TRANSITION-METAL-CATALYZED REACTIONS OF DIAZOCOMPOUNDS, EFFICIENT SYNTHESIS OF FUNCTIONALIZED ETHERS BY CARBENE INSERTION INTO THE HYDROXYLIC BOND OF ALCOHOLS

A. F. NOELS,* A. DEMONCEAU, N. PETINIOT, A. J. HUBERT and PH. TEYSSIÉ

Laboratory of Macromolecular Chemistry and Organic Catalysis, University of Liège, Sart Tilman 4000 Liege, Belgium

Abstract—An efficient catalytic synthesis of unsaturated ethers by carbene insertion (with diazoesters as carbene precursors) into the OH bond of unsaturated alcohols is reported. The regioselectivity for the OH insertion is high. However, depending on the catalyst counter-ions and the diazoester alkoxy group, addition to the unsaturated centre can be promoted to some extent, yielding then cyclopropyl and cyclopropenyl carbinols. The mechanistic aspects of the reactions are discussed.

The insertion reaction of carbenes into the hydroxylic bond of alcohols quite generally suffers from low yields and poor selectivities,[1] especially with functionalized carbenes and/or alcohols.[2]

We report an efficient catalytic process for promoting OH insertion reactions, with diazoesters as carbene precursors, permitting a ready and regioselective access to functionalized ethers under mild conditions (Scheme 1).

RESULTS AND DISCUSSION

Reactions with saturated alcohols. We have previously briefly reported on the high efficiency of rhodium(II) acetate for catalyzing carbalkoxycarbene insertion into the OH bond of aliphatic alcohols[3] and enols[4] to yield ethers (Scheme 1). Table 1 summarizes some typical results for simple alkanols. For purposes of comparison, copper catalyzed insertions are also reported. Indeed, the copper ion, when associated with anions of very poor coordinating ability such as the trifluoromethanesulfonate anion (triflate anion), proved to be also an excellent OH insertion catalyst.

The yields are good; the other reaction products are carbene oligomers and dimers (maleate and fumarate). Although OH bonds are thermodynamically stronger than CH bonds, products resulting from CH insertion are not observed. Moreover, in rhodium(II) catalyzed reactions, competitive experiments between equimolecular mixtures of two alcohols revealed that the relative reactivities were in fact related to steric hindrance in the alcohol (order of relative reactivities: EtOH = 1, propan-2-ol = 0.83, t-BuOH = 0.47).

With ethyl diazoacetate (EtDA), the apparent activation parameters for the Rh(II) acetate catalyzed insertion into the OH bond of ethanol are $\Delta H\ddagger = 18 \pm 1.5\,kcal\,mol^{-1}$ and $\Delta S\ddagger = -2.2 \pm 0.5$ eu (see experimental section). The reaction is first order in

$$ROH + N_2CH\text{-}CO_2Alk$$

$$\xrightarrow{\text{catalyst}} RO\text{-}CH_2\text{-}CO_2Alk + N_2$$
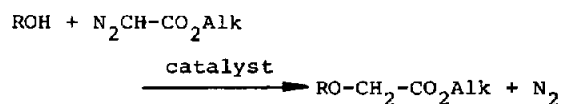
Scheme 1.

Table 1. Yields of insertion of carbetoxycarbenes[a] into O–H bonds of saturated alcohols ROH

Catalyst	R	Ether[b] Yield, %
$Rh_2(O_2C\text{-}CH_3)_4$	C_2H_5	89
	$i\text{-}C_3H_7$	83
	$t\text{-}C_4H_9$	82
$Cu\ (OTf)_2$	C_2H_5	97
	$t\text{-}C_4H_9$	62

Reaction conditions: 22°C; alcohol 5.10^{-2} mol; diazoester, 3.10^{-3} mol; catalyst, 10^{-5} mol. a: generated by decomposition of Ethyldiazoacetate (EtDA). b: yields based on EtDA.

rhodium and in its early stages, also first order in diazoester.

