170. Asymmetric Palladium-Assisted Alkylation of Alkenes

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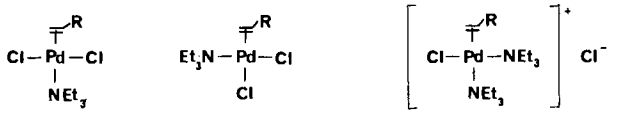
(28.II.83)

Summary

Palladium-promoted alkylation of alkenes using chiral sulfoxide-containing carbanions and chiral lithiated oxazolines results in asymmetric induction (AI) ranging from 3–5% (1,5 induction), 20–40% (1,3 induction) to 44–52% (1,4 induction). No general trend allowing predictions of results was found. With 1-hexene, attack at C(1) is almost exclusive but propene gives a mixture of attack at C(1) and C(2). The use of a chiral ligand together with malonate anion also leads to some asymmetric induction (*ca.* 20%).

Alkene-palladium(II) chelates (such as those obtained with dialkenes, allylic and homoallylic amines and sulfides) readily undergo reaction with stabilized carbanions [1–4]. Palladium-assisted alkylations of simple monoalkenes proceeding through unstable σ-alkylpalladium(II) complex intermediates have been studied later [5a–c]. We reported recently that asymmetric induction of up to 40% could be obtained during these palladium-assisted alkylations of alkenes [6]. Until now asymmetric induction had only been studied in alkylation of allylic-Pd complexes [7–11] using optically pure ligands. We report herein the full details of our study of these asymmetric alkylations, using *chiral nucleophiles* and optically pure ligands.

Results and Discussion. – The generally accepted route for the Pd-assisted alkylation of alkenes involves, in a one-pot, three-step reaction, formation of π-complexes of type **I** and/or **II** [5b] followed by nucleophilic attack on the coordinated alkene *(Eqn. 1)*.



trans-I *cis*-I II

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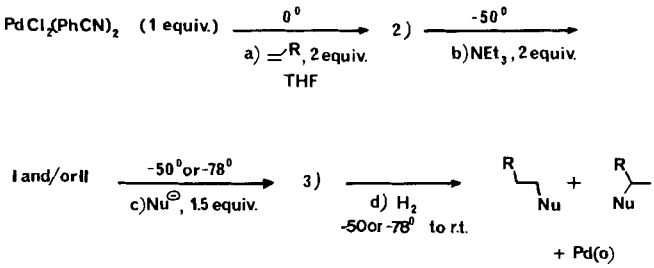
Reductive cleavage (by H_2) of the Pd-C bond in the intermediate σ-complexes gives the products and a copious black precipitate of Pd(O) which is removed and converted back to $PdCl_2$ [12].



In these reactions chirality may be introduced either by the use of a chiral nucleophile (step c), or by the use of a chiral amine in the place of NEt_3 (step b) or by the use of a chiral nucleophile together with a chiral amine.

Unless the starting alkene belongs to D_{2h}- or C_{2v}-point groups, the reactive alkene-Pd complexes **I** and/or **II** are chiral but racemic: $y = 1 - y = 0.5$, *(Scheme 1)*. From attack of a chiral nucleophile at C(1) (Nu* in *Scheme 1*), a mixture of unequally populated diastereoisomers **III** is obtained after reduction ($x \neq 1\text{-}x$). However, the percentage of asymmetric induction (1-2x) depends *(Scheme 1)* on the relative rates of enantiomer interconversion *(v)* and of alkylation (v_1 and v'_1) of each of the enantiomeric complexes. Unless exchange between the enantiomers is fast enough compared to the rates of alkylations[4][5]), these reactions behave like kinetic resolutions and would need 2 equiv. of alkene-Pd complex and 1 equiv. of the chiral nucleophile [13].

When the nucleophile is achiral and the chirality is introduced by the use of a chiral amine (L* as ligand L, *Scheme 1*) the reactive π-complex is now a mixture of unequally populated diastereoisomers ($y \neq 1\text{-}y$) and the reaction leads to a mixture of enantiomers **III** which may depend on v, v_1, v'_1 and y, if the rate of diastereoisomer interconversion is slow compared to the rates of alkylation[5]).

Several features of this reaction warrant comments. Foremost is the necessity to perform step a *(Eqn. 1)* at a temperature such that the π-complex is rapidly formed but isomerization minimized [16a–c], migration along the chain leading to modification of the regioselectivity and/or to formation of more than two adducts. *cis-trans* isomerization would also decrease the percentage of asymmetric induction.

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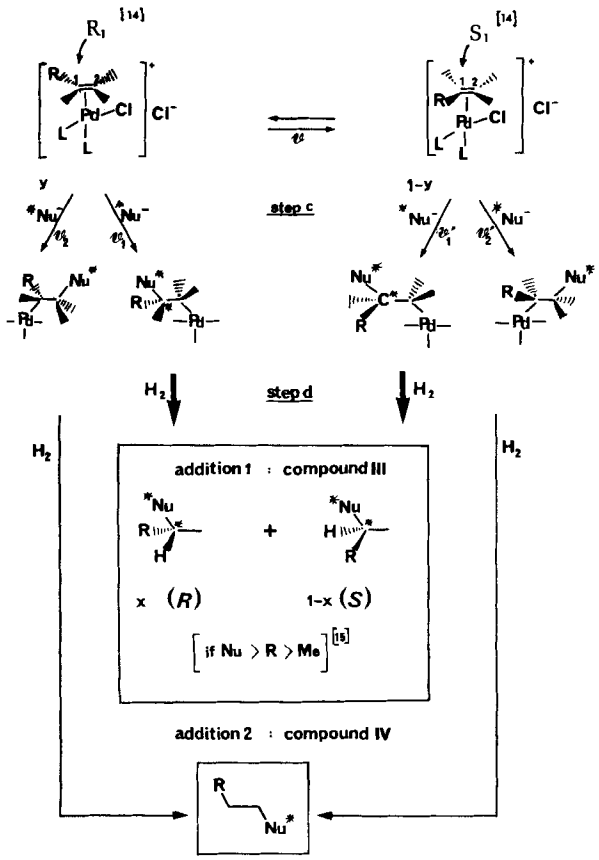
[2]) An unreactive dimeric alkene-Pd complex is formed during step a.

[3]) An unstable (*i.e.* difficult to isolate and cristallise) σ-complex is formed *(Scheme 1)*.

[4]) In the case of *trans*- and *cis*-Pt(alkene-α-methylbenzylamine)Cl_2 complexes, pure diastereoisomers epimerize in solution and epimerization rates are strongly increased by the presence of free alkene (see [14a,b]). Ligand exchanges are faster for Pd than for Pt. Thus in our reaction conditions, the two possible isomers of the chiral π-complexes (**I** or **II**) may undergo exchange (the rate of exchange is under study by NMR).

