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Oxidation of olefins by palladium(II) Part 17. An asymmetric chlorohydrin synthesis catalyzed by a bimetallic palladium(II) complex

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Abstract

Previous studies showed that oxidation of α-olefins with monometallic catalysts containing chiral diphosphines and diamines gave chlorohydrins with poor to good enantioselectivites (28–82% ee). The present studies demonstrate that bimetallic catalysts containing a β-triketone and bridging chiral diphosphine and diamines are excellent catalysts for this reaction giving enantioselectivites considerably higher than the monometallic catalysts. Enantioselectivities were more than 50% for most olefins tested. The highest optical purities were 94% ee for propene and 93% ee for allylphenyl ether. A useful feature of this asymmetric synthesis is the fact it is a net air oxidation. © 2000 Elsevier Science S.A. All rights reserved.

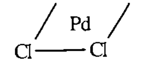
Keywords: Palladium(II); Catalysis; Asymmetric; Olefins; Chlorohydrins

1. Introduction

Paper 16 of this series describes the preparation of enantiomeric chlorohydrins from olefins using a combination of monometallic Pd(II) complexes containing chiral auxiliaries (**A** and **B** shown below), plus $CuCl_2$ as catalyst [1].

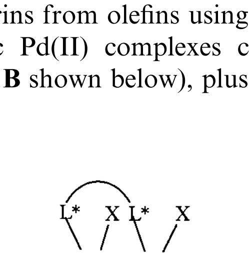
monometallic

A



monometallic

B



bimetallic

C

As shown in Scheme 1, the reaction is an air oxidation since the CuCl formed in the first step is readily reoxidized by dioxygen to give back $CuCl_2$. Thus, the reaction has potential for a continuous commercial process for chlorohydrin production.

As expected, the enantioselectivities were low (% ee = 8–12%) for catalyst **A** containing monodentate chiral ligands. Catalyst **B**, containing bidentate chiral ligands, gave modest to good enantioselectivities, ranging from ee = 28 to 82%. For propene the **1**:**2** ratio was 6–12, while for more substituted olefins the **2** isomer was not detected.

The present paper examines the effectiveness of a novel bimetallic Pd(II) complex, **C**, containing a 1,3,5-β-triketone ligand and a bridging bidentate chiral auxiliary. In the present study the chiral bidentate ligands were (1*R*,2*R*)-(−)-1,2-diaminocyclohexane (1*R*,2*R*-DACH), (+)- and (−)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (DIOP), and (*S*)-(−)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl [(*S*)-BINAP]. These bimetallic catalysts are homogeneous analogues of the bimetallic heterogeneous catalysts studied previously in these laboratories [2–4].

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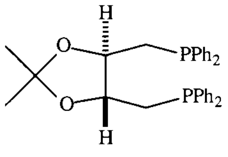
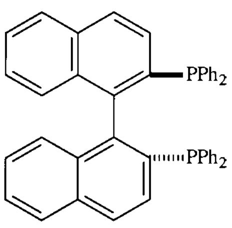
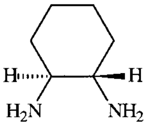


(R,R)-DIOP



(R)-BINAP



(R,R)-DACH

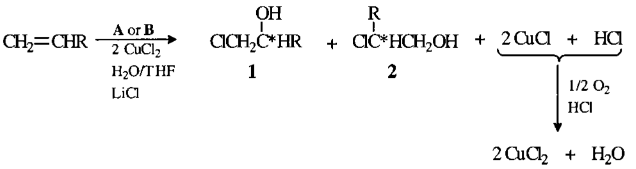
Some of the results of the present study have been reported in a preliminary communication [5].

2. Results

2.1. Synthesis and characterization of ligands

The triketones, 1-phenyl-1,3,5-hexanetrione (PHT) and 1-phenyl-6.6.6-trifluoro-1,3,5-hexanetrione (PFHT), were prepared by a literature procedure that recommends the use of sodium hydride as base [6]. 2,4,6,-Heptanetrione (HpT) was prepared by the reaction of dehydroacetic acid with concentrated HCl [7]. Yields were in the range of 50–80%. The preparation of the sodium salts of 1-phenyl-1,3,5-hexanetrione (Na_2[PHT]) and 1-phenyl-6,6,6-trifluoro-1,3,5-hexanetrione (Na_2[PFHT]), involved the reaction of the di- or triketone with sodium metal in THF at room temperature (r.t.).

The ^{1}H-NMR spectra of the β-triketones had signals due to both $-CH_2-$ (3.28–4.32 ppm) and $=CH-$ (5.02–6.31 ppm) protons indicating that enol forms of the triketones are present. There are a number of possible enol forms for these triketones. The signals arising from the phenyl protons for PHT and PFHT occur between 7.46 and 7.86 ppm.



Scheme 1.

The ^{13}C-NMR spectra also had signals for vinyl carbons of the enol form at 79.2–113.3 ppm as well as methylene protons at 50.1–66.0 ppm confirming the presence of several isomers.

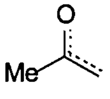
2.2. Synthesis and characterization of palladium(II) catalysts

The preparation of the bimetallic catalysts involved mixing $[Pd(CH_3CN)_4](BF_4)_2$ and the β-triketone in a 2:1 ratio, followed by addition of the chiral diamine or diphosphine. The ratio of chiral ligand to Pd(II) was 1:2.

Tables 1 and 2 summarize the ^{1}H- and ^{13}C-NMR data for the Pd(II) catalysts. The signals arising from the phenyl and binaphthyl groups of the diphosphines are not listed. These occur between 6.90–7.95 ppm in the ^{1}H-NMR and 121.8–157.3 ppm in the ^{13}C-NMR. Also omitted from Tables 1 and 2 are the signals arising from the methylene groups in the (−)-DACH containing catalysts. These signals occur between 1.54–2.35 ppm in the ^{1}H-NMR and 23.4–32.6 ppm in the ^{13}C-NMR. Finally the CH_3CN ^{13}C-NMR signals are missing from Table 2. These occur between 1.13–1.20 and 117.9–119.0 ppm.

The signals in the ^{31}P-NMR spectra for the DIOP and BINAP palladium(II) catalysts appear between 22.8 and 32.3 ppm in Table 2. The shift in these signals from those in the free ligand is strong evidence for the coordination of the phosphine to Pd(II). In the free ligands the signals occur in the range −25 to −10 ppm.

Table 1
^{1}H-NMR chemical shifts for palladium(II) catalysts[a]

Compound		MeCN	$P(CH_2)_2P$/or $H_2NC^*HC^*HNH_2$/or $PCH_2CH^*CH^*CH_2P$
$[Pd_2(MeCN)_2(PHT)(-)DACH](BF_4)_2$	1.78	2.06	3.04, 4.52, 4.90, 5.15
$[Pd_2(MeCN)_2(HpT)(-)DACH](BF_4)$	1.75	2.06	3.09, 4.56, 5.13, 5.50, 5.60
$[Pd_2(MeCN)_2(PFHT)(-)DIOP](BF_4)_2$		2.05	2.20, 2.30, 4.10, 4.37
$[Pd_2(MeCN)_2(PFHT)(+)DIOP](BF_4)_2$		2.06	2.22, 2.28, 4.15, 4.36
$[Pd_2(MeCN)_2(HpT)(-)DIOP](BF_4)_2$	1.75	2.05	2.92, 4.14
$[Pd_2(MeCN)_2(PHT)(S)BINAP](BF_4)_2$	1.76	2.06	

[a] All spectra were run in DMSO.

