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HYDROCARBONYLATION OF UNSATURATED NITROGEN COMPOUNDS. SYNTHESIS OF *N*-PROTECTED AMINOACID DERIVATIVES FROM *N*-SUBSTITUTED PHTHALIMIDES

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Summary

The hydrocarbonylation of some β-substituted *N*-vinylphthalimides catalysed by Rh or Pd complexes has been investigated. The reaction is strongly affected by the nature of the substituent and is completely prevented when two substituents are present. The addition of carbon monoxide, when it occurs, takes place with complete selectivity and its direction can be regulated to a large extent by selecting the reaction parameters.

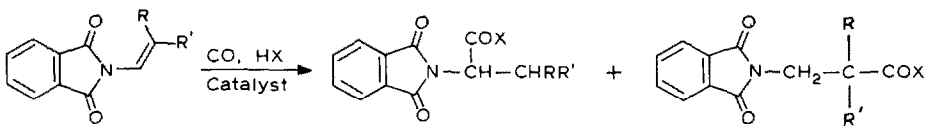
The hydrocarbonylation of *N*-allylphthalimide occurs under mild conditions but the control of the regioselectivity is much less efficient.

Introduction

The hydrocarbonylation of easily available *N*-alkenylimides provides a ready entry to *N*-protected aminoacid derivatives and constitutes a valuable synthetic tool for the preparation of these kinds of compounds.

Recent works in this field have pointed out that the hydroformylation of unsubstituted *N*-vinylimides (Scheme 1; $R = R' = H$, $HX = H_2$), catalyzed by

SCHEME 1



(1a. R = H, R' = CH_3,
1b R = H, R' = Ph,
1c R = CH_3, R' = CH_3)

(3)

(4)

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rhodiumdiphosphine complexes [1], takes place in a regiospecific mode, affording in high yield the branched aldehyde which is easily oxidized to the corresponding alanine derivative. Fair optical yields, up to 41%, have also been obtained when chiral bidentate phosphines were employed as ligands for the metal in the asymmetric process.

The same substrates can be converted into *N*-protected aminoesters by hydrocarbalkoxylation in the presence of palladium catalysts [1,2,3] (Scheme 1; HX = ROH). In this case the regioselectivity of the carbon monoxide insertion is dictated by the nature of the phosphine used as ligand and a selectivity higher than 90% for the branched, as well as for the linear product, is easily attainable in the presence of mono- or bi-dentate phosphines, respectively [2,3].

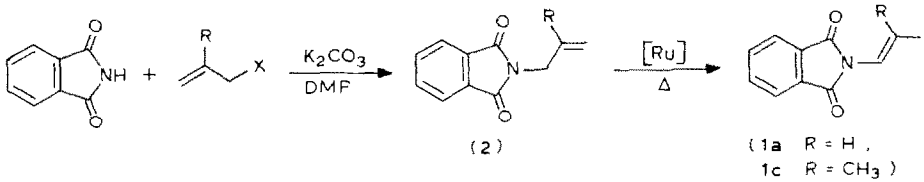
To extend the potential of this process, and to obtain an insight into the factors that regulate the regioselectivity of the carbon monoxide addition to these substrates, we have investigated the hydrocarbonylation of some β-substituted *N*-vinylphthalimides **1** and of *N*-allylphthalimide **2**.

On carbon monoxide addition, substrates **1b** and **1c** would give rise directly to derivatives of the natural α-aminoacids, phenylalanine (**3c**) and valine (**3b**) (Scheme 1), while the linear products arising from **2** are of interest because they can easily be converted into either 2-pyrrolidone derivatives or proline [1].

Results

The required substrates were prepared as depicted in Scheme 2. The alkylation of

SCHEME 2



phthalimide with the suitable allylic halide was quickly accomplished through a solid-liquid phase-transfer catalyzed process. The reaction was carried out in dimethylformamide in the presence of anhydrous potassium carbonate and a 5 mol% amount of methyltrioctylammonium chloride (Aliquat 336). Pure allylphthalimides **2** could be recovered in high yield simply by dilution with water after 15–20 h stirring at room temperature.