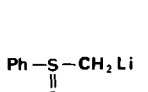
[5]) Normal asymmetric synthesis is involved only if the *Curtin-Hammett* principle holds, that is if enantiomer or diastereoisomer interconversion is fast compared to the rates of alkylations.

Scheme 1

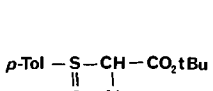


Competition between reductive cleavage of the C-Pd bond (H_2) and β-elimination have also to be minimized in step d[6]).

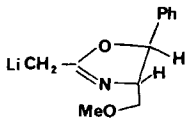
1. Addition of Chiral Nucleophiles. The results are presented in *Tables 1* and *2*. Sulfoxide-containing carbanions **A** (racemic) and **B** (optically pure) [17] as well as optically pure lithiated oxazolines **C** and **D** [18] have been used as chiral nucleophiles.



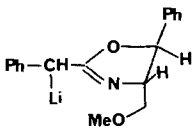
A



B



C



D

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[6]) Addition of the anion of ethyl phenylacetate to 1-hexene followed by β-elimination showed, when the alkene-Pd(II) complex is prepared at 20° that at least 11 different unsaturated esters are formed (studied by GC/MS coupling: capillary column *SE 30*, 20 m, *LKB 9000 S* mass spectrometer coupled with a digital *11E/10* computer).

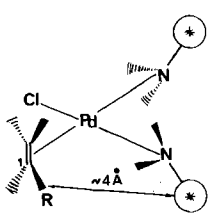
The role of the pK_a of carbanions is not clear in the cases studied. **A**, the less stabilized anion, gives very poor chemical yields: 20 to 0% (*Table 1*, runs 1 to 4). Anion **C**, which can be considered less stabilized than anions **B** and **D** react satisfactorily: 70% yield (*Table 1*, run 9) but anion **B**, more stabilized [19], gives poor yields (40–20%; *Table 1*, runs 5 to 7) as well as anion **D** *(Table 2)*. The relationship of the sulfoxide group with the low yields is not clear as this group usually gives good yields in the alkylation of π-allyl-Pd complexes [20]. However when alkylations involve sulfoxide-containing carbanions (**A** and **B**) the reduction (by H_2) of the σ-complex (last step of the reaction, *Scheme 1*) is clearly slowed down (from 1 or 2 h with anions **C** and **D** to 2 days for anions **A** and **B**).

The nature of the alkene, the anion, the amine and the temperature play important roles in these wayward reactions and no general trend could yet be established. Runs 1 to 4, 6 and 9 to 11 *(Table 1)* correspond to creation of an asymmetric carbon on the complexed-alkene and 20% to 40% asymmetric induction are obtained with carbanion **A** where 1,3-induction is involved, but 3% to 5% asymmetric induction are obtained with carbanion **C** where the induction is 1,5. Runs 5 and 7 *(Table 1)* as well as runs 1 to 6 *(Table 2)* correspond to creation of the asymmetric carbon on the already chiral nucleophile leading respectively to 1,2 and 1,4 inductions. The addition of 1-hexene and ethylene to carbanion **B** leading to 18% to 20% of asymmetric induction may be compared to alkylations of this carbanion which proceed with poor stereospecificity [21].

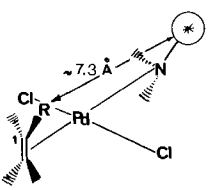
The addition of ethylene and propene to carbanion **D** may also be compared to alkylation, however RX-alkylations usually lead to higher enantiomeric excess (50 to 65%) [22], while in our case the asymmetric induction varies from 15% to 52%. A very high asymmetric induction of about 100% (only one doublet is seen, *cf.* below) was obtained in run 1, *Table 1*, but with a very low chemical yield of the product (0.5%), which makes this result not significant.

2. Use of a Chiral Amine as Ligand. Chiral and optically pure (−)-(*S*)-*N*,*N*-dimethyl-α-methylbenzylamine was used in place of NEt_3 and the results are presented in *Table 3*. Diethyl malonate anion gives poor chemical yields, 0% to 30%, although much higher yields are usually reported [1–5]. The nature of the chiral amine may be only partly responsible for these falls in chemical yields since we observed that alkylation of 1-hexene with sodium diethyl malonate in presence of NEt_3 occurs in only 42% yield under the same conditions. The influence of the cation is not straightforward either in these capricious reactions. When Na^+ is

Scheme 2

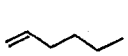
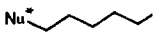
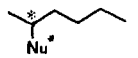
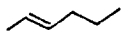
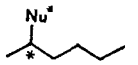
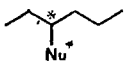
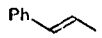
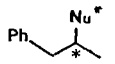
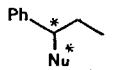
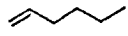
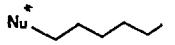
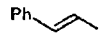
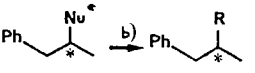
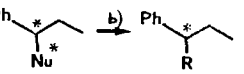
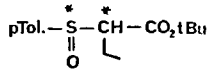
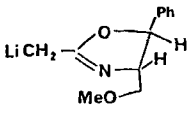
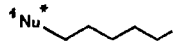
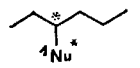
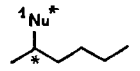


II



trans-I

Table 1. *Pd-Assisted Alkylation of Alkenes by Chiral Carbanions*[a])

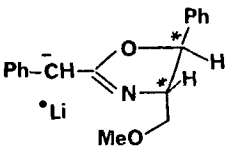
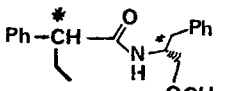
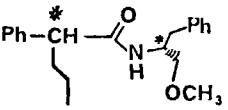
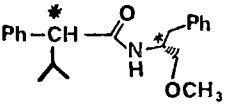
Run	Alkene	Nucleophile: Nu*	Step c (t°)	Yield (%)	Compound ratio	Products		AI (%)
1		Ph–S–CH_2Li ‖ O	–50°	13	96		**1**	–
					4		**2**	100
2		**A**	–50°	10	73		**2**	36
					27		**3**	?
3		**A**	–50°	15	15		**4**	20
					85		**5**	40
4		**A**	–50°	0	–	———		–
5		*p*-Tol–S–CH–CO_2tBu ‖ | O Li	–50°	31	100		**6**	20
6		**B**	–50°	17	64		**7** / **7**$_1$	20
					36		**8** / **8**$_1$	?
7		**B**	–50°	40	100		**9**	18
8			–78°	44	100		**10**[a]	–
					95		**11**[a]	5
9		**C**	–78°	70	5		**12**[a]	?
10		**C**	–78°	0	–	———		–
11		**C**	–78°	25	100		**13**[a]	3

[a]) The oxazoline ring is opened during the reduction step *(cf. Exper. Part)*:

$^1Nu^* = -CH_2-CO-NH-\overset{*}{C}H-CH_2-Ph$
$\qquad\qquad\qquad\qquad\qquad\quad |$
$\qquad\qquad\qquad\qquad\quad CH_2-OCH_3$

[b]) After desulfurization *(cf. Exper. Part)* R = $-CH_2-CO_2t$Bu.