Table 2
^{13}C- and ^{31}P-NMR chemical shifts for palladium(II) catalysts [a]

Compound	^{31}P signal (ppm)	^{13}C Signals		
		$P(CH_2)_2P$/or $H_2NC*HC*HNH_2$/or $PCH_2CH*CH*CH_2P$	=CH–	C=O
$[Pd_2(MeCN)_2(PHT)(-)DACH](BF_4)_2$		45.7, 46.8	88.7, 99.2	165.4, 174.8, 99.2, 181.3
$[Pd_2(MeCN)_2(HpT)(-)DACH](BF_4)$		45.7	85.9	167.8, 171, 183
$[Pd_2(MeCN)_2(PFHT)(-)DIOP](BF_4)_2$	22.8, 22.9	26.45, 29.30, 74.82, 75.94	97.8, 98.2, 99.0	167.4, 177.7, 188.1
$[Pd_2(MeCN)_2(PFHT)(+)DIOP](BF_4)_2$	22.9, 23.1	26.5, 29.3, 74.8, 75.8	98.1, 98.9, 99.1	167.5, 178.1, 188.9
$[Pd_2(MeCN)_2(HpT)(-)DIOP](BF_4)_2$	28.3	29.4, 75.7	97.9, 99.1	172.6, 179.4, 189.0
$[Pd_2(MeCN)_2(PHT)(S)BINAP](BF_4)_2$	32.2		91.6, 95.7	171.3, 174.7, 175.4

[a] All spectra were run in DMSO.

Table 3
Results for the oxidation of several olefins by chiral bimetallic Pd(II) catalysts in the presence of $CuCl_2$ [a]

Run	Chiral ligand	Triketone	[LiCl] (M)	THF (%)	Substrate	Carbonyl (%)	**1**:**2** ratio	% ee of **1**
1	(*S*)-BINAP	HpT	0.10	45	Propene	5.5	3.5	94
2	(+)-DIOP	PFHT	0.08	54	Propene	5.5	2.8	68
3	(−)-DACH [e]	PHT	0.085	60	Propene	6.5	2.7	50
4	(+)-DIOP	PFHT	0.10	MeOH	Propene	ND	90 [b]	75
5	(+)-DIOP	PFHT	0.08	30	1-Pentene	6.9	3.1	74
6	(−)-DACH	PHT	0.12	34	1-Pentene	6.0	2.3	54
7	(+)-DIOP	PFHT	0.00	50	1-Pentene	21 [c]	2.8	15
8	(*S*)-BINAP	PHT	0.22	50	1-Pentene	19 [c]	4.0	89
9	(+)-DIOP	PFHT	0.10	20	$CH_2=CHC(O)CH_3$	ND	>90	84
10	(+)-DIOP	PFHT	0.15	20	$CH_2=CHCH_2OH$	20 [d]	4.5	50
11	(−)-DACH	PHT	0.20	86	$CH_2=CHCH_2OPh$	20	>95	60
12	(−)-DIOP	HpT	0.20	86	$CH_2=CHCH_2OPh$	12	>95	85
13	(*S*)-BINAP	PHT	0.30	92	$CH_2=CHCH_2OPh$	8.5	>95	93
14	(−)-DIOP	PHT	0.20	90	$CH_2=CHCH_2O$(1-Naph)	12	>95	76
15	(*S*)-BINAP	PHT	0.20	90	$CH_2=CHCH_2O$(1-Naph)	11	>95	80

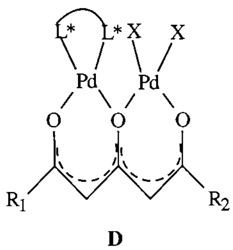
[a] All runs contain 0.1–0.3 mmol of chiral catalyst in 25–50 ml of solvent and are 3–5 M in $CuCl_2$. Temperature = 25°C. The solvent was a H_2O–THF mixture containing 30–92% THF by volume.

[b] 2-Methoxy-1-chloropropane was the product.

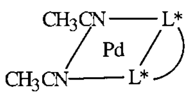
[c] The carbonyl products also included 1- and 3-hydroxy-2-pentanone.

[d] The product was a 1:1 mixture of 1-hydroxyacetone and 3-hydroxypropanal.

The lack of $^{31}P-^{31}P$ coupling provides evidence for the bridging nature of the diphosphine. It is possible that the bimetallic complex containing a chiral diphosphine has a structure in which both Ps of the diphosphine are complexed to one Pd(II) of the dimer (structure **D**). If this were the case a $^{31}P-^{31}P$ would be observed.



D



E

In the monometallic catalyst (structure **E**) containing (S)-BINAP a $^{31}P-^{31}P$ coupling constant of 10.59 Hz was observed [8]. This is consistent with the coupling observed in other *cis* bis(monophosphine) complexes [9]. In the bimetallic catalysts no coupling was observed, indicating the phosphines were on two different Pd(II)s. Of course, another reason for believing that the phosphine is bridging is the fact that the bimetallic catalyst gives high enantioselectivities. If structure **D** were the correct one, the Pd(II) with the diphosphine ligand would be unreactive because it is coordinately saturated. The other Pd(II) would be the reactive species but would give no chiral induction.

2.3. Oxidation of olefins by the chiral bimetallic palladium(II) catalysts

Table 3 summarizes the product distributions and optical yields, while Table 4 lists the quantities of reagents, gas uptake and yields for the oxidation of several olefins by the bimetallic catalysts containing

Table 4
Experimental details, gas uptake and yields

Run	Reactants (mmol)				Solvent (ml)	Gas uptake (mmol) [a]	% Total yield based on gas uptake [b]
	Catalyst	LiCl	$CuCl_2$	Substrate			
1	0.122	2.4	132		30	13.8	93
2	0.19	4.25	206		50	11.6	91
3	0.07	5.0	115		50	13.7	88
4	0.122	2.4	109		30	10.3	90
5	0.13	4.0	170	10	50	7.0	89
6	0.19	6.0	145	10	50	5.4	91
7	0.13	0.0	110	7.3	30	5.2	
8.	0.075	6.6	90	11	30	7.5	
9	0.11	5.0	275	24	50	15.6	
10	0.11	3.75	109	19	25	2.0	
11	0.14	6.0	37.5	3.7	25	2.8	
12	0.045	6.0	54	3.7	30	3.4	
13	0.045	9.0	54	3.7	30	2.9	
14	0.075	6.0	93	3.7	30	6.0	96
15	0.10	6.0	87	6.5	30	8.8	95

[a] For runs 1–4 the gas was propene. The gas was dioxygen for the remaining runs.
[b] Yields are calculated assuming dioxygen is a 4-electron oxidant.

different bridging bidentate chiral ligands. As expected from the previous results with monometallic Pd(II) complexes [1], propene, 1-pentene and allyl alcohol produced both the 1-chloro-2-hydroxy (**1**) and 2-chloro-1-hydroxy (**2**) isomers with **1** predominating. The course of the reaction was monitored by measuring either propene or dioxygen uptake with gas burets. The gas uptake was always linear with time, indicating no induction period.