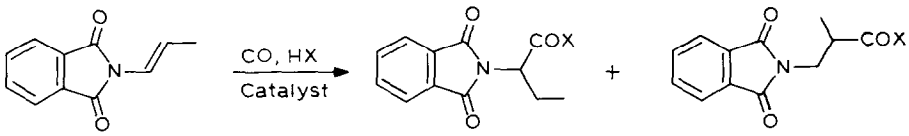
Ruthenium complexes promoted the irreversible double bond migration in *N*-allylphthalimides **2** to give the *N*-propenyl-derivatives **1**. The reaction was best affected by heating the substrate with a catalytic amount (1 : 100) of a ruthenium compound under a nitrogen atmosphere at 150°C.

The isomerization of **2a** (Scheme 2; R = H), catalyzed by $RuCl_2(PPh_3)_3$, was completed in a few h and was highly stereoselective, affording pure (*E*)-*N*-propenylphthalimide, **1a**, after one crystallization from ethanol.

The substituted allylic derivative **2b** (Scheme 2; R = CH_3) did not undergo double bond migration in the presence of $RuCl_2(PPh_3)_3$ and the use of a more active catalyst, namely $H_4Ru_4(CO)_{12}$, was necessary. Although the reaction took more than 100 h to reach a satisfactory conversion, this catalytic isomerization

TABLE 1

HYDROCARBONYLATION OF (*E*)-*N*-PROPENYLPHTHALIMIDE



(1) (3) (4)

Catalyst	Conversion [a] (%)	Selectivity [b] (%)	Regioselectivity [c] (%)	Optical yield (Config.) (%)
Hydroformylation (HX = H_2) [d]				
$HRh(CO)(PPh_3)_3$/(−)-DIOP (1:2)	98	100	100	0
$HRh(CO)(PPh_3)_3$/(−)-DIOCOL (1:2)	90	100	100	0
Hydrocarbethoxylation (HX = EtOH) [e]				
$PdCl_2$/(−)-DIOP (1:1)	70	100	15	1.5 (*S*) [f]
$PdCl_2$/(−)-DIOCOL (1:1)	78	100	12	3 (*R*)
$PdCl_2/PPh_3$ (1:2)	52	90	61	–

[a] Determined by GLC. [b] Mol aldehydes (esters)/mol reacted substrate ×100. [c] Mol of **3**/mol of **3**+mol of **4**×100. [d] Substrate 0.02 mol, benzene 20 ml, substrate/catalyst 300:1, *p*(total) ($CO:H_2$ = 1:1) 100 atm at 25°C, 24 h at 100°C. [e] Substrate 0.02 mol, MEK 20 ml, EtOH 4 ml, substrate/catalyst 100 1; *p*(CO) 100 atm at 25°C, 110 h at 100°C. [f] Determined by converting **4** into 2-methyl-3-*N*-phthalimidopropanoic acid, $[\alpha]^{17°}_{D(max)} = 24.4$ ($c = 0.98$, $CHCl_3$).

compares favourably with the previously reported preparation of **1c**, involving the treatment of **2b** with a stoichiometric amount of pentacarbonyliron [4,5].

The hydrocarbonylation experiments of substrates **1** and **2** were carried out under a total pressure of 100 atm and at temperatures in the range 70–100°C. The hydroformylations were usually performed in benzene solution using rhodiumphosphine complexes as catalysts, at a substrate-to-metal ratio of 300:1. In the asymmetric reactions one of the two optically active diphosphines (−)-DIOP * or (−)-DIOCOL ** was added to the catalytic precursor.

The catalysts for the asymmetric hydrocarbethoxylation were prepared in situ from palladium dichloride and the above-mentioned diphosphines and the reactions were performed in methyl ethyl ketone solution at a substrate-to-metal ratio of 100:1.

The reactivity of the investigated substrates towards carbon monoxide insertion varied over a wide range: the β-disubstituted vinylimide **1c** was quite unreactive and failed to give any carbonylation product even in the most drastic conditions employed.

N-Styrylphthalimide **1b** was hydroformylated only to a small extent (5%) at 100°C, giving only one aldehyde, probably the one arising from the addition of the formyl group to the carbon linked to the nitrogen. No reaction took place in the presence of palladium catalysts.