Table 2. *Pd-Assisted Alkylation of Alkenes by Chiral Carbanions in Presence of NEt_3 of Chiral Ligands*

Run	Alkene	Nucleophile	Step c (t°)	Ligand[a])	Yield (%)	Compound ratio	Products[b])		AI (%)
1	=		−50°	NEt_3	30	100			15
2	"		−78°	NEt_3	20	100		**14**	25
3	=/	**D**	−50°	NEt_3	62	27		**15**	12
						73		**16**	46
4	"	**D**	−78°	NEt_3	25	28		**15**	12
						72		**16**	52
5	=/	**D**	−50°	L*(−)-(*S*)	35	30		**15**	8
						70		**16**	26
6	"	**D**	−78°	L*(−)-(*S*)	25	25		**15**	8
						75		**16**	28
7	=/	**D**	−50°	L*(+)-(*R*)	56	30		**15**	8
						70		**16**	44

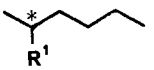
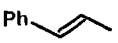
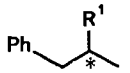
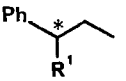
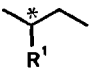
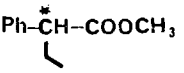
[a]) L*(−)-(*S*)=(−)-(*S*)-*N*,*N*-dimethyl-α-methylbenzylamine; L*(+)-(*R*)=(+)-(*R*)-*N*,*N*-dimethyl-α-methylbenzylamine *(cf. Exper. Part)*.

[b]) The oxazoline ring is opened during reduction step *(cf. Exper. Part)*.

replaced by Li^+ the chemical yield decreases (compare runs 2 and 3, *Table 3*) or increases (compare runs 4 and 5, *Table 3*), moreover the regioselectivity changes as well as the percentage of asymmetric induction (compare runs 2 and 3, *Table 3*). Again the highest asymmetric induction 40% corresponds to the lowest chemical yield (1%, run 3, *Table 3*) and the lowest asymmetric induction 0% with the highest chemical yield (32%, run 5, *Table 3*).

The percentage of asymmetric induction is lower in those experiments where a chiral ligand is used as chirality inducer *(Table 3)* compared to the use of a chiral nucleophile (*Table 1* and *2*). In view of *Ugi*'s and *Salem*'s models [23] and of the distances between the chirality inducer and the asymmetric C(1), determined on models [24] according to X-ray results [25], one could predict that higher asymmetric induction should be obtained if the reacting species are *cis*-**I** and **II** than *trans*-**I**

Table 3. *Pd-Assisted Alkylation of Alkenes by Achiral Carbanions, in Presence of Chiral Ligand (−)-(S)-N,N-Dimethyl-α-methyl-benzylamine at −50°*

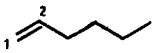
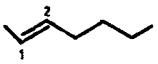
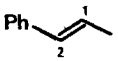
Run	Alkene	Nucleophile: R^1	Cation	Yield (%)	Compound ratio	Products		ee (%)
1		$^-CH[CO_2Et]_2$	^+Na	20	50		**17**	–
					50		**18**	30
2		$^-CH[CO_2Et]_2$	^+Na	25	68		**19**	10
					32		**20**	20
3			^+Li	15	93		**19**	12
					7		**20**	40[a])
4		$^-CH[CO_2Et]_2$	^+Na	0	–			–
5			^+Li	32	100		**21**	0
6		$Ph-\bar{C}H-COOCH_3$	^+Li	60	100		**22**	10

[a]) This result is non-significant, as the chemical yield in **20** is 1%.

(Scheme 2). This is supported by the observations of *Paiaro & Panunzi* [14a, b] on *cis* and *trans* Pt(alkene-α-methylbenzylamine)Cl_2, where nearly equal quantities of the two possible diastereoisomers are present at equilibrium in solution for the *trans*-species but where one diastereoisomer may predominate to the extent of 40% in the *cis*-species.

3. Addition of a Chiral Nucleophile in the Presence of a Chiral Ligand. Chiral *N,N*-dimethyl-α-methylbenzylamines have been used in the place of NEt_3; (−)-(*S*) was optically pure but (+)-(*R*) was only 98% (+) based on the starting material (see below). The lithiated oxazoline **D** was used as nucleophile and the results are given in *Table 2.* Opposed to a (4*S*, 5*S*)-oxazoline anion the (*S*)-amine-ligand leads to a notable decrease of the percentage of asymmetric induction for addition at C(2): 46% (−50°) and 52% (−78°) in presence of NEt_3 drop to 26% (−50°) and 28% (−78°); the effect during addition at C(1) is smaller, from 12% to 8%, but is still present. However, replacement of the (*S*)-amine by the (*R*)-amine only

Table 4. *Regioselectivity of Various Nucleophilic Additions*

Run	Alkene	Anion	Step c (t°)	Add. 1	Add. 2	Cation
1		[a] **D**	−50°	27	73	Li
2	"	[a] **D**	−78°	28	72	Li
3		[a] **A**	−50°	96	4	Li
4	"	[a] **B**	−50°	100	0	Li
5	"	[a] **C**	−78°	100	0	Li
6	"	[b] mal.	−50°	40	60	Na
7	"	[a] mal.	−50°	50	50	Na
8		[b] **A**	−50°	10	90	Li
9	"	[a] **A**	−50°	73	27	Li
10	"	[a] **C**	−78°	95	5	Li
11		[a] **A**	−50°	15	85	Li
12	"	[a] **B**	−50°	64	36	Li
13	"	[a] mal.	−50°	63	37	Na
14			−50°	93	7	Li

[a] Step a *(Eqn. 1)* is performed at 0°.

[b] Step a *(Eqn. 1)* is performed at 20°.

restores the asymmetric induction: 44% (−50°) obtained in presence of NEt_3 (runs 3 and 7, *Table 2*).