2.4. Absolute configuration and stereochemistry of the chlorohydrin products

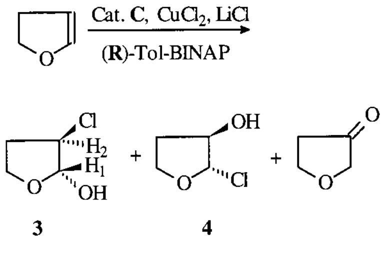
In run 1 of Table 3, the enantioselectivity of the **1** and **2** isomers was 94 and 68% ee and the absolute configuration of the 2-chloro-1-propanol product (**2**) was found to be (*R*) by comparison with an authentic sample in the presence of $Eu(hfc)_3$. The original reaction mixture for run 1 containing 78% **1** and 22% **2** was reacted with 4% NaOH and then the product extracted by $CDCl_3$. The ^{1}H- and ^{1}C-NMR spectra indicated the formation of propylene oxide. The % ee of propylene oxide was determined by ^{1}H- and ^{1}C-NMR to be 84%. The % ee of propylene oxide indicated that the two isomers, **1** and **2**, gave epoxide with the same absolute configuration. The absolute configuration of propylene oxide was determined by comparison with an authentic sample of (*S*)-(−)-propylene oxide in the presence of $Eu(hfc)_3$. The absolute configuration was found to be (*S*).

The absolute configuration of the chlorohydrin from allylphenyl ether (run 13) was also (*S*), while that of the same chlorohydrin in run 12 was (*R*).

The overall stereochemistry of the reaction was determined using 2,3-dihydrofuran. Oxidation of 2,3-dihydrofuran gave the three products shown in Scheme 2. The three products were identified as 3-chloro-2-hydroxy-tetrahydrofuran (**3**), 2-chloro-3-hydroxytetrahydrofuran (**4**) and 3-oxo-tetrahydrofuran in relative yields of 80, 15 and 5% respectively. The ee of **3** was found to be 72% and its stereochemistry was determined to be (*E*) from the coupling constant ($J_{1,2} = 2.96$ Hz) [10].

2.5. Control experiments

To ensure that the bimetallic catalyst **C** is the actual catalyst, two control experiments were run. First the oxidation of propene was attempted using all reactants but the catalyst **C**. No propene uptake occurred and no chlorohydrin product was detected by GLC. Second, the reaction was run until the usual amount of product was accumulated. The catalyst was isolated from the reaction mixture as the bromide complex. It was shown to be catalyst **C** by ^{1}H and ^{13}C analysis.



Scheme 2.

3. Discussion

3.1. Catalyst system

This paper describes the oxidation of olefins to chiral chlorohydrins by a novel bimetallic palladium(II) complex containing a bridging chiral diphosphine ligand. This system could be of commercial utility because it is a net air oxidation. Thus, the CuCl formed in the reaction is readily reoxidized back to $CuCl_2$ by dioxygen. More than 300 catalyst turnovers have been achieved to date and many more are possible since the catalyst had not lost any activity at this point.

The control experiments leave little doubt that the bimetallic catalyst, **C**, is the actual catalyst. Since the [Cu(II)] to [Pd(II) catalyst] ratio is about 1000, it is possible that the actual catalyst is either Cu(II) or a dimer containing both Pd(II) and Cu(II). The fact that no reaction occurs in the absence of Pd(II) proves that Cu(II) alone cannot be the catalyst. A Pd(II)–Cu(II) dimer is eliminated as catalyst by the fact that the dimeric Pd(II) catalyst can be recovered from a spent reaction mixture. Another indication that **C** is the catalyst is the fact that the oxygen uptake is linear throughout the whole reaction. If another catalyst were being formed, an induction period would be expected.

The yields listed in Table 4 are in the 90% range for propene and 1-butene and close to 100% for the allyl-α-naphthyl ether runs (14 and 15). These yields show that the gas uptake procedure is an accurate measure of the extent of reaction.

3.2. Enantio- and regioselectivity

These bimetallic catalysts are superior to the monometallic Pd(II) catalysts containing a chiral diphosphine ligand studied previously [1]. Direct comparison between the two systems is difficult because in most of the monometallic catalysts contained sulfonated ligands to increase the solubility. It is known that sulfonation decreases the enantioselectivity[11]. However, in two cases where the monometallic catalyst was not sulfonated, the enantioselectivities were not as high as with the bimetallic catalyst. Thus, in run 1 of Table 3, the corresponding monometallic catalyst gave a enantioselectivity of 56% ee as opposed to 94% ee in the present study. For run 13, the values are 80% for the monometallic and 93% for the bimetallic. The high asymmetric induction obtained with the bimetallic catalysts is probably the most unexpected and interesting result of the present work.

The closest comparison to the present reaction is the Pd(II) catalyzed synthesis of chiral chlorohydrins using an olefin containing a chiral allylic amine ligand [12]. This very interesting conversion gives a chiral chlorohydrin containing the chiral amine in poor to modest optical purities (ee = 1–77%). As the chiral agent is monodentate, the system is analogous to catalyst A. The fact that the optical yields were generally higher than those obtained with **A** can be rationalized by the fact that the system is rigid in the same fashion as the bimetallic catalyst in the present studies.

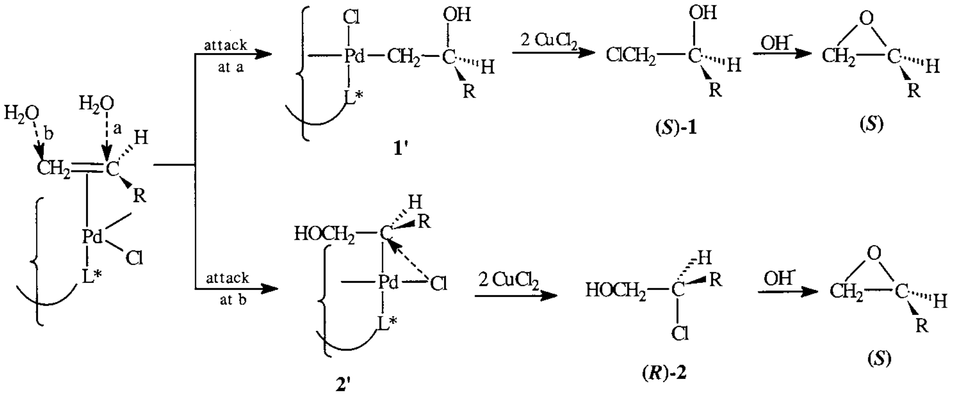
Of the three chiral ligands tested, catalysts containing (*S*)-BINAP gave the highest enantioselectivities with DIOP next and DACH a poor third. This order can readily be seen by comparing runs 1–3 and runs 11–13. The optical purity would have been expected to be higher in run 15 based on this order and the % ee in run 14. This result is disappointing since the chlorohydrin product is a potential intermediate in the preparation of propranolol, the β-adrenergic blocker [13].