* DIOP = 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane [6].

** DIOCOL = 2,3-*O*-(5′α-cholestan-3′,3′-ylidene)-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane [7].

On the other hand, (*E*)-*N*-propenylphthalimide **1a** reacted smoothly at 100°C, giving in high yield the expected carbonylation products with complete selectivity (Table 1). The addition of carbon monoxide in the rhodium-catalyzed hydroformylation occurred in a regiospecific mode to the carbon linked to the nitrogen (α-insertion) so that 2-*N*-phthalimidobutanal **3a** (Scheme 1; X = H) was obtained in an almost quantitative yield. The reaction was however lacking in stereoselectivity and the isolated aldehyde was racemic.

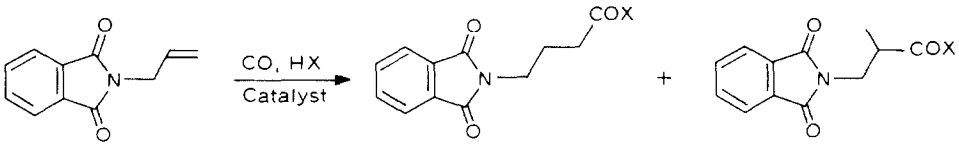
Quite different behaviour was observed in the hydrocarbethoxylation, where palladium-chiral-diphosphine-complexes strongly favoured the β-insertion of carbon monoxide, affording a reaction product containing about 85–90% of the optically active β-phthalimido ester **4a** (Scheme 1; X = OEt). The optical purity of this compound was established on the corresponding acid, prepared by saponification [8], and ranged between 1 and 3%.

The direction of the carbon monoxide addition in the hydrocarbethoxylation could be regulated to a large extent by the choice of the phosphine ligand: in the presence of triphenylphosphine the predominant product (60%) was, in fact, the α-phthalimido-derivative **3a** (Scheme 1; X = OEt).

The rhodium-catalyzed hydroformylation and the palladium-catalyzed hydrocarbethoxylation of *N*-allylphthalimide **2** exhibited some common features: in both cases the insertion of carbon monoxide took place readily under mild conditions, giving only the two expected carbonylation products (Table 2). Conversely, both the reactions were poorly regioselective since the linear/branched isomer-ratio ranged from 0.67 to 1.7 in the hydroformylation and was only slightly better, up to 3, in the hydrocarbethoxylation.

TABLE 2

HYDROCARBONYLATION OF *N*-ALLYLPHTHALIMIDE



(2) (5) (4)

Catalyst	Conversion [a] (%)	Selectivity [b] (%)	Ratio **5**/**4**	Optical yield (Config.) [c] (%)
Hydroformylation (HX = H_2) [d]				
$HRh(CO)(PPh_3)_3$/(−)-DIOP (1:2)	95	100	1.3	1 (*R*)
$HRh(CO)(PPh_3)_3$/(−)-DIOCOL (1.2)	90	100	1.7	1.5 (*R*)
$RhCl(CO)(PPh_3)_2/PPh_3$ (1:50) [e]	98	100	0.7	—
$Co_2(CO)_8$ [f]	94	48	4	—
$PtCl_2(PPh_3)_2/SnCl_2$ (1:5) [g]	90	88	1.5	—
Hydrocarbethoxylation (HX = EtOH) [h]				
$PdCl_2$/(−)-DIOP (1:1)	98	100	3	4 (*R*)
$PdCl_2$/(−)-DIOCOL (1:1)	99	100	2.4	4 (*R*)

[a] Determined by GLC. [b] Mol aldehydes (esters)/mol reacted substrate ×100. [c] Determined by converting **4** into the corresponding acid. [d] Substrate 0.02 mol, benzene 20 ml, substrate/catalyst 300·1, p(total) (CO:H_2 = 1.1) 100 atm at 25°C, 15–20 h at 70°C. [e] Substrate/catalyst 1000:1. [f] Substrate/catalyst 50:1, 43 h at 120°C. [g] Solvent MEK (20 ml). [h] Substrate 0.02 mol, MEK 16 ml, EtOH 4 ml, substrate/catalyst 100.1, p(CO) 100 atm at 25°C, 24 h at 100°C.

