-phenylpropan-2-ol, which in turn was prepared by reaction of phenylmagnesium bromide with acetone-d_6.

The mass spectrum of deuterated olefin showed an isotopic purity $\geqslant$83%. The composition (%) of this olefin determined by mass spectral analysis at 15 eV was: $d_0 = 0$, $d_1 = 1.0$, $d_2 = 6.0$, $d_3 = 18.0$, $d_4 = 28.0$, $d_5 = 47.0$.

Hydroformylation experiments

All experiments were carried out in a 150-ml stainless-steel rocking autoclave heated in a thermostated oil-bath; the temperature could be maintained to within ±1°C. The $Co_2(CO)_8$ (0.190 g) was placed in the autoclave and the vessel evacuated; then a solution of 5.5 g of olefin in 40 ml benzene was introduced by suction. In the experiments in the presence of the catalyst activator the added solution contained 80 μl of pyridine. An equimolecular mixture of hydrogen and carbon monoxide was introduced in the autoclave up to the desired pressure value, and the vessel was rocked in the oil-bath. After the reaction was stopped, the autoclave was rapidly cooled with ice-water, gases were discharged and the solutions immediately analysed.

Hydroformylation of styrene with octacarbonyldicobalt in the presence of (+)-(S)-3-s-butylpyridine

Styrene (5.5 g, 0.053 mol) in 40 ml benzene was hydroformylated with $Co_2(CO)_8$ (0.190 g) in the presence of (+)-(*S*)-3-s-butylpyridine (0.140 g),

$[\alpha]_D^{25}$ + 26.7 (60% optical purity) [6], at 60°C and 80 atm ($CO/H_2 = 1$) as described above. After 17 h 50% of olefin had reacted (GLC). Evaporation of the solvent and distillation of the residue gave 1.2 g of hydratropaldehyde (95% pure by GLC analysis). This product was dissolved in 10 ml pentane and extracted three times with 10% aqueous HCl at 0°C. Drying (Na_2SO_4), evaporation of the pentane and distillation gave practically pure hydratopaldehyde, b.p. 45°C (0.05 mmHg), which was optically inactive.

Hydroformylation of α-ethylstyrene with octacarbonyldicobalt in the presence of (+)-(S)-3-s-butylpyridine

α-Ethylstyrene (2 g, 0.015 mol) in 15 ml benzene was hydroformylated with $Co_2(CO)_8$ (0.106 g) in the presence of the same chiral pyridine (80 μl) at 50°C and 80 atm ($CO/H_2 = 1$). After 18 h more than 95% of substrate had reacted. The usual working up gave pure optically inactive 2-phenylbutane, b.p. 105—106°C (28 mmHg).

Hydroformylation reactions of 2-phenylpropene-1d_2-3d_3 under various conditions

Hydroformylations of deuterated α-methylstyrene were carried out by the general procedures described above. Conversions and yields obtained were comparable with those reported in Table 1 for the undeuterated olefin under corresponding conditions. After each hydroformylation, the reaction mixture was distilled bulb-to-bulb under vacuum in order to remove the catalyst and then the unreacted olefin and each product was separated in pure form by preparative GC. Inspection of molecular peak measured at 15 eV indicated the following compositions (%) of the recovered olefin:

(1) Experiment carried out at 60°C and 80 atm ($CO/H_2 = 1$) in the presence of pyridine (see Table 1): $d_1 = 0.8$, $d_2 = 2.6$, $d_3 = 14.4$, $d_4 = 51.4$, $d_5 = 30.8$.

(2) Experiment carried out at 110°C and 80 atm ($CO/H_2 = 1$) in the presence of pyridine (see Table 1): $d_0 = 1.0$, $d_1 = 3.0$, $d_2 = 18.5$, $d_3 = 36.7$, $d_4 = 24.5$, $d_5 = 16.3$.

(3) Experiment carried out at 110°C and 80 atm ($CO/H_2 = 1$) without pyridine (see Table 1): $d_1 = 4.0$, $d_2 = 9.5$, $d_3 = 27.0$, $d_4 = 36.5$, $d_5 = 23.0$.

(4) Experiment carried out at 110°C, $p(CO) = 90$ atm and $p(H_2) = 20$ atm without pyridine: $d_0 = 4.5$, $d_1 = 7.8$, $d_2 = 16.7$, $d_3 = 28.0$, $d_4 = 28.0$, $d_5 = 15.0$.

Oxidation of a mixture of deuterated cumenes to benzoic acid

2-Phenylpropene-1d_2-3d_3 (3.2 g, 0.025 mol) in 20 ml benzene were hydroformylated with $Co_2(CO)_8$ (0.09 g) in the presence of pyridine (40 μl) at 110°C and 80 atm ($CO/H_2 = 1$). After 6 h the conversion was practically quantitative. After the usual working up, vacuum distillation gave a mixture of deuterated cumenes (2.54 g, 80% yield), which was converted into benzoic acid by potassium permanganate oxidation [12]. This acid was obtained in pure form (m.p. 121°C) in 25% yield and found by mass spectrometry to contain no deuterium.

Identification of the reaction products

The identities of the hydroformylation and hydrogenation products obtained from the olefins investigated were confirmed by comparison of their physical properties with those of authentic samples.

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