Besides the effect of the chiral ligand there are no obvious trends in carbonyl yields and enantioselectivity. The identity of the triketone ligand and the solvent composition has little effect on these variables. Run 4 was run in methanol solvent to give the methyl ethers as products. The enantioselectivity in run 4 is that expected in comparison with run 2. However, none of the Wacker product, 2,2-dimethoxypropane, was detected. One factor that may be important is the chloride concentration. In run 7 no LiCl was added the optical purity was only 15% ee.

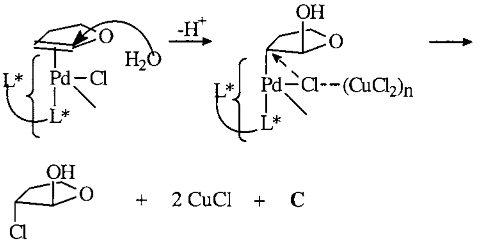
The regioselectivity was a problem only with the simple α-olefins, propene, 1-pentene and allyl alcohol. For methyl vinyl ketone and the allyl ethers only the **1** isomer was observed. The formation of the two isomers may not be a serious problem if they are converted to epoxide of the same configuration. With propene, both isomers gave epoxide with the (*S*) configuration when (*S*)-BINAP was the ligand.

3.3. Mechanism

These results discussed in Section 2.4 provide some mechanistic insight into the reaction. Molecular models indicate that the formation of (*S*)-**1** is consistent with anti addition to the most stable π-complex. Anti addition is expected for Pd(II) catalysts containing a neutral ligand [14]. The formation of (*R*)-**2** is consistent with decomposition occurring from the coordination sphere of the Pd(II) or a $CuCl_2$ attached to the Pd(II). The reaction sequence is shown in Scheme 3. With cyclic olefins this scheme predicts chlorohydrin products with the (*E*) configuration. 2,3-Dihydrofuran indeed did give chlorohydrins with the *E* configuration. If the hydroxypalladation is *anti*, the decomposition must occur from the coordination sphere of the Pd(II) in order to give the overall *E* configuration. This last result is inconsistent with studies on the decomposition of hydroxypalladation adducts formed by exchange of hydroxymercuration adducts with $PdCl_4^{2-}$ in the presence of $CuCl_2$ [15]. However these last experiments



Scheme 3.



Scheme 4.

were conducted at high [Cl$^-$] where the mode of decomposition may be different from the conditions of the present experiment. A plausible reaction sequence is shown in Scheme 4. Although the Cl$^-$ is shown arising from the coordination sphere of Pd(II), it is also possible that it comes from the coordination sphere of the copper(II).

One uncertain aspect of the reaction pathways in Schemes 3 and 4 is the source of the coordination sites for chloride and/or $CuCl_2$ binding. The bimetallic catalyst **C** has only one coordination site available for bonding. There is no problem with the original addition of water if the addition is *anti* since only one site is required to bind the olefin. However, once the hydroxypalladation has occurred, the one coordination site is required to bind to the carbon of the hydroxypalladation adduct. If decomposition occurs by chloride transfer from the coordination sphere of the Pd(II), one of the other ligands must dissociate to make room for the chloride. This could be either a phosphine or an oxygen from the triketone. Another possibility is that the Pd(II) becomes five coordinate. Because of the uncertainty, the coordination sphere of the Pd(II) is not specified exactly in Schemes 3 and 4.

3.4. Summary

An improved catalytic system for synthesis of chiral chlorohydrins has been developed. The catalyst for this new synthesis is a bimetallic Pd(II) complex containing a triketone and a chiral bridging bidentate ligand. Since it a net air oxidation, this system could be a means of producing small-molecule chiral compounds in commodity quantities from inexpensive feedstocks. Future work will be aimed at exploring the scope of the reaction. In particular, the bromide containing system is presently under investigation to determine if chiral bromohydrins can be synthesized. Because of the greater lability of the carbon–bromine bond, these species could be of more synthetic value than the chlorohydrins.

4. Experimental

All ^1H-, ^{13}C-, ^{31}P-NMR spectra were recorded on a 300 MHz Varian VXR 300 spectrometer. Chemical shifts for ^1H and ^{13}C are relative to $(CH_3)_4Si$. ^{31}P chemical shifts are relative to 85% H_3PO_4 at 0.0 ppm. IR spectra were recorded on a Perkin–Elmer Model 1310 Infrared spectrometer or an ATI Mattson Genesis series FTIR spectrometer. Melting points were recorded on a Laboratory Devices Mel-Temp apparatus using a calibrated thermometer. Elemental analyses were performed by Midwest Microlab, Indianapolis, Indiana 46250. GLC analyses were carried out on a GOW-MAC gas chromatograph (Model 350).

Palladium sponge, sodium tetrafluoroborate, (+)- and (−)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis-(diphenylphosphino)butane (DIOP), (1*R*,2*R*)-(−)-1,2-diaminocyclohexane (1*R*,2*R*-DACH), tris[3-(heptafluoropropyl-hydroxymethylene)-(+)-camphoratol], europium(III) derivative (Eu(hfc)$_3$), sodium hydride (60% dispersion in mineral oil), (*S*)-(−)-propylene oxide, (*S*)-(+)-2-chloro-1-propanol, 1,1,1-trifluoro-2,4-pentanedione, 2,4-pentanedione, dehydroacetic acid, and propene, were obtained from Aldrich Chemical Co. (*S*)-(−)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl [(*S*)-BINAP] was obtained either from Fisher Scientific or Strem Chemicals. Allylphenyl ether was obtained from Fluka Chemical Corp. All chemicals were used as received. Solvents were reagent grade. Dichloromethane, diethyl ether, tetrahydrofuran, and acetonitrile were dried over calcium hydride (CaH_2) and distilled and stored under argon. The preparation of the polyketones required moisture exclusion techniques. All reaction glassware was dried overnight at 110°C before use. The apparatus was assembled and lightly flamed, while passing argon through the system. Moisture sensitive solvents and solutions were transferred via cannulas and/or syringes. Reflux reactions under nitrogen or argon were normally performed in a three-neck round bottom flask fitted with a condenser, an inert gas adapter and a suba seal septum. Reagents were introduced through the neck with the septum. The reactions were accomplished under a slight positive pressure of the inert gas.