By comparison with the previously reported mechanism for olefin cyclopropanation,[5] a bimolecular nucleophilic attack of an alcohol molecule on a Rh carbenoid is proposed for those reactions.[12]

Reactions with unsaturated alcohols. Rhodium(II) alkanoates are also very efficient for promoting regioselective insertion into the OH bond of olefinic and acetylenic alcohols.[6]

Ethylenic alcohols. Tables 2 and 3 summarize the results of intramolecular competitions, as well as the influence of the diazoester alkoxy group, for insertion into the OH bond or cycloaddition to the double bond of olefinic alcohols with a variety of rhodium(II) catalysts. There is always a high preference for insertion (yielding olefinic ether 1, Scheme 2) over cyclopropanation (products 2 or 3). Interestingly, the yield of ether regularly increases with the number of carbon atoms of the diazoester alkoxy group. On the other hand, best

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Table 2. Relative yields of O–H insertion and double bond addition in catalyzed decomposition of alkyl-diazoacetate (Alk-DA) in allyl alcohol

Entry n°	Catalyst Rh$_2$(O$_2$C-R)$_4$	Diazoester Alk-	O-H Insertion Yield, %	Cyclopropanation[a] Yield, %
1	R= -CH$_3$	- CH$_3$	54	14
2		- C$_2$H$_5$	66	15
3		n-C$_4$H$_9$	85	14
4		t-C$_4$H$_9$	84	15
5	-C(CH$_3$)$_3$	- C$_2$H$_5$	46	19
6	-n C$_6$H$_{13}$	- C$_2$H$_5$	63	14 (6/8)
7		- t-C$_4$H$_9$	49	27 (13/14)
8	-CH$_2$-O-CH$_3$	- C$_2$H$_5$	46	11
9	-CF$_3$	- C$_2$H$_5$	64	6
10		- t-C$_4$H$_9$	77	23 (9/14)
11	-C$_7$F$_{15}$	- CH$_3$	82	17 (8/9)
12		- C$_2$H$_5$	63	16 (7/9)
13		- t-C$_4$H$_9$	49	28 (13/15)
14	-C$_6$F$_5$	- C$_2$H$_5$	62	19
15		- t-C$_4$H$_9$	62	31 (13/18)
16	-Ferrocenyl	- C$_2$H$_5$	66	34 (13/21)
17		- t-C$_4$H$_9$	63	36 (11/25)
18	-1-Adamantyl	- C$_2$H$_5$	53	17
19	-C$_{10}$H$_4$Cl$_4$NO$_2$[b]	- CH$_3$	60	35 (15/20)
20		- C$_2$H$_5$	62	32 (14/18)
21		- t-C$_4$H$_9$	66	27 (12/15)
22	-C$_{16}$H$_8$Cl$_4$NO$_2$[c]	- CH$_3$	70	30 (10/20)
23		- C$_2$H$_5$	69	30 (13/17)
24		- t-C$_4$H$_9$	57	24 (11/13)
25	Cu(II)triflate	- C$_2$H$_5$	67	6
26		- t-C$_4$H$_9$	97	3

Same reaction conditions as in Table 1, Yields based on Alk-DA. a: Values in (brackets) refer respectively to the Z- and E-isomers (ratio of areas in the GLC peaks). The Z-isomer spontaneously cyclises into a γ-lactone.[7] b: R is the (L(+)-2-(tetrachlorophtalimido)propionato)group. c: R is the (L(+)-2-(tetrachlorophtalimido)-3-phenyl propionato)group.