4. Regioselectivity of the Alkylation. The results are summarized in *Table 4.* In contrast with literature reports [5b,c] propene led to a mixture: addition at C(1) and C(2) and not only at C(2). With 1-hexene and 2-hexene alkylations occur mainly on C(1) except for malonate anion. The most important factor is the influence of alkene isomerization (when the first step, *Eqn. 1,* is performed at 20°) on the regioselectivity (compare entries 6 and 7, 8 and 9, *Table 4*).

Experimental Part

General. IR spectra were measured with a *Perkin-Elmer 1310* spectrophotometer and are reported in cm^{-1}. NMR spectra were measured with a *Perkin-Elmer R 24A* (60 MHz) a *WH-90,* a *WP-200 SY* or a *WM-400 Bruker* spectrophotometer; determinations of the percentages of diastereoisomers are described below. TMS was used as internal standard; chemical shifts are given in ppm, and coupling constants *J* in Hz. Purification was performed by flash column chromatography using medium pressure. Columns were packed with silica gel *60 (Merck)* (230–400 mesh) [26]. Analytical thin layer chromatography (TLC) was performed using silica gel *60* F_{254} plates. UV light, iodine vapor, or phosphomolybdic acid in EtOH were used to visualize the products. The yields are given for pure, isolated products.

Materials. Solvents were freshly distilled under Ar and stored under Ar. THF was refluxed over $LiAlH_4$, and distilled under atmospheric pressure. Diisopropylamine and NEt_3 were refluxed over KOH and distilled under atmospheric pressure. Alkenes were used without further purification. BuLi purchased from *Aldrich* as a 1.7M hexane solution was titrated using the diphenylacetic acid method [27]. Palladium chloride, anh., was purchased from *Fluka* and converted to its bis-benzonitrile complex by stirring for 3 days in benzonitrile and collecting the resulting orange-yellow crystals by filtration. (−)-(*S*)-*N,N*-Dimethyl-α-methylbenzylamine was prepared from commercially pure (−)-(*S*)-α-methylbenzylamine *(Fluka)* by dimethylation using the *Eschweiler-Clark* reaction [28] and distilled under reduced pressure (26–28°/0.3 Torr); yield 61%, $[\alpha]_D^{21} = -67.3°$ (neat) [29]. ^{1}H-NMR ($CDCl_3$, 60 MHz): 7.3 (*s*, 5 H, C_6H_5); 3.25 (*q*, $^3J = 7$, 1 H, CH); 2.15 (*s*, 6 H, $N(CH_3)_2$); 1.35 (*d*, $^3J = 7$, 3 H, CH_3). (+)-(*R*)-*N,N*-Dimethyl-α-methylbenzylamine was prepared from (+)-(*R*)-α-methylbenzylamine (*EGA*-Chemie, 98% (+)) in the same way, yield: 60%, $[\alpha]_D^{21} = +64.3°$ (neat). Diethyl malonate was purchased from *Fluka* and used without further purification.

General Procedure for Alkylation. The $PdCl_2(PhCN)_2$ (0.383 g, 1 mmol) was weighed in a 50 ml two-necked, round-bottomed flask fitted with a magnetic stirring bar, a thermometer and serum cap. The flask was alternatively evacuated and filled with Ar (through a needle). Addition of THF (5 ml) at 0° and stirring for 10 min at 0° (ice bath) produced an amber suspension. Addition of the alkene followed by stirring for 20 min at 0° gave generally a homogeneous amber solution. Gazeous alkenes were introduced by bubbling into the THF-solution until homogeneous. The flask was then cooled to −50°, when the colour became somewhat lighter. NEt_3, or the optically active *N,N*-dimethyl-α-methylbenzylamine (2 equiv. per Pd) was added dropwise, slowly, and the mixture was stirred for 10 min at −50° (in the case of the ethylene-Pd complex, addition of NEt_3 afforded a lemon-coloured slurry. With other alkenes, no change of colour or aspect could be observed). The flask was cooled to −78° (or kept at −50°, according to the reaction). The anion (1,5 equiv. per Pd) was then added as a THF-solution (cooled to −78° before addition) over 10 min using a precooled syringe. The reaction flask was stirred for 4 h at −50° or −78°. The flask was then flushed with H_2 (H_2 balloon with a needle through the rubber cap) and the cold bath removed. The mixture was allowed to warm to r.t. and stirred vigorously overnight under H_2. The black Pd(0) suspension was filtered off, and the solvent concentrated with a rotary evaporator. The products were analyzed by NMR and TLC, then separated by flash-chromatography, all the fractions being checked by 60 MHz ^{1}H-NMR to be sure that the mixtures were not enriched (when dealing with diastereoisomers as products of the reaction).

Preparation of the Carbanions. Lithium diisopropylamide was prepared by dropwise addition of a stoichiometric amount of BuLi solution to diisopropylamine (1,5 mmol) in THF (3 ml) at −78° under Ar; the mixture was then stirred 15 min at r.t. and kept at −78°. Li-carbanions were generated by dropwise addition of a solution of the substrate in THF (1 ml) to the LDA-solution at −78°, followed by stirring at −78° for 45 min.

Na-carbanions were generated by dropwise addition of the substrate to a NaH (1,5 mmol) suspension in THF (3 ml) at r.t. and stirred until homogeneous. The resulting carbanion was cooled to −78° just before addition to the Pd complex.

Determination of Asymmetric Induction (% AI). Diastereoisomeric Ratios. When diastereoisomers were obtained (addition of chiral nucleophiles, *Tables 1* and *2*) the ratios were determined by ^{1}H-NMR using non-equivalences between diastereotopic signals (external comparison); one example is given in the *Figure.* When the chiral centres were separated by 1, 2 or 3 bonds (*Table 1* and *2*) non equivalence of some signals (see below: description of spectra) were large when using *WP-200* or *WM 400* NMR spectrophotometers. When the chiral centers were separated by 4 bonds (1,5 position, runs 9 and 11 in

Table 1) it was necessary to use $Eu(fod)_3$. The ^{1}H-NMR spectra of compound **11** (400 MHz) and **13** (90 MHz), *Table 1*, show only one NH-signal but ^{1}H-NMR spectra of compounds **14** (200 MHz) and **15** + **16** (400 MHz), *Table 2*, show respectively 2 and 3 NH-signals. In the case of compound **14** no coalescence occurred when the sample was heated to 130° (in $C_2D_2Cl_4$), so the 2 signals presumably correspond to the two possible diastereoisomers, the amide being *trans*. The three NH-signals in compounds **15** + **16** thus correspond to the 4 possible diastereoisomers (with *trans*-amide), 2 of them having identical NH chemical shift.