The % ee was determined by using ^{1}H- or ^{13}C-NMR in the presence of chiral Eu(hfc)$_3$. A range of 0.1–0.3 molar ratio of Eu(hfc)$_3$ with respect to the chiral material was used.

4.1. Oxidation procedure

To provide good gas liquid mixing, the reactions were run in creased flasks at 25°C at a constant pressure of 1 atmosphere. The progress of the oxidations was followed by gas (propene or dioxygen) uptake measured by gas burets thermostated at 25°C. The reaction vessel was a 250 ml two-necked coned shaped flask with the sided indented at four places to increase stirring efficiency. The apparatus is similar to that previously described [16]. In a typical run the flask containing 30–50 ml of reaction mixture was placed in a constant temperature bath and connected to the gas buret. The system was then evacuated for 10 min on the vacuum line with stirrer running. The stirring was stopped and the system pressurized to 1.0 atmosphere with dioxygen. The mercury in the gas buret and the leveling bulb were equalized and a reading taken. The stirrer was then activated. Atmospheric pressure was maintained by continuously leveling the mercury in the gas buret. The volume of dioxygen consumed was measured at regular time intervals (t) to give a series of readings (V_t).

4.2. Preparation of reactants and ligands

4.2.1. Allyl-α-naphthyl ether [17]

α-Naphthol (20.0 g, 0.139 mmol), allyl bromide (16.8 g, 0.139 mmol), potassium carbonate (19.2 g, 0.139 mmol), and acetone (150 ml) were heated under reflux for 2 h. The acetone was removed under reduced pressure, the slurry treated with 0.1 N aqueous sodium hydroxide and extracted with ether. The ether extracts were washed with water, dried, and evaporated to give a light brown oil. This oil product was charged on an alumina column. The column was eluted with petroleum ether to give an almost colorless oil. The solvent was removed by vacuum: yield 20.4 g (80%). ^{1}H-NMR (CDCl$_3$): δ 4.56 (d, 2H), 5.27 (dd, 1H), 5.47 (dd, 1H), 6.13 (m, 1H), 6.74 (d, 1H), 7.25–7.43 (m, 4H), 7.71 (t, 1H), 8.23 (t, 1H). ^{13}C-NMR (CDCl$_3$): δ 35.8, 116.9, 117.8, 120.3, 121.2, 125.2, 125.7, 127.5, 128.3, 133.7, 136.0, 149.5.

4.2.2. 1-Phenyl-1,3,5-hexanetrione (PHT) [6]

To a stirred slurry of sodium hydride (5.00 g, 0.208 mol) in 150 ml of 1,2-dimethoxyethane (DME) at reflux, under argon, was added a solution of 2,4-pentanedione (0.0585 mol) in 50 ml of DME, followed, after 1 h, by methylbenzoate (7.30 ml, 0.0587 mol). The reaction mixture was refluxed for 7 h. Most of the solvent was removed under reduced pressure and the pasty residue was cooled to 0°C in an ice-water bath. Diethyl ether (150 ml) was added. After stirring the mixture for a few minutes, 100 ml of cold water was added. Initially, the water was added dropwise until the excess sodium hydride was destroyed. The two layers were separated. The ethereal layer was extracted with two 100-ml portions of cold water and with 100 ml of cold 1% aqueous sodium hydroxide. The extracts combined with the original aqueous layer and then poured onto a mixture of 40–50 ml of 12 N HCl and 200 g of crushed ice. The resulting precipitate was collected on a funnel. The product was recrystallized from 95% ethanol: yield 7.30 g (61.2%); m.p. 97–98°C. ^{1}H-NMR (CDCl$_3$): δ 2.05 (s), 2.07 (s), 2.33 (s), 3.58 (s), 3.99 (s), 5.35 (s), 5.85 (s), 6.26 (s), 7.47 (m), 7.85 (dd). ^{13}C-NMR (CDCl$_3$): δ 22.1, 30.6, 50.1, 55.0, 96.0, 97.3, 99.6, 100.9, 119.4, 126.4, 127.2, 128.6, 128.7, 28.8, 129.2, 130.2, 131.6, 132.8, 133.7, 133.8, 174.0, 178.8, 183.5, 189.4, 194.0.

4.2.3. 1-Phenyl-6,6,6-trifluoro-1,3,5-hexanetrione (PFHT)

The preparation of this yellow compound was accomplished using the procedure for PHT with 1,1,1-trifluoro-2,4-pentanedione and methylbenzoate as starting materials. The final product recrystallized from hot 80% ethanol: yield 48%; m.p. 67–69°C. ^{1}H-NMR (CDCl$_3$): δ 4.10 (s), 6.16 (s), 7.48 (m), 7.86 (dd). ^{13}C-NMR (CDCl$_3$): δ 25.8, 54.2, 66.0, 96.7, 127.0, 128.6, 128.8, 132.2, 134.9, 183.3, 193.7.

4.2.4. 2,4,6-Heptanetrione (HpT) [7]

A mixture of dehydroacetic acid (10.0 g, 0.0595 mol) and 50.0 ml concentrated HCl were boiled until the evolution of carbon dioxide ceased (1 h) and refluxed for an additional 5 h. The solution was then evaporated under reduced pressure, leaving a semisolid mass that was dissolved in 10% sodium hydroxide solution. A solution of barium hydroxide (24 g) in boiling water was added and a yellow precipitate was collected and dissolved at once in an excess of 15% HCl. This acid solution was extracted with diethyl ether. Evaporation of the ether gave an oil, which was distilled to give 2,4,6-heptanetrione: yield 5.05 g (60%); b.p. 105–107°C (30 mmHg); m.p. 45–46°C. ^{1}H-NMR ($CDCl_3$): δ 1.84 (s), 1.94 (s), 2.10 (s), 2.12 (s), 3.28 (s), 3.58 (s), 5.02 (s), 5.45 (s), 5.93 (s). ^{13}C-NMR ($CDCl_3$): δ 19.4, 21.5, 24.3, 30.1, 53.5, 57.4, 98.4, 100.9, 113.3, 165.5, 178.3, 180.0, 186.7, 190.9, 194.0, 202.0. IR (CH_3CN): 2980, 2900, 1705, 1657, 1585, 1230, 1180, 1150, 1138, 1000, 936, 887, and 820 cm^{-1}.

4.2.5. 1-Phenyl-6,6,6-trifluoro-1,3,5-hexanetrione; disodium salt (Na$_2$[PFHT])

A sample of 1-phenyl-6,6,6-trifluoro-1,3,5-hexanetrione (0.570 g, 2.21 mmol) and sodium (0.100 g, 4.35 mmol) were stirred in 25 ml of THF. The reaction was stirred for 48 h at r.t. Hydrogen gas was evolved during the reaction. THF was removed by vacuum and the golden solid was dried: yield 0.642 g (96%); m.p. 235–237°C decomposed. ^{1}H-NMR (DMSO): δ 5.60 (s), 7.28 (br.s), 7.72 (br.s), 7.91 (t). ^{13}C-NMR (DMSO): δ 79.2, 93.5, 126.3, 127.1, 127.4, 128.4, 129.0, 170.3, 179.9, 188.1.