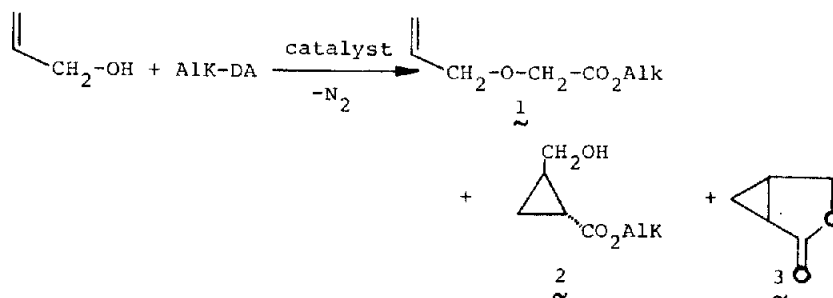Table 3. Relative yields of O–H insertion and ≡ addition in catalyzed decomposition of Alk-DA in unsaturated alcohols

	Catalyst	Substrate	Alk-DA Alk-	Insertion, yield, %	Addition, yield % [a]
1	$Rh_2(O_2C-CH_3)_4$	$CH_2=CH-CH_2OH$	$-C_2H_5$	66	15
2	$Cu(OTf)_2$	"	$-C_2H_5$	67	6
3	$Rh_2(O_2C-CH_3)_4$	$CH_2=CH-CH(CH_3)-OH$	$-C_2H_5$	62	13
4	"	"	$n-C_4H_9$	68	20
5	"	"	$t-C_4H_9$	64	23
6	$Cu(OTf)_2$	"	$-C_2H_5$	46	15
7	$Rh_2(O_2C-CH_3)_4$	$CH_2=CH-C(CH_3)_2-OH$	$-C_2H_5$	56	14
8	"	"	$n-C_4H_9$	64	18
9	"	"	$t-C_4H_9$	64	23
10	$Cu(OTf)_2$	"	$-C_2H_5$	33	14
11	"	"	$n-C_4H_9$	38	28
12	"	"	$t-C_4H_9$	20	12
13	"	$CH_2=CH+CH_2+_2OH$	$-C_2H_5$	53	14
14	$Rh_2(O_2C-CH_3)_4$	"	$-C_2H_5$	68	14
15	"	$CH_2=CH+CH_2+_3OH$	$-C_2H_5$	57	15
16	$Cu(OTf)_2$	"	$-C_2H_5$	19	15
17	$Rh_2(O_2C-CH_3)_4$	$HC≡C-CH_2OH$	$-CH_3$	60	12
18	"	"	$-C_2H_5$	77	6
19	"	$HC≡C+CH_2)_2OH$	$-CH_3$	50	19
20	"	$HC≡C-CH(C_2H_5)-OH$	$-CH_3$	54	21
21	"	"	$-C_2H_5$	56	20
22	"	$HC≡C-C(CH_3)(C_2H_5)-OH$	$-CH_3$	37	36
23	"	$HC≡C-C(CH_3)_2OH$	$-CH_3$	36	56
24	"	"	$-C_2H_5$	38	58

Same reaction conditions as in Table 1. a: Overall yield of (E + Z) isomers.

yields in addition compounds (cyclopropylcarbinols) are obtained with Rh(II) alkanoates of rather lipophilic character (Table 2, entries 16, 19, 22), especially when the diazoester is itself bulky (compare in Table 2, 6 and 7, 9 and 10, 14 and 15).

It is worthy of notice that the Z-isomers of cyclopropylcarbinols spontaneously rearrange into the γ-lactones 3, an observation previously reported by Ando and coworkers.[7]

As illustrated in Table 3, rhodium catalysis is relatively

$$CH_2-OH + AlK-DA \xrightarrow[-N_2]{catalyst} CH_2-O-CH_2-CO_2Alk$$

1

$$+ \quad \overset{CH_2OH}{\triangle}_{CO_2AlK} \quad + \quad \text{3}$$

2 **3**

Scheme 2.

insensitive to steric hindrance at the OH level (compare in Table 3, 1, 3, 7), although substitution α to an OH group decreases to some extent the benefit of using diazoesters with a long alkyl chain (Table 2, compare 1 to 4 with Table 3, 7 to 9). Steric effects are revealed only in competitive experiments, as for saturated alcohols (Table 4, 1, ratio of inserted 1-hydroxy-2-propene to 2-hydroxy-2-methyl-3-butene = 2.7). Besides, an allylic OH is always more reactive than a non-allylic OH (Table 4, 2), although chelation does not seem to be operative, as indicated by the results of competitions between potentially bidantate ligands (Table 4, 3).