A higher yield of the straight chain isomer (80%) could be obtained in the cobalt-catalyzed hydroformylation but, unfortunately, the product selectivity in this case was poor and the oxo-products consisted of an almost equal mixture of alcohols and aldehydes while about 5% of the substrate was hydrogenated to *N*-propylphthalimide.

A higher amount of this by-product (12%) was formed when the hydroformylation was carried out in the presence of a platinum–tin based catalyst: in this case the reaction was selective for the aldehydes, but the yield of the linear isomer (60%) was no better than those obtained with rhodium catalysts.

The branched isomer produced in the asymmetric hydrocarbonylations of *N*-allylphthalimide was found to be optically active in every case (Table 2). The optical yields were determined by relating the chiral reaction product to the relevant acid of known configuration and were slightly higher in the hydrocarbethoxylation (~ 4%) than in the hydroformylation.

Discussion

The hydrocarbonylation of *N*-alkenylphthalimides is strongly affected by the substituent(s) present on the carbon remote from the nitrogen. The insertion of carbon monoxide readily occurs on unsubstituted substrates [1,2,3] and its rate is only slightly reduced when an unhindered substituent like methyl is present. When the steric hindrance of the substituent increases, the reaction is strongly hampered and it is completely prevented when two substituents are present.

These results are qualitatively in keeping with the behaviour observed in the rhodium-catalyzed hydroformylation of the corresponding phenyl-substituted olefins, although the range of reactivity displayed by the latter substrates is more restricted as they are affected by substitution to a lesser extent than phthalimides [11].

The addition of carbon monoxide to *N*-alkenylimides, when it occurs, can be directed with high regioselectivity either to the α- or to the β-carbon atom by the choice of a suitable combination of metal catalyst-ligand-hydrogen donor, and this allows the process to be useful for synthetic purposes.

Also in this respect, the phthalimido-olefins behave similarly to the phenyl-substituted substrates, with the noticeable exception of the rhodium-catalyzed hydroformylation, which is quite regiospecific for *N*-alkenylphthalimides and only regioselective to a variable extent for alkenylbenzenes [11].

When the substituent is moved one carbon atom further away from the double bond, as in *N*-allylphthalimide, the reactivity increases, but the control over the regioselectivity is much less efficient.

These facts seem to indicate that the reactivity of these compounds is dependent mostly on steric effects, while electronic factors are more likely to be involved in determining the regioselectivity of the reaction.

The optical yields obtained in the asymmetric reactions are very low and are slightly higher for the chiral products arising from *N*-allyl- rather than *N*-propenylphthalimide. Although these results do not allow any sound conclusion, the low stereoselectivity may indicate that *N*-alkenylphthalimides do not act as polydentate ligands in the hydrocarbonylation, as otherwise occurs in the rhodium-catalyzed hydrogenation of the structurally-related α-acylaminoacrylic acids.

As a final remark, our results confirm that the exclusive formation of α-CO insertion products in the hydroformylation of enimides is the general behaviour of these compounds and this provides a straightforward method for the preparation of *N*-protected α-aminoaldehydes, a class of products of increasing interest [12].

Experimental

Materials

Reagents and solvents were commercial products. *N*-Styrylphthalimide was prepared as reported in the literature [13]. $HRh(CO)(PPh_3)_3$, $RhCl(CO)(PPh_3)_2$, $Co_2(CO)_8$, $PtCl_2(PPh_3)_2$, (−)-DIOP (Strem Chemicals) and $PdCl_2$ (Fluka) were used as received. (−)-DIOCOL was available in our laboratories and $H_4Ru_4(CO)_{12}$ was prepared according to the literature [14].

Carbon monoxide was obtained from GMBH (Ludwigshafen, West Germany) and hydrogen from NIGS (Porto Torres, Italy).