4.3. Catalyst preparation

4.3.1. Tetraacetonitrilepalladium(II) tetrafluoroborate [18]

A sample of Pd sponge (1.00 g, 9.40 mmol) and $NOBF_4$ (2.20 g, 18.8 mmol) were stirred in 50 ml of CH_3CN under argon. NO generated in the course of the reaction was removed periodically. After stirring for 24 h, the mixture was filtered to yield a yellow filtrate. Addition of anhydrous Et_2O produced a yellow solid, which was dried under vacuum: yield 4.00 g (96%). ^{1}H-NMR (CD_3NO_2): δ 2.65 (s). IR (Nujol): 2335 (s), 1100–1000 (vs.br), 760 cm^{-1}.

4.3.2. Diacetonitrile-1-phenyl-1,3,5-hexanetrione-μ-(1R,2R)-(−)-1,2-diaminocyclohexane dipalladium(II) tetrafluoroborate ([Pd$_2$(MeCN)$_2$(PHT)(−)-DACH](BF$_4$)$_2$)

$[Pd(CH_3CN)_4](BF_4)_2$ (0.880 g, 2.00 mmol) and 1-phenyl-1,3,5-hexanetrione (0.204 g, 1.00 mmol) were stirred in 50 ml of CH_3CN in the presence of $(C_2H_5)_3N$. After stirring for 12 h, (1*R*,2*R*)-(−)-1,2-diaminocyclohexane (0.114 g, 1.00 mmol) was added and the mixture stirred for an additional 12 h and filtered. The filtrate was concentrated by vacuum to 10 ml. An orange solid was precipitated by addition of anhydrous Et_2O. The product was washed with anhydrous Et_2O and dried under vacuum: yield 0.560 g (72%). Anal. Calc. for $Pd_2C_{24}H_{33}N_5B_2F_8O_3$: C, 34.90; H, 4.03; N, 8.48. Found: C, 35.30; H, 4.31; N, 8.78%. M.p. 138–140°C decomposed. ^{1}H-NMR (DMSO): δ 1.13 (t), 1.25 (m.br), 1.52 (m), 1.75 (s), 1.95 (m), 2.07 (s), 2.15–2.37 (m), 5.05 (m.br), 5.15 (m.br), 5.42 (m.br), 5.77 (m.br), 6.40 (s), 6.62 (s), 7.52 (m.br), 7.80 (m). ^{13}C-NMR (DMSO): δ 1.14, 18.8, 22.9, 23.4, 32.5, 32.6, 45.7, 46.8, 88.7, 99.2, 118.9, 121.8, 126.9, 128.9, 134.8, 144.6, 165.4, 174.8, 181.3. FTIR (KBr): 3355 (vs), 3260 (s), 3035 (m), 2976 (s), 2335 (vs), 1635 (m), 1605 (s), 1546 (vs), 1519 (s), 1485 (s), 1465 (s), 1450 (s), 1405 (m), 01365 (m), 1100–1000 (vs.br), 765 (vs) cm^{-1}.

4.3.3. Diacetonitrile-2,4,6-heptanetrione-μ-(1R,2R)-(−)-1,2-diaminocyclohexanedipalladium(II) tetrafluoroborate ([Pd$_2$(MeCN)$_2$(HpT)(−)-DACH](BF$_4$)$_2$)

A sample of $[Pd(CH_3CN)_4](BF_4)_2$ (1.00 g, 2.26 mmol) and 2,4,6-heptanetrione (0.160 g, 1.13 mmol) were stirred in 50 ml CH_3CN in the presence of $(C_2H_5)_3N$. After stirring for 12 h, (1*R*,2*R*)-(−)-1,2-diaminocyclohexane (0.120 g, 1.05 mmol) was added. The reaction mixture was stirred for an additional 12 h and filtered. The filtrate was concentrated by vacuum to 10 ml. Addition of anhydrous Et_2O precipitated a yellowish-brown compound, which was washed with anhydrous Et_2O and dried under vacuum: yield 0.540 g (71%); m.p. 150–152°C decomposed. Anal. Calc. for $Pd_2C_{17}H_{28}N_4B_2F_8O_3$: C, 28.25; H, 3.90; N, 7.75. Found: C, 27.27; H, 4.14; N, 8.67%. ^{1}H-NMR (DMSO): δ 1.54 (m.br), 1.75 (s), 1.88–1.95 (m), 2.06 (s), 2.25 (s), 4.67 (t.br), 5.13 (m.br), 5.50 (s.br), 5.60 (s.br), 6.06 (s). ^{13}C-NMR (DMSO): δ 1.2, 18.9, 23.7, 32.5, 45.7, 85.9, 95.6, 119.0, 167.8, 171.2, 183.2. FTIR (KBr): 3320–3270 (vs), 3250 (s), 3005 (w), 2987 (s), 2335 (vs), 1650 (vs), 1590 (s), 1550 (s), 1490–1420 (s.br), 1380 (m), 1200–1000 (vs.br) cm^{-1}.

4.3.4. Diacetonitrile-1-phenyl-6,6,6-trifluoro-1,3,5-hexanetrione-μ-(−)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane-dipalladium(II) tetrafluoroborate ([Pd$_2$(MeCN)$_2$(PFHT)(−)DIOP](BF$_4$)$_2$)

To a stirred solution of $[Pd(CH_3CN)_4](BF_4)_2$ (0.880 g, 2.00 mmol) in 30 ml of dry CH_3CN, was added a solution of 1.00 mmol of 1-phenyl-6,6,6-trifluoro-1,3,5-hexanetrione, disodium salt in 10 ml CH_3CN. The reaction mixture was stirred for 24 h at r.t. Then (−)-DIOP (0.498 g, 1.00 mmol) in 10 ml CH_3CN was added to the reaction mixture. The reaction mixture was stirred for 12 h at r.t. The solvent was removed by a rotary evaporator. The solid was collected, washed with Et_2O dried under vacuum: yield 1.00 g (81.8%). M.p. 119–121°C decomposed. Anal. Calc. for $Pd_2C_{47}H_{45}O_5N_2P_2B_2F_{11}\cdot CH_3CN\cdot 1.5NaBF_4$: C, 41.19;

H, 3.38; N, 2.94; P, 4.34. Found: C, 40.37; H, 3.76; N, 2.91; P, 4.34%. ^{1}H-NMR (DMSO): δ 1.63 (s), 1.75 (s), 2.05 (s), 2.20 (dd), 2.30 (s.br), 4.10 (td.br), 04.37 (td.br), 6.31 (s), 6.57 (s), 6.87 (d), 7.14 (t), 7.37 (m), 7.56 (m), 7.84 (m), 7.95 (d). ^{13}C-NMR (DMSO): δ 1.13, 22.40, 26.45, 29.30, 74.82, 75.94, 97.02, 97.80, 99.00, 108.68, 118.10, 126.29, 127.20, 127.37, 127.50, 127.86, 128.13, 128.59, 128.97, 129.27, 130.76, 131.73, 132.66, 132.89, 133.16, 133.72, 135.85, 136.43, 167.36, 177.74, 188.11. ^{31}P-NMR (DMSO): δ 22.8 and 22.9. FTIR (Nujol): 3030 (w), 02984 (vs), 2932 (vs), 2890 (m), 2365 (m), 2350 (m), 1660 (vs), 1582 (vs), 1482 (vs), 1438 (vs), 1386 (m), 1244 (m), 1160– 998 (vs.br), 881 (s), 818 (m), 746 (s), 693 (vs), 525 (vs) cm^{-1}.