Acetylenic alcohols. No insertion into the C-H sp bond is observed. The same general trends seen with olefinic alcohols are otherwise apparent, namely preference for OH insertion over triple bond addition (Table 3, 17-21 and Table 5). However, sensitivity to steric hindrance is more pronounced and in some cases, a reverse regioselectivity obtains, cyclopropenation predominating over OH insertion (Table 3, compare 17, 20 and 23-24), a fact *not* observed with allylic alcohols, and permitting in those particular cases a ready access to cyclopropenylcarbinols with satisfactory yields.

Role of the diazoester. Rhodium(II) alkanoates promote gentle and complete decomposition of all the diazoesters studied. However, it appears that (as far as insertion into OH bonds of olefinic alcohols is concerned) n-BuDA (n-butyl diazoacetate) or t-BuDA generates more efficient species that MeDA or EtDA with rhodium acetate (see Table 2, 1-4 and Table 3 3-5 and 7-9). This trend is by no means general. In fact, every "catalyst-diazoester" couple shows a relatively different chemoselectivity according to the substrate, seen also in intermolecular competitions. Typically, with rhodium acetate as catalyst, competitions between equimolecular amounts of 1-hexanol and 1-hexene give ratios of OH insertion to double bond addition of 6.7 with MeDA, 3.9 with EtDA and 2.7 with n-BuDA, methyl diazoacetate being thus about three times more selective than n-BuDA. However, using another rhodium(II) alkanoate (Rh ferrocenate, all other parameters unchanged) relative ratios of 1.0, 1.9 and 2.6 are obtained. Since purely electronic effects can hardly be invoked when using similar diazoesters, the above observations are indicative of control by weak (or lyophobic) interactions at the catalytic centre (e.g. specific solvations), an hypothesis also strongly supported by the role of the catalyst counter-ions (bulkiness, lipophilicity etc.) on the regioselec-

Table 4. Competition for O-H insertion between pairs of unsaturated alcohols

| R_1OH | R_2OH | Ratio R_1OR/R_2OR [a] | |
		$Rh_2(O_2C-CH_3)_4$	$Cu(OTf)_2$
1. $CH_2=CH-CH_2OH$	$CH_2=CH-C(CH_3)_2OH$	2.7	3.1
2. $CH_2=CH-CH_2OH$	$CH_2=CH(CH_2)_2OH$	2	1
3. $CH_2=CH(CH_2)_2OH$	$CH_2=CH(CH_2)_3OH$	1	1.4
4. $CH_2=CH-CH_2OH$	$HC\equiv C-CH_2OH$	0.8	–
5. $HC\equiv C-CH_2OH$	$HC\equiv C-C(CH_3)_2OH$	2.7	–
6. $HC\equiv C-CH_2OH$	$HC\equiv C(CH_2)_2OH$	1.2	–

Same Experimental conditions as in Table I, except that there is 5.10^{-2} mol of each alcohol- Diazoester is EtDA -
a : ratio of GLC areas.

Table 5. Relative yields of O–H insertion and triple bond addition in catalyzed decomposition of Alk-DA in propargyl alcohol

Catalyst Rh$_2$(O$_2$C–R)$_4$	Alk-DA Alk–	O–H Insertion Yield, %	Cyclopropenation Yield, %
R = –CH$_3$	–CH$_3$	60	12
	–C$_2$H$_5$	77	6
	–n-C$_4$H$_9$	62	11
– C(CH$_3$)$_3$	–CH$_3$	53	11
n-C$_3$H$_7$	–CH$_3$	64	10
1-adamantyl	–CH$_3$	52	12
–CF$_3$	–CH$_3$	40	3
–C$_2$F$_5$	–CH$_3$	45	2
n-C$_7$F$_{15}$	–CH$_3$	68	11
C$_{10}$H$_4$Cl$_4$NO$_2$ [b]	–CH$_3$	82	9
	–C$_2$H$_5$	78	10

b : see note b in Table II.