Enantiomeric Excess. When enantiomers were obtained (*Table 1*, run 6, and *Table 2*) chiral shift reagent $Eu(hfc)_3$ was used and was better than $Eu(tfc)_3$.

A. Chiral Carbanions (*Tables 1* and *2*). – *Reaction of Methyl Phenyl Sulfoxide.* The racemic sulfoxide was prepared by oxidation of thioanisole with $NaIO_4$.

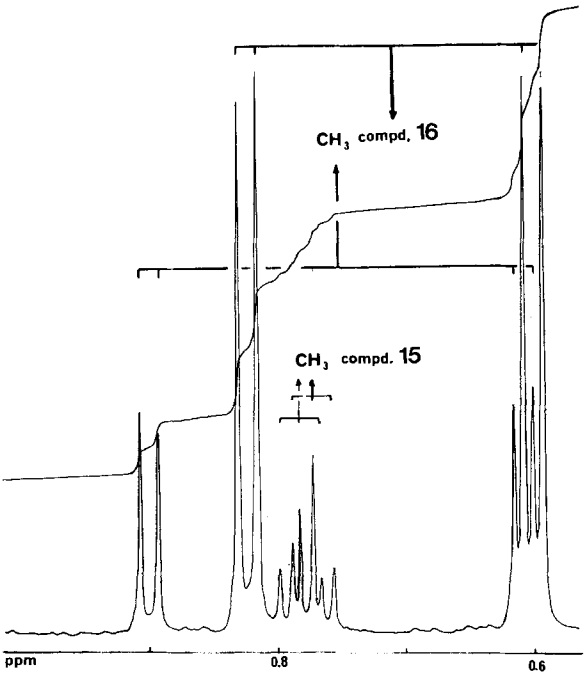


Figure. *400-MHz ^{1}H-NMR* ($CDCl_3$) *of* **15** + **16** (run 3 in *Table 2*)

1. With 1-Hexene. Purification by flash column chromatography (70:30 ether/hexane) gave a mixture of 2 regioisomers in 13% yield: heptyl phenyl sulfoxide (**1**, 96%) and (2-methylhexyl) phenyl sulfoxide (**2**, 4%). IR ($CHCl_3$): 1090(SO). ^{1}H-NMR ($CDCl_3$, 400 MHz) of **1**: 7.68–7.45 (*m*, 5 H, C_6H_5); 2.79 (*ABXY*..., 2 H, CH_2SO); 1.75 (*m*, 1 H, *H*CH–CH_2SO); 1.62 (*m*, 1 H, H–C*H*–CH_2SO); 1.40 (*m*, 2 H, CH_2–CH_2–CH_2SO); 1.35–1.20 (*m*, 6 H, $(CH_2)_3$); 0.88 (*t*, ^3J = 7, 3 H, CH_3). NMR ($CDCl_3$, 400 MHz) of **2**: all signals of **2** were under those of **1** except *d* of CH–CH_3: 1.05 (*d*, ^3J = 6.5) (spectrum of **2** is given in the next experiment).

2. With 2-Hexene. Isolation by flash column chromatography (70:30 ether/hexane) gave a mixture of (2-methylhexyl) phenyl sulfoxide (**2**, 73%) and (2-ethylpentyl) phenyl sulfoxide (**3**, 27%) in 10% overall yield. IR ($CHCl_3$): 1090(SO). ^{1}H-NMR ($CDCl_3$, 400 MHz) of **2**: 7.38–7.24 (*m*, 5 H, C_6H_5); 2.88 (*A*BX, 1 H, CH_2SO diast. **a**); 2.75 (*A*BX, ^2J(AB) = – 15, ^3J(AX) = 0, 1 H, *H*CHSO diast. **b**); 2.60 (AB*X*, 1 H, *H*CHSO diast. **b**); 2.42 (AB*X*, 1 H, *H*CHSO diast. **a**); 2.14 (AB*X*..., 1 H, C*H*–CH_2–SO diast. **a**); 2.04 (AB*X*..., 1 H, C*H*–CH_2SO diast. **b**); 1.45–1.24 (*m*, 6 H, $(CH_2)_3$); 1.18 (*d*, ^3J = 6.5, 3 H, CH–CH_3 diast. **a**); 1.07 (*d*, ^3J = 6.5, 3 H, CH–CH_3 diast. **b**); 0.90 (*t*, ^3J = 7, 3 H, CH_3). ^{1}H-NMR

($CDCl_3$, 400 MHz) of **3**: 7.38–7.24 (*m*, 5 H, C_6H_5); 2.81 (*A*BX, 1 H, CH_2SO); 2.57 (A*B*X, 1 H, CH_2SO); 1.92 (*m*, 1 H, $CHCH_2SO$); 1.45–1.24 (*m*, 6 H, $(CH_2)_2$ and CH_2CH_3); 0.90–0.80 (2*t*, 6 H, CH_3). The diastereoisomer ratio was determined on **2** by integration of the doublets from $CH-CH_3$ as 68% **a**/32% **b** (36% AI). Determination on **3** was not possible.

3. With β-Methylstyrene. Isolation by flash column chromatography (80:20 ether/hexane) gave a mixture of (2-phenylbutyl) phenyl sulfoxide (**5**, 85%) and (2-methyl-3-phenylpropyl) phenyl sulfoxide (**4**, 15%) in 15% yield. IR ($CHCl_3$) 1090(SO). ^{1}H-NMR ([D_6]acetone, 250 MHz) of **5**: 7.65–7.12 (*m*, 10 H, C_6H_5); 3.2–2.9 (*ABX*, 2 H, CH_2SO); 2.75–2.55 (AB*X*, 1 H, $CH-CH_2SO$); 1.3 (*ABX*$_3$Y, 2 H, CH_2CH_3); 0.8 (*t*, $^3J = 7.5$, 3 H, CH_3 diast. **a**); 0.78 (*t*, $^3J = 7.5$, 3 H, CH_3 diast. **b**). NMR ([D_6]acetone, 250 MHz) of **4**: 7.65–7.12 (*m*, 10 H, C_6H_5); 3.2–2.9 (*ABX*, 2 H, CH_2SO); 2.6 (AB*X*, 1 H, $CHCH_2SO$); 1.75 (*m*, 2 H, $PhCH_2$); 1.15 (*d*, $^3J = 6.5$, 3 H, CH_3 diast. **a**); 1.03 (*d*, $^3J = 6.5$, 3 H, CH_3 diast. **b**). ^{1}H-NMR integration gave 70% **a**/30% **b** for **5** (40% AI) and 60% **a**/40% **b** for **4** (20% AI).