4.3.5. Diacetonitrile-2,4,6-heptanetrione-μ-(−)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane dipalladium(II) tetrafluoroborate ([$Pd_2(MeCN)_2(HpT)$(−)DIOP]$(BF_4)_2$)

The preparation of this yellowish-brown compound was accomplished using the previous procedure with 2,4,6-heptanetrione, [$Pd(CH_3CN)_4$]$(BF_4)_2$, triethylamine and (−)-DIOP as starting materials: yield 71%; m.p. 108–110°C (decomposed). This compound was characterized by ^{1}H-, ^{13}C- and ^{31}P-NMR.

4.3.6. Diacetonitrile-1-phenyl-6,6,6-trifluoro-1,3,5-hexanetrione-μ-(+)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)-butanedipalladium(II)tetrafluoroborate ([$Pd_2(MeCN)_2$(PFHT)(+)DIOP]$(BF_4)_2$)

This yellow compound was prepared using the procedure described above with 1-phenyl-6,6,6-trifluoro-1,3,5-hexanetrione, [$Pd(CH_3CN)_4$]$(BF_4)_2$, triethylamine and (+)-DIOP as starting material: yield 76%; m.p. 87–89°C. This compound was characterized by ^{1}H-, ^{13}C- and ^{31}P-NMR.

4.3.7. Diacetonitrile-1-phenyl-1,3,5-hexanetrione-μ-(S)-(−)-2,2-bis(diphenylphosphino)-1,1-binaphthyl dipalladium(II) tetrafluoroborate ([$Pd_2(MeCN)_2$(PHT)(S)BINAP]$(BF_4)_2$)

To a stirred solution of [$Pd(CH_3CN)_4$]$(BF_4)_2$ (0.238 g, 0.536 mmol) in 15 ml of dry CH_3CN under argon, was added dropwise 1-phenyl-1,3,5-hexanetrione (0.0547 g, 0.268 mmol), followed by 10 drops of $(CH_3)_3N$. The color changed immediately to orange. The reaction mixture was stirred for 30 min at r.t. Then (S)-(−)-BINAP (0.167 g, 0.268 mmol) in 3 ml of C_6H_6 was added to the reaction mixture. The reaction mixture was stirred for an additional 12 h. The solvent was removed by a rotary evaporator to give a pasty red residue. The residue was washed with anhydrous Et_2O (3 × 30 ml). The greenish-yellow solid was dried under vacuum: yield 0.310 g (92.9%). M.p. 135–136°C decomposed. Anal. Calc. for $Pd_2C_{60}H_{48}O_3N_2P_2B_2F_8$: C, 55.72; H, 3.74; N, 2.17; P, 4.79. Found: C, 56.72; H, 3.83; N, 2.16; P, 4.91%. ^{1}H-NMR (DMSO): δ 1.76 (s), 2.06 (s), 6.53 (s), 6.87 (dd), 7.05 (t), 7.20 (t), 7.52 (m), 7.65 (m), 7.74 (br,d), 7.80 (t), 7.91 (m.br). ^{13}C-NMR (DMSO): δ 1.2, 22.5, 91.9, 95.7, 117.9, 118.9, 122.7, 123.6, 123.8, 124.6, 125.3, 125.9, 126.0, 126.1, 126.4, 126.5, 126.7, 127.0, 127.1, 127.2, 127.3, 127.4, 127.6, 127.7, 127.8, 127.8, 128.0, 128.2, 128.3, 128.4, 128.8, 129.0, 129.1, 130.0, 131.6, 132.2, 132.9, 133.8, 134.1, 135.0, 135.1, 139.0, 161.8, 162.5, 171.3, 174.7, 175.4. ^{31}P-NMR (DMSO): δ 34.37 (s). FTIR (Nujol): 3028 (w), 2971 (vs), 2882 (vs), 2842 (vs), 2328 (m), 2293 (m), 1658 (m), 1608 (m), 1584 (m), 1554 (m), 1462 (vs), 1377 (vs), 1311 (m), 1161 (sh), 1130–995 (vs.br), 872 (m), 815 (m), 745 (s), 719 (s), 695 (vs), 522 (vs), 500 (m) cm^{-1}.

4.3.8. Diacetonitrile-2,4,6-heptanetrione-μ-(S)-(−)-2,2-bis(diphenylphosphino)-1,1′-binaphthyl dipalladium(II) tetrafluoroborate ([$Pd_2(MeCN)_2$(HpT)(S)BINAP]$(BF_4)_2$)

This yellow compound was prepared using the procedure described above using 2,4,6-heptanetrione disodium salt, [$Pd(CH_3CN)_4$]$(BF_4)_2$, and (S)-(−)-BINAP as starting materials: yield 87%. This compound was characterized by ^{1}H-, ^{13}C- and ^{31}P-NMR.

4.4. Oxidation reactions

4.4.1. General procedure

The mmoles of reagents and the total amount of gas uptake for each run are given in Table 4. Enantioselectivities were measured using about a 0.3 mol ratio if Eu(hfc)$_3$ to product. The yields of the chlorohydrins for the propene and 1-butene runs were calculated from the areas of the of the GLC peaks using internal standards.

4.4.2. Oxidation of propene

In the aqueous mixed solvent runs (1–3), acetone was isolated as 2,4-dinitrophenylhydrazone derivative and identified by ^{1}H-NMR. The chlorohydrin products were isolated by continuous extraction with Et_2O for 3 days. The ether was dried over anhydrous $MgSO_4$ and then evaporated. Two products with similar retention times were detected by GLC in a 2.8:1.0 ratio. The first product was collected by preparative GLC and identified as 1-chloro-2-propanol. ^{1}H-NMR ($CDCl_3$): δ 1.26 (d, 3H), 2.19 (d.br, OH), 3.43 (dd, 1H), 3.57 (dd, 1H), and 3.99 (m, 1H). ^{13}C-NMR ($CDCl_3$): δ 20.24, 51.61, 67.66. Because of similar retention times preparative GLC gave a 1:1 mixture of 1-chloro-2-propanol and the second product. The second product was identified as 2-chloro-1-propanol. ^{1}H-NMR ($CDCl_3$) for the mixture: δ 1.26 (d, 3H), 1.50 (d, 3H), 2.00 (br, OH), 2.19 (br, OH), 3.43 (dd, 1H), 3.57 (dd, 1H), 3.65 (dd, 1H), 3.74 (dd, 1H), 3.99 (m, 1H), and 4.15 (m, 1H). ^{13}C-NMR ($CDCl_3$) for the mixture: δ 20.24, 20.30, 51.61, 65.75, 66.78, 67.66.