tivities in intramolecular competitions. Similar effects were previously observed in rhodium catalyzed cyclopropanation of alkenes,[5,8] addition to aromatic molecules,[9] and insertion into C–H bonds of alkanes.[10]

The copper triflate catalyzed reactions indicate by comparison a much higher sensitivity to steric effects (see Table 3). Moreover, at least partial reduction of Cu(II)–Cu(I) species was revealed by EPR; at the end of the diazoester addition (EtDA), the original Cu(II) signals in allylalcohol ($g_\perp$ = 2.0553, $g_\parallel$ = 2.3536) remained only as a shoulder in the spectrum. The ability of diazoesters to reduce Cu(II) is well established.[11] On the other hand, the propensity of Cu(I) to complex with alkenes is also well documented, especially when the copper ion is associated with very weak ligands such as the triflate anion. Thus, Cu(I) species could be responsible for the cyclopropanation reaction of olefinic alcohols via a coordination type of mechanism similar to that reported for the cyclopropanation of simple olefins.[9] Actually when Cu(I) triflate was used as catalyst (instead of Cu(II) triflate), the cyclopropanation of the allyl alcohol double bond (EtDA) increased from 6 to 30% and the OH insertion yield went down to 55%. So, with copper catalysis, the relative ratio of cyclopropanation to insertion probably results from competitions between carbenoid and coordination-types of mechanisms.

In conclusion, rhodium(II) alkanoates and copper(II) triflate, a family of air-stable, easily synthesized compounds, are efficient catalysts for promoting a regioselective insertion of carbenes into the hydroxylic bonds of a variety of alcohols under mild conditions. On a synthetic point of view, an easy high-yield access to functionalized unsaturated ethers is potentially interesting for the synthesis of a variety of heterocyclic systems. Moreover, the methodology also permits the one step synthesis of 3-membered cyclic carbinols with satisfactory yields.

EXPERIMENTAL

General methods and preparative procedures were previously reported.[5] The alcohols were distilled prior to use, and the reaction performed by slow addition of the diazoester through a syringe pump (Sage, model 352) to a combination of the catalyst and an excess of the alcohol at room temperature. The reactions were run in the atmosphere and the products identified by comparison of their VPC retention times with those of authentic samples and/or comparison with data of the literature[7] and by coupled GC-MS. Most of the rhodium(II) alkanoates used as catalysts were prepared from the corresponding carboxylic acids according to published procedures.

Typical reaction conditions are given for the reaction of EtDA with allyl, propargyl and α,α-dimethylpropargyl alcohols.

Reaction with allyl alcohol: ethyl 2-allyloxyacetate (1). To 150 mmol of the unsaturated alcohol, containing 0.04 mmol of Rh(II) acetate, 7.5 mmol of ethyl diazoacetate was added with an automatic syringe pump within approximatively 3 h, while stirring magnetically at room temperature. The reaction mixture was then distilled under vacuum and the product corresponding to OH insertion submitted to a second distillation (18 torr, b.p.

Table 6. Kinetics of Rh(II) acetate catalyzed insertion into the hydroxylic bond of ethanol (EtDA)

[Ethanol] M	10^3[Rh(II)acetate] M	EtDA M	T,°K	k_{obsvd}
17.1	2.4	1.170	248	0.403
17.1	2.4	1.170	303	0.626
17.1	2.4	1.170	308	0.925
17.1	2.4	1.170	313	1.766
17.1	4.8	1.170	298	0.434
17.1	9.6	1.170	298	0.387
17.1	2.4	0.585	298	0.417
17.1	2.4	2.340	298	0.382

70–75°). Anal ($C_7H_{12}O_3$): C, H. IR (neat, ν cm^{-1}): 3035 (w), 1747 (S), 1640 (w), 1430 (w) 1200 (S). NMR (60 MHz, neat, HMDS): δ (ppm) = 6.2–4.88 (m, 3H, olefinic H), 3.95 (S, 2H, –O–CH$_2$–CO$_2$–), 4.15–3.85 (m, 4H, –CH$_2$–CH$_3$+–O–CH$_2$–CH=), 1.16 (t, 3H, –CH$_3$).