General procedure

Melting points are uncorrected. GLC analyses were performed on a Perkin-Elmer 3920B instrument using 6 ft columns of 2.5% OV-17 and 2.5% SE-30 on Chromosorb W. ^1H NMR spectra were recorded on a Varian T-60 instrument in $CDCl_3$ solution using tetramethylsilane as internal standard ($\delta = 0$ ppm). Mass spectra were recorded on a Hitachi Perkin–Elmer RMU-6L mass spectrometer. Optical rotations were obtained with a Perkin–Elmer 241 polarimeter.

Preparation of N-allylphthalimide

Freshly distilled allyl bromide (91 g, 0.75 mol) was added dropwise to a well-stirred suspension of phthalimide (100 g, 0.68 mol), anhydrous potassium carbonate (190 g, 1.37 mol) and Aliquat 336 (10 g, 0.027 mol) in dimethylformamide (350 ml), while maintaining the temperature at 20°C in a water bath. After 20 h stirring, the slurry was poured into water (1.5 l), the resulting precipitate was filtered, dried and crystallized from ethanol to give pure *N*-allylphthalimide (115 g, 90% yield), m.p. 70°C (lit. 70°C [15]). ^1H NMR: 7.65 (m, 4H, aromatic), 6.20–5.53 (m, 1H, –CH=), 5.35–4.95 (m, 2H, $=CH_2$), 4.25 (m, 2H, $=N-CH_2-$).

Preparation of N-(2-methyl)allylphthalimide

Following the same procedure, *N*-(2-methyl)allylphthalimide was obtained from 2-methylallyl chloride in 99% yield: m.p. 87–88°C (lit. 87–88°C [4]); ^1H NMR: 7.65 (m, 4H, aromatic), 4.82 (m, 2H, $=CH_2$), 4.15 (s, 2H, $=N-CH_2-$), 1.80 (s, 3H, $-CH_3$).

Preparation of (E)-N-propenylphthalimide

N-Allylphthalimide (10 g, 5.3×10^{-2} mol) and $RuCl_2(PPh_3)_3$ (0.508 g, 5.3×10^{-4} mol) were heated at 150°C under nitrogen for 13 h. The resulting yellow solid was dissolved in benzene, filtered through a short column of silica gel and crystallized from n-hexane to give pure (*E*)-*N*-propenylphthalimide (9 g, 90% yield), m.p. 150°C (lit. m.p. 149–150°C [13]). ^1H NMR: 7.65 (m, 4H, aromatic), 6.50 (m, 2H, –CH=CH–N=), 1.85 (d, 3H, $-CH_3$).

Preparation of N-(2-methylpropenyl)phthalimide

N-(2-Methyl)allylphthalimide (12 g, 6×10^{-2} mol) and $H_4Ru_4(CO)_{12}$ (0.113 g, 1.5×10^{-4} mol) were heated under nitrogen at 175°C for 100 h. At this time the conversion, determined by GLC, was 66%. The reaction mixture was filtered through silica gel (benzene), a new aliquot of $H_4Ru_4(CO)_{12}$ was added to the eluted product and the mixture was heated again at 175°C for 45 h, when a satisfactory conversion (88%) was reached. Three crystallizations from methanol gave pure *N*-(2-methylpropenyl)phthalimide (5.8 g; 48% yield) m.p. 89°C (lit. m.p. 90–91°C [4]) ^{1}H NMR: 7.65 (m, 4H, aromatic), 5.78 (m, 1H, CH=), 1.92 (d, 3H, $-CH_3$), 1.65 (d, 3H, $-CH_3$).

Hydroformylation experiments: general procedure

The complex and the phosphine ligand, if any, were placed in a stainless steel autoclave. The autoclave was rocked and the air removed (0.1 mmHg).

A solution of the substrate in benzene was introduced by suction and the vessel was pressurized with 1/1 CO/H_2 at 100 atm at room temperature and then heated in an oil bath at the required temperature until a satisfactory conversion was reached. The products were purified by crystallization and their structures confirmed by NMR and mass spectrometry.