4. With trans-*2-Butene.* TLC and the NMR spectrum showed only the presence of methyl phenyl sulfoxide, no alkylation product could be obtained even in the presence of HMPA [5a–c].

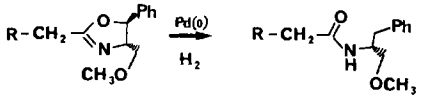
Reaction of (+)-(R)-t-Butyl-α-(p-tolylsulfinyl)acetate. The optically active ester was prepared by reaction of menthyl *p*-toluenesulfinate with $BrMgCH_2CO_2tBu$ [17].

1. With 1-Hexene. Isolation by flash column chromatography afforded *t*-butyl α-(*p*-tolylsulfinyl)-octanoate (**6**) as the only product (100% regioselectivity). IR ($CHCl_3$): 1710(CO), 1090(SO). ^{1}H-NMR ($CDCl_3$, 250 MHz) of **6**: 7.7–7.1 (*m*, 4 H, C_6H_4); 3.5 (*d*×*d*, $^3J = 5$, $^3J = 9$, 1 H, $CH-CO_2t$-Bu diast. **a**); 3.3 (*idem*, diast. **b**); 2.4 (*s*, 3 H, CH_3Ph); 1.5–1.1 (*m*, 19 H, $(CH_2)_5$ and *t*-Bu); 1.0–0.8 (br. *t*, 3 H, CH_3). Integration of the *ABX*-system gave 60% **a**/40% **b** (20% ee).

2. With β-Methylstyrene. Isolation by flash column chromatography gave a mixture of *t*-butyl 3-phenyl-2-(*p*-tolylsulfinyl)pentanoate (**8**, 36%) and *t*-butyl 3-benzyl-2-(*p*-tolylsulfinyl)butanoate (**7**, 64%). The diastereoisomeric ratio of each regioisomer could not be measured directly by NMR (3 chiral centres). The products were therefore treated with *Raney* nickel in ethanol, affording *t*-butyl 3-phenylpentanoate ($\mathbf{8_1}$) and *t*-butyl 3-benzylbutanoate ($\mathbf{7_1}$). The enantiomeric excess could only be determined on the latter using chiral shift reagent (20% ee, 60/40). IR ($CHCl_3$): 1710(CO). ^{1}H-NMR (C_6D_6, 250 MHz) of $\mathbf{7_1}$: 7.15–6.19 (*m*, 5 H, C_6H_5); 2.48 (*ABX*, $^2J(AB) = -9$, 2 H, $PhCH_2$); 2.2 (*m*, 1 H, CH); 2.12 and 1.92 (*ABX*, $^2J(AB) = -14$, $^3J(AX) = 5$, $^3J(BX) = 7$, 2 H, CH_2-CO_2tBu); 1.34 (*s*, 9 H, CO_2tBu); 0.85 (*d*, $^3J = 6.5$, 3 H, $CH-CH_3$).

3. With Ethylene. Isolation by flash column chromatography afforded 2 diastereoisomers of *t*-butyl 2-(*p*-tolylsulfinyl)butanoate (**9**) in 40% yield. ^{1}H-NMR ($CDCl_3$, 200 MHz): 7.6–7.25 (*m*, 4 H, C_6H_4); 3.45 (*d*×*d*, $^3J = 6$, $^3J = 11$, 1 H, CH diast. **b**); 3.30 (*d*×*d*, $^3J = 4$, $^3J = 7$, 1 H, CH diast. **a**); 2.4 (*s*, 3 H, CH_3Ph); 2.1 (*m*, 2 H, CH_2CH_3 diast. **a**); 1.72 (*idem*, diast. **b**); 1.40 (*s*, 9 H, *t*-Bu diast. **b**); 1.25 (*idem*, diast. **a**); 1.03 (*t*, $^3J = 7$, 3 H, CH_3 diast. **a**); 0.96 (*idem*, diast. **b**). Integration of signals which showed a non-equivalence between the 2 diastereoisomers gave AI = 18%.

Reaction of (−)-(4S,5S)-4-Methoxymethyl-2-methyl-5-phenyl-2-oxazoline. Isolation by flash column chromatography gave the opened oxazoline. During the hydrogenation step debenzylation occurred as Pd(0) was formed:



and an amide was obtained in every case[7]).

1. With 1-Hexene. *N*-[(1-methoxymethyl)-2-phenylethyl]octanamide (**10**, 100%, regioselectivity) was obtained in 44% yield as a white solid, m.p.: 33–36°. IR ($CHCl_3$): 3420(NH), 1665(CO). ^{1}H-NMR ($CDCl_3$, 200 MHz): 7.2 (*s*, 5 H, C_6H_5); 5.8 (br. *d*, 1 H, NH); 4.25 (*m*, 1 H, CHNH); 3.3 (*s*, 3 H, OCH_3);

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[7]) These reactions of oxazolines with alkenes can afford, after hydrolysis, optically active saturated acids. In our case, however, as we obtain amides, this hydrolysis was very difficult (sometimes impossible) and moreover, the chiral entity could not be recovered. $NaBH_4$ instead of H_2 was used in the complex hydrogenation step. The reaction product was thus obtained as an oxazoline in good yield (72%). Hydrolysis afforded the corresponding 3-methylheptanoic acid and the chiral entity (+)-(1*S*,2*S*)-2-amino-3-methoxy-1-phenyl-1-propanol.

3.3–3.2 (*m*, 2 H, OCH_2); 2.85 (*d*, $^3J = 6.5$, 2 H, CH_2Ph); 2.3–2.0 (*m*, 2 H, CH_2CO); 1.8–0.7 (*m*, 13 H, C_6H_{13}).

2. With 2-Hexene. Isolation by flash column chromatography gave 2 regioisomers in 70% overall yield: *N*-[(1-methoxymethyl)-2-phenylethyl]-3-methylheptanamide (**11**, 95%) and *N*-[(1-methoxymethyl)-2-phenylethyl]-3-ethylhexanamide (**12**, 5%), m.p.: 38–42°. IR ($CHCl_3$): 3420(NH), 1665(CO). ^{1}H-NMR ($CDCl_3$, 400 MHz) of **11**: 7.35–7.15 (*m*, 5 H, C_6H_5); 5.75 (br. *d*, 1 H, NH); 4.30 (*m*, 1 H, NHC*H*); 3.35 (*s*, 3 H, CH_3O); 3.30 (*AB*X, 2 H, CH_2O); 2.90 (*AB*X, $^2J(AB) = -13.5$, $^3J(AX) = 6.5$, 1 H, *H*CHPh); 2.83 (AB*X*, $^2J(AB) = -13.5$, $^3J(BX) = 8$, 1 H, *H*CHPh); 2.16 (*m*, 1 H, CH); 1.97–1.82 (*m*, 2 H, CH_2CO); 1.35–1.20 (*m*, 6 H, $(CH_2)_3$); 0.88 (br. *t*, 3 H, CH_3); 0.85 (*d*, $^3J = 6.5$, 3 H, CH–CH_3). With Eu(fod)$_3$ non-equivalence was observed on methyl doublets: 5% AI.