The carbinol 2 and the bicyclic lactone 3 were identical with the products described in Ref. 7.

Reaction with propargyl alcohol: ethyl 2-propynyl-oxyacetate. B.p. 0.1 mm, 35°. Anal ($C_7H_{10}O_3$): C, H. IR (neat, ν cm^{-1}) 3285 (m) 2102 (m), 1744 (S), 1442 (m), 1115 (S), 1020 (S). NMR (60 MHz, neat, HDMS): δ (ppm) 4.36–3.81 (m, 6H), including 4.07 (S, 2H, –O–CH$_2$–C̈–), 2.69 (t, 1H, ^4J = 2.5 Hz, ≡C–H), 1.20 (t, 3H, CH$_3$). Methyl 2-hydroxymethyl-2-cyclopropene-1-carboxylate, the product of cycloaddition to the triple bond, was reduced in situ by Pd on C, yielding quantitatively the bicyclic lactone 3.

Reaction with α,α-dimethylpropargylalcohol. Ethyl (1,1-dimethyl-2-propynyl) oxyacetate had b.p. (4 × 10^{-2} mm) 41°. IR (neat, ν cm^{-1}) 3250 (m), 2100 (w), 1740 (S), 1200 (S) 1110 (S). NMR (60 MHz, CCl$_4$, TMS): δ (ppm): 4.06 (q, 2H, ^3J = 7.2 Hz, O–CH$_2$–CH$_3$), 4.00 (S, 2H, –O–CH$_2$–CO$_2$), 2.46 (S, 1H, C≡C–H) 1.46 (S, 6H, CH$_3$), 1.25 (t, 3H, –CH$_2$–CH$_3$).

Ethyl(1-hydroxy-1-methyl-2-ethyl-2-cyclopropene-1-carboxylate had b.p. (4 × 10^{-2} mm) 70°. IR (neat, ν cm^{-1}): 3420 (S, broad), 3130 (m), 1800 (m), 1720 (S), 1200 (S). NMR (60 MHz, CCl$_4$, TMS), δ (ppm): 6.30 (d, 1H,^3J = 1.7 Hz, H olefin), 4 (q, 2H, CH$_2$–CH$_2$–CH$_3$), 3.93 (S, 1H OH), 2.16 (d, 1H, ^3J = 1.7 Hz), 1.38 (S, 6H, CH$_3$), 1.20 (t, 3H, CH$_2$–CH$_3$).

L(+)-2-(*tetrachlorophthalimido*)*propionic acid.* 28.6 g Tetrachlorophthalic anhydride, 10.1 mL triethylamine and 8.9 g of L(+) alanine in 250 mL of toluene were refluxed with a Dean-Stark trap until complete water evolution had occurred. The solvent was evaporated under vacuum and the residue was washed once with HCl (1.2% conc HCl), and twice with distilled water. The resulting solid was crystallized from aq MeOH, dried first at 110° and overnight under vacuum at 25°. Yield 97%, m.p. 305°C. Anal ($C_{11}H_5Cl_4NO_4$): C, H, N.

Tetra {L(+)-2-(*tetrachlorophthalimido*)*propionato*}*dirhodium(II).* 50 mg Hydrated Rh(III) chloride, 500 mg of L(+)-2-(tetrachlorophthalimido)propionic acid and 61 mg of sodium bicarbonate were refluxed for 1 h in 20 mL of ethanol under N$_2$. On cooling, a green solid precipitated out of the green solution.

The solid was chromatographed on silica (elution with toluene-ethyl acetate: 100–0 followed by 85–15). The solid was further crystallized from acetone. Anal ($C_{44}H_{16}Cl_{16}N_4O_{16}Rh_2$): C, H, N. IR ($\nu$, cm^{-1}): 1780 (m), 1727 (S), 1610 (s), 1410 (mS), 1400–1350 (S), 738 (m). ORD (25°, CHCl$_3$, C=O, 366): max at 525 nm with $[\alpha]_{525}$ = 273, min at 472 nm $[\alpha]_{472}$ = 148; $[\alpha]_{600}$ = 153.