Asymmetric hydroformylations

(a) (E)-N-Propenylphthalimide. Following the above procedure, the reaction was carried out at 100°C for 24 h in the presence of $HRh(CO)(PPh_3)_3$ and a chiral diphosphine in a ratio of 1:2. Racemic 2-phthalimidobutanal was purified by crystallization (benzene); m.p. 104–105°C (lit. m.p. 106°C [16]). ^{1}H NMR: 9.62 (s, 1H, –CHO), 7.75 (m, 4H, aromatic), 4.82–4.42 (m, 1H, =N–CH=), 2.38–2.02 (m, 2H, $-CH_2-$), 1.02 (t, 3H, $-CH_3$). Mass spectrum: 217 (1%, M^+), 188 (base peak, $M^+ - CHO$).

(b) N-Allylphthalimide. Following the general procedure, the reaction was carried out for 19 h at 70°C in the presence of $HRh(CO)(PPh_3)_3$ and a chiral diphosphine. 4-*N*-Phthalimidobutanal **5** and 2-methyl-3-*N*-phthalimidopropanal **4** were purified by column chromatography followed by fractional crystallization (benzene-hexane).

Compound **5**: m.p. 74–75°C (lit. m.p. 76°C [15]). ^{1}H NMR: 9.68 (s, 1H, –CHO), 7.68 (m, 4H, aromatic), 3.75 (t; 2H, $=N-CH_2-$), 2.72–2.40 (m, 2H, $-CH_2CHO$), 2.30– –1.75 (m, 2H, $-CH_2-$). Mass spectrum: 218 (2%, MH^+), 188 (base peak, $M - CHO$).

Compound **4**: m.p. 78°C. ^{1}H NMR: 9.70 (d, 1H, –CHO), 7.65 (m, 4H, aromatic), 4.22–3.52 (m, 2H, $=N-CH_2-$), 3.05–2.40 (m, 1H, $=CHCH_3$), 1.18 (d, 3H, $-CH_3$). Mass spectrum: 217 (25%, M^+), 188 (base peak, $M^+ - CHO$).

Ag_2O oxidation of the compound **4** gave 2-methyl-3-*N*-phthalimidopropanoic acid: m.p. 161–162°C (lit. 161°C [17]).^{1}H NMR: 7.67 (m, 4H, aromatic), 4.10–3.70 (m, 2H, $=N-CH_2-$), 3.23–2.80 (m, 1H, =CHCOOH), 1.21 (d, 3H, $-CH_3$). This compound showed $[\alpha]_D^{17}$ −0.24 ($c = 0.968$, $CHCl_3$) when prepared from the aldehyde obtained in the presence of (−)-DIOP and $[\alpha]_D^{17}$ −0.35 when in the presence of (−)-DIOCOL.

Hydrocarbethoxylation experiments: general procedure

Palladium dichloride and the phosphine ligand were placed in a stainless steel autoclave. The autoclave was rocked and the air was removed (0.1 mmHg).

A solution of the substrate in methyl ethyl ketone-ethanol (4:1) was introduced

by suction, the vessel was pressurized whith carbon monoxide at 100 atm at room temperature and was then heated in an oil bath at 100°C until a satisfactory conversion was reached. The products were purified by crystallization and their structures were confirmed by NMR spectroscopy and mass spectrometry.

Asymmetric hydrocarbethoxylation

(a) (E)-N-Propenylphthalimide. Following the above procedure the reaction was stopped after 110 h.

Ethyl 2-methyl-3-*N*-phthalimidopropanoate, **4**, was isolated after fractional crystallization (ethanol-ether): m.p. 56–57°C; ^{1}H NMR: 7.68 (m, 4H, aromatic), 4.05 (q, 2H, $-OCH_2-$), 3.93–3.67 (m, 2H, $=N-CH_2-$), 3.20–2.70 (m, 1H, =CHCOOEt), 1.33–1.02 (m, 6H, $-CH_3$). Mass spectrum: 261 (6%, M^+), 160 (base peak, $M^+ - CH_3CHCOOEt$). Stirring overnight a tetrahydrofuran solution of the ester with aqueous 1 : 1 hydrochloric acid gave the corresponding acid for the polarimetric determination of the optical purity.

(b) N-Allylphthalimide. According to the general procedure, the reaction was stopped after 24 h.

The branched ester **4** was isolated in pure form after several crystallizations (ether-pentane) and its optical purity was determined after hydrolysis to the acid as reported in the previous experiment.

Acknowledgment

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