3. With β-Methylstyrene. No reaction occurred with this alkene, only *N*-[(1-methoxymethyl)-2-phenylethyl]acetamide being obtained, m.p.: 87–90°. IR ($CHCl_3$): 3340(NH), 1665(CO). ^{1}H-NMR ($CDCl_3$, 60 MHz): 7.2 (*s*, 5 H, C_6H_5); 5.7 (br. *d*, 1 H, NH); 4.2 (*m*, 1 H, C*H*–NH); 3.3–3.1 (*m*, 2 H, CH_2O); 3.25 (*s*, 3 H, CH_3O); 2.85 (*d*, $^3J = 7$, 2 H, CH_2Ph); 1.95 (*s*, 3 H, $COCH_3$).

4. With trans-*2-Butene.* Isolation by flash column chromatography gave *N*-[(1-methoxymethyl)-2-phenylethyl]-3-methylpentanamide) (**13**) as a white solid in 25% yield, m.p.: 44–54° (mixture of diastereoisomers). IR ($CHCl_3$): 3450(NH), 1675(CO). ^{1}H-NMR ($CDCl_3$, 90 MHz): 7,2 (*s*, 5 H, C_6H_5); 6.0–5.6 (*m*, 1 H, NH); 4.2 (*m*, 1 H, NHC*H*); 3.25 (*s*, 3 H, CH_3O); 3.2 (*m*, 2 H, CH_2O); 2.85 (*d*, $^3J = 7$, 2 H, CH_2Ph); 2.0 (*m*, 2 H, CH_2CO); 1.9–0.6 (*m*, 9 H, iC_4H_9). With addition of Eu(fod)$_3$ non-equivalence was observed on CH_3 from C_4H_9 and CH_3O: AI = 3%.

*Reaction of (–)(4*S*,5*S*)-2-Benzyl-4-methoxymethyl-5-phenyl-2-oxazoline.*

1. With Ethylene. a) Reaction at –50° afforded *N*-[(1-methoxymethyl)-2-phenylethyl]-2-phenylbutanamide (**14**) in 30% yield after isolation by flash column chromatography, m.p.: 60–63°. IR ($CHCl_3$): 3415(NH), 1665(CO). ^{1}H-NMR ($CDCl_3$, 250 MHz): 7.4–7.2 (*m*, 10 H, C_6H_5); 5.73 (*d*, $^3J = 8.5$, 1 H, NH diast. **a**); 5.61 (*idem*, diast. **b**); 4.36–4.14 (*m*, 1 H, NH–C*H*); 3.39–3.11 (*m*, 3 H, PhC*H* and CH_2O); 3.3 (*s*, 3 H, OCH_3 diast. **b**); 3.23 (*idem*, diast. **a**); 2.85–2.67 (*m*, 2 H, CH_2Ph); 2.23–2.03 (*m*, 2 H, CH_2–CH_3, diast. **b**); 1.86–1.64 (*idem*, diast. **a**); 0.86 (*t*, $^3J = 7.8$, CH_2CH_3, diast. **b**); 0.84 (*idem*, diast. **a**). Integration gave 57% **a**/43% **b** (15% AI).

b) Reaction at –78° afforded **14** in 20% yield. Diastereoisomeric ratio: 63% **a**/37% **b** (25% AI).

2. With Propene. a) Reaction at –50° afforded, after isolation by flash column chromatography, *N*-[(1-methoxymethyl)-2-phenylethyl]-3-methyl-2-phenylbutanamide (**16**, 73%) and *N*-[(1-methoxymethyl)-2-phenylethyl]-2-phenylpentanamide (**15**, 27%) in 62% overall yield, m.p.: 77–82°. IR ($CHCl_3$): 3415(NH), 1665(CO). ^{1}H-NMR ($CDCl_3$, 400 MHz) of **16**: 7.4–7.0 (*m*, 10 H, C_6H_5); 5.85 (*d*, $^3J = 8.5$, 1 H, NH diast. **a**); 5.72 (*idem*, NH diast. **b**); 4.22 (*m*, 1 H, C*H*–NH); 3.34–3.08 (*m*, 3 H, CH_2O and C*H*Ph); 3.24 (*s*, 3 H, CH_3O); 2.96–2.67 (*m*, 2 H, CH_2Ph); 2.38 (*m*, 1 H, C*H*$(CH_3)_2$ diast. **a**); 2.05 (*idem*, diast. **b**); 1.02 and 0.7 (2*d*, $^3J = 6.5$, $(CH_3)_2$–CH diast. **b**); 0.94 and 0.68 (*idem*, diast. **a**). Integration gave: 73% **a**/27% **b** (46% AI). ^{1}H-NMR ($CDCl_3$, 400 MHz) of **15**: 7.4–7.0 (*m*, 10 H, C_6H_5); 5.72 (*d*, $^3J = 8.5$, 1 H, NH diast. **a**); 5.58 (*idem*, diast. **b**); 4.30 (*m*, 1 H, C*H*NH); 3.34–3.08 (*m*, 3 H, CH_2O and C*H*Ph); 3.24 (*s*, 3 H, CH_3O); 2.96–2.67 (*m*, 2 H, CH_2Ph); 1.76–1.62 (*m*, 2 H, CH_2–CH_2CH_3); 1.28–1.15 (*m*, 2 H, CH_2–CH_2CH_3); 0.88 (*t*, $^3J = 7.5$, 3 H, $CH_2CH_2CH_3$ diast. **b**); 0.86 (*idem*, diast. **a**). The diastereoisomeric ratio was measured by integration of the *n*-propyl methyl group: 56% **a**/44% **b** (12% AI).

b) Reaction at –78° afforded **15** and **16** with 25% yield. Compound **16** (72%): 76% **a**/24% **b** (52% AI). Compound **15** (28%): 56% **a**/44% **b** (12% AI).

3. With Propene, in the presence of (–)-(*S*)-*N*,*N*-dimethyl-α-methylbenzylamine as ligand. a) Reaction at –50° gave a mixture of **16** (70%) and **15** (30%) in 35% overall yield; **16**: 63% **a**/37% **b** (26% AI); **15**: 54% **a**/46% **b** (8% AI).

b) Reaction at –78° gave **16** (75%) and **15** (25%) in 25% yield; **16**: 64% **a**/36% **b** (28% AI); **15**: 54% **a**/46% **b** (8% AI).