Tetra(ferrocenycarboxylato)dirhodium(II). 250 mg Hydrated rhodium(III) chloride and 0.370 g of sodium bicarbonate in 70 mL ethanol were refluxed during 90 min under argon. After cooling, the solution was filtered. More rhodium chloride (~ 100 mg) and sodium bicarbonate were added to the filtrate which was refluxed to yield a second crop of rhodium(II) ferrocenylcarboxylate. Crude yield 80%, relative to rhodium trichloride. The khaki precipitate of rhodium complex was washed with methanol and ether. For analytical purpose, part was recrystallized from DMSO and dried *in vacuo.* Anal for Rh (O$_2$C–Fc)$_2$·DMSO: C, H. IR (ν, cm^{-1}) 1550 (S), 1480 (S), 1388 (S), 1353 (mS), 1345(m), 1185 (m), 1100 (m), 1020 (w), 995 (w), 865 (w), 808, 795, 770 (m).

REFERENCES

[1]For reviews, see A. P. Marchand and N. McBrockway, *Chem. Rev.* 4, 431 (1974); D. S. Wulfman and B. Poling, *Reactive Intermediates,* Vol. 1, p. 424. Plenum Press, New York (1980); W. Kirmse, K. Loosen and H. D. Sluma, *J. Am. Chem. Soc.* 103, 5935 (1981).

[2]T. Saegusa, Y. Ito, S. Kobayashi, K. Hirota and T. Shimizu, *J. Org. Chem.* 33, 545 (1968).

[3]R. Paulissen, E. Hayez, A. J. Hubert and Ph. Teyssié, *Tetrahedron Letters,* 2233 (1973).

[4]R. Paulissen, E. Hayez, A. J. Hubert and Ph. Teyssié, *Ibid.* 607 (1974).

[5]A. J. Anciaux, A. J. Hubert, A. F. Noels, N. Petiniot and Ph. Teyssié, *J. Org. Chem.* 45, 695 (1980).

[6]For acetylenic alcohols, see N. Petiniot, A. J. Anciaux, A. F. Noels, A. J. Hubert and Ph. Teyssié, *Tetrahedron Letters* 1239 (1978).

[7]W. Ando, I. Imai and T. Migita, *J. Chem. Soc. Chem. Commun.* 822 (1972); *J. Org. Chem.* 37, 3596 (1972).

[8]A. J. Hubert, A. F. Noels, A. J. Anciaux and Ph. Teyssié, *Synthesis,* 600 (1976), see also Ref. 5.

[9]A. J. Anciaux, A. Demonceau, A. F. Noels and R. Warin, *J. Org. Chem.* **46**, 873 (1981).

[10]A. Demonceau, A. F. Noels, A. J. Hubert and Ph. Teyssié, *J. Chem. Soc. Chem. Commun.* 688 (1981).

[11]P. G. Moniotte, A. J. Hubert and Ph. Teyssié, *J. Organometal. Chem.* **88**, 115 (1975); D. Bethell, K. L. Handoo, S. A. Fairhurst and L. H. Sutcliffe, *J. Chem. Soc. Chem. Commun.* 326 (1977); T. Saegusa, Y. Ito, T. Shimizu and S. Kobayashi, *Bull. Chem. Soc. Japan* **42**, 3535 (1969); T. Shirafuji, Y. Yamamoto and H. Nozaki, *Tetrahedron* **27**, 5353 (1971).

[12]Besides a lack of products corresponding to C–H insertion, so typical of free carbene processes, the presence of carbenoid intermediates was further supported by the observation of chiral recognition during the insertion into the OH bond of racemic 1-phenylethanol catalyzed by a chiral rhodium(II) catalyst (to be published).