4. With Propene, in presence of (+)-(*R*)-*N*,*N*-dimethyl-α-methylbenzylamine. Reaction at –50° gave a mixture of compounds **16** (70%) and **15** (30%) in 56% yield; **16**: 72% **a**/28% **b** (44% AI); **15**: 54% **a**/46% **b** (8% AI).

B. Achiral Carbanions in Presence of Chiral Ligands *(Table 3). – Reaction of Diethyl Malonate.*

1. With 1-Hexene. Reaction of sodium diethyl malonate on 1-hexene afforded ethyl 2-ethoxycarbonyl-3-methylheptanoate (**18**, 50%) and ethyl 2-ethoxycarbonyloctanoate (**17**, 50%) in 20% overall yield.

IR ($CHCl_3$): 1720(CO). ^{1}H-NMR ($CDCl_3$, 60 MHz) of **18**: 4,15 (*q*, $^3J=7$, 4 H, OCH_2); 3.1 (*d*, $^3J=7$, 1 H, $CH(CO_2Et_2)$; 1.8–1.6 (*m*, 1 H, CH_3-CH); 1.25 (*t*, $^3J=7$, 6 H, OCH_2CH_3); 1.4–1.0 (*m*, 6 H, $(CH_2)_3$); 1.0–0.8 (*m*, 6 H, CH_2-CH_3 and $CH-CH_3$, not separated in 60 MHz). The enantiomeric excess in **18** was determined by addition of Eu(hfc)$_3$; the non-equivalence of the signals of $CH-CH_3$ (*d*) reached $\Delta\nu=13$ Hz and gave on integration: 65/35 (30% ee). ^{1}H-NMR ($CDCl_3$, 60 MHz) of **17**: 4.15 (*q*, $^3J=7$, 4 H, OCH_2); 3.15 (*t*, $^3J=7$, 1 H, $CH(CO_2Et)_2$); 1.25 (*t*, $^3J=7$, 6 H, OCH_2CH_3); 1.4–0.8 (*m*, 13 H, C_6H_{13}).

2. With β-Methylstyrene. a) Reaction of sodium diethyl malonate afforded ethyl 2-ethoxycarbonyl-3-methyl-4-phenylbutanoate (**19**, 68%) and ethyl 2-ethoxycarbonyl-3-phenylpentanoate (**20**, 32%) in 25% yield. ^{1}H-NMR ($CDCl_3$, 250 MHz) of **20**: 7.36–7.15 (*m*, 5 H, C_6H_5); 4,21 (*q*, $^3J=7$, 4 H, OCH_2); 3.62 (*d*, $^3J=7$, 1 H, $CH(CO_2Et)_2$); 3.24 (*m*, 1 H, PhC*H*); 1.30 (*m*, 2 H, $PhCH-CH_2$); 1.30 (*t*, $^3J=7$, 6 H, CH_2CH_3); 0.74 (*t*, $^3J=7.5$, 3 H, CH_3). Addition of Eu(hfc)$_3$ and non-equivalence of the CH_3-triplets led to 60/40 (20% ee). ^{1}H-NMR ($CDCl_3$, 400 MHz) of **19**: 7.36–7.15 (*m*, 5 H, C_6H_5); 4.21 (*q*, $^3J=7$, 4 H, OCH_2); 3.30 (*d*, $^3J=7$, 1 H, $CH(CO_2Et)_2$); 2.85 (*ABX*, $^2J(AB)=-13$, $^3J(AX)=5$, $PhCH_2$); 2.57 (AB*X*Y$_3$, 1 H, CH); 2.43 (A*B*X, $^2J(AB)=-13$, $^3J(BX)=9$, $PhCH_2$); 1.30 (2*t*, $\Delta\nu=3$, $^3J=7$, 6 H, OCH_2CH_3); 0.96 (*d*, $^3J=6.5$, 3 H, $CHCH_3$). Addition of Eu(hfc)$_3$ and non-equivalence of the methyl doublets gave 55/45 (10% ee).

b) Reaction of lithium diethyl malonate afforded **19** (93%) and **20** (7%) in 15% yield; **20**: 70/30 (40% ee); **19**: 56/44 (12% ee). IR ($CHCl_3$): 1720(CO).

3. With (E)-2-Butene. a) No reaction occurred with sodium diethyl malonate which was recovered.

b) Reaction of lithium diethyl malonate with (*E*)-2-butene afforded ethyl 2-ethoxycarbonyl-3-methylpentanoate (**21**) in 32% yield. IR ($CHCl_3$): 1720(CO). ^{1}H-NMR ($CDCl_3$, 60 MHz): 4.15 (*q*, $^3J=7$, 4 H, OCH_2); 3.25 (*d*, $^3J=8$, 1 H, $CH(CO_2Et)_2$); 2.4–2.0 (*m*, 1 H, CH); 1.25 (*t*, $^3J=7$, 6 H, OCH_2CH_3); 1.2–0.8 (*m*, 8 H, $CH_3-CH_2-CH-CH_3$). The enantiomeric excess was determined by addition of Eu(hfc)$_3$, and the doublet of CH_3 gave 50/50 (0% ee). The product showed the same NMR and IR spectra as an authentic sample prepared by reaction of 2-bromobutane on sodium diethyl malonate in DMF.

Reaction of Lithium Methyl Phenylacetate with Ethylene. After isolation by flash column chromatography, methyl 2-phenylbutanoate (**22**) was obtained in 60% yield. IR ($CHCl_3$): 1730(CO). ^{1}H-NMR ($CDCl_3$, 90 MHz): 7.29 (*s*, 5 H, C_6H_5); 3.65 (*s*, 3 H, CH_3O); 3.45 (*t*, $^3J=8$, 1 H, PhC*H*); 2.25–1.6 (*AB*X$_3$Y, 2 H, $CH-CH_2-CH_3$); 0.88 (*t*, $^3J=7$, 3 H, CH_2-CH_3). By addition of Eu(hfc)$_3$ splitting of the methyl singlet of OCH_3 occurred giving 55/45 (10% ee).

We gratefully acknowledge Prof. *H. Kagan* for fruitful discussions, *M.E. Guittet* (Prof. *Lallemand* Laboratory, CNRS-ICSN, Gif-Sur-Yvette) for the 400 MHz ^{1}H-NMR spectra in presence of Eu(fod)$_3$ and *Bruker*-spectrospin (Dr. *C. Brevard*) for providing facilities in the recording of the other 400 MHz ^{1}H-NMR spectra.

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