In run 1 a mixture of 1-chloro-2-propanol and 2-chloro-1-propanol was isolated by preparative GLC in a 4.0:1.0 ratio, respectively, and characterized by ^{1}H- and ^{13}C-NMR. The ees of the 1-chloro-2-propanol and 2-chloro-1-propanol were found to be 94 and 68%, respectively. The absolute configuration of 2-chloro-1-propanol was found to be (*R*) by comparison with the ^{1}H-NMR spectrum of an authentic sample of (*S*)-(+)-2-chloro-1-propanol in the presence of $Eu(hfc)_3$. Another sample of the original mixture of the two isomers isolated by preparative GLC was reacted with 4% NaOH solution (5 ml). The mixture was stirred for 10 m at r.t. and extracted with $CDCl_3$. The ^{1}H- and ^{13}C-NMR indicated the formation of propylene oxide. The optical purity of the propylene oxide was found to be 84%. The absolute configuration of the propylene oxide was determined by comparison of its ^{13}C-NMR with that of an authentic sample of (*S*)-propylene oxide, both in the presence of 0.1 molar ratio of $Eu(hfc)_3$. It was found to be (*S*).

In run 4, for which the solvent was methanol, GLC analysis indicated two products were formed. The product that eluted first was present in very low yield (< 5%) and was not isolated. The second peak was isolated by preparative GC and confirmed to be 2-methoxy-1-chloropropane. ^{1}H-NMR ($CDCl_3$): δ 1.24 (d, 3H), 3.38 (s, 3H), 3.50 (dd, 2H), and 3.55 (m, 1H). ^{13}C-NMR ($CDCl_3$): δ 17.42, 47.34, 56.63, 56.75.

4.4.3. Oxidation of 2,3-dihydrofuran

Three products were detected by GLC in relative yields of 5, 15 and 80%, respectively. ^{1}H- and ^{13}C-NMR identified the products 3-oxo-tetrahydrofuran, 2-chloro-3-hydroxytetrahydrofuran and 3-chloro-2-hydroxytetrahydrofuran, respectively. Spectral data of the products were as follows: 3-chloro-2-hydroxy-tetrahydrofuran: ^{1}H-NMR ($CDCl_3$): δ 5.47 (d, $J_{1,2} = 2.96$ Hz, 1H), 4.25 (dt, $J = 2.93, 7.30$ Hz, 1H), 4.19 (m, 2H), 2.78 (bs, 1H, OH), 2.65 (m, 1H), 2.15 (m, 1H); ^{13}C-NMR ($CDCl_3$): δ 103.1, 67.0, 61.1, 32.9. 3-oxo-tetrahydrofuran: ^{1}H-NMR ($CDCl_3$): δ 5.10 (dd, 2H), 3.70 (m, 2H), 2.02 (m, 2H). ^{13}C-NMR ($CDCl_3$): δ 207.2, 103.6, 62.7, 32.5. The ee of 3-chloro-2-hydroxy-tetrahydrofuran was determined to be 72%. ^{1}H-NMR analysis showed that H_1 and H_2 have an *E* conformation ($J_{1,2} = 2.96$ Hz) [14].

4.4.4. Oxidation of 1-pentene

In runs 5 and 6 the 2-pentanone was isolated as 2,4-dinitrophenylhydrazone derivative and identified by ^{1}H-NMR. The chlorohydrin products were isolated by continuous extraction with Et_2O for 3 days. Two products of similar retention times were detected by GLC in about a 3:1 ratio. The first product was collected by preparative GLC and identified as 1-chloro-2-pentanol. ^{1}H-NMR ($CDCl_3$): δ 0.93 (t, 3H), 1.48 (m, 4H), 2.15 (s.br., OH), 3.45 (dd, 1H), 3.60 (dd, 1H), 3.79 (m.br, 1H). ^{13}C-NMR ($CDCl_3$): δ 13.93, 18.76, 36.30, 50.60, 71.18. Because of the similar retention times, collection by preparative GLC gave a 1:1 mixture of 1-chloro-2-pentanol and the second product. The second product was identified as 2-chloro-1-pentanol. ^{1}H-NMR ($CDCl_3$) for the mixture: δ 0.93 (t, 6H), 1.48–1.72 (m, 8H), 2.05 (t.br, OH), 2.14 (d.br, OH), 3.65 (dd, 2H), 3.79 (m.br, 1H), 4.08 (m, 1H). ^{13}C-NMR ($CDCl_3$) for the mixture: δ 13.53, 13.94, 18.76, 19.56, 36.26, 36.31, 50.61, 66.13, 67.06, 71.18.

In runs 7 and 8, GLC analysis of the ether extract indicated five products were formed. These products were collected by preparative GLC and identified as 2-pentanone, 3-hydroxy-2-pentanone, 1-chloro-2-pentanol, 2-chloro-1-pentanol and 1-hydroxy-2-pentanone, respectively.

The first product was 2-pentanone. ^{1}H-NMR($CDCl_3$): δ 0.90 (t, 3H), 1.56 (m, 2H), 2.11 (s, 2H), 2.38 (t, 2H). ^{13}C-NMR($CDCl_3$): δ 13.77, 17.38, 29.92, 45.73, 209.00. The second product was 3-hydroxy-2-pentanone. ^{1}H-NMR($CDCl_3$): δ 1.02 (t, 3H), 1.81–2.03 (m, 2H), 2.29 (br, OH), 2.30 (s, 3H), 4.11 (dd, 1H) ^{13}C-NMR($CDCl_3$): δ 10.69, 26.10, 27.33, 66.79, 183.18. The third and fourth peaks were 1-chloro-2-pentanol and 2-chloro-1-pentanol, respectively. The fifth product was 1-hydroxy-2-pentanone. ^{1}H-NMR($CDCl_3$): δ 0.93 (t, 3H), 1.63 (m, 2H), 2.56 (t, 2H), 4.06 (s, 2H). ^{13}C-NMR($CDCl_3$): δ 13.69, 17.19, 41.62, 67.07, 202.45.

4.4.5. Oxidation of methyl vinyl ketone

The products were isolated by continuous extraction with ether for 3 days. Et_2O was distilled off and the solution concentrated to 2–3 ml. The solution was charged on a silica gel chromatography column. The column was eluted first with petroleum ether–Et_2O (90% petroleum ether) to afford a yellow product, the ^{1}H-NMR of which indicated it was a mixture of starting material and a new product in low yield. The column was next eluted with 45% Et_2O–petroleum ether. A wide yellowish-red band was collected under nitrogen. The product was identified as 1-chloro-2-hydroxy-3-butanone. FTIR (neat): 3625–3401 (vs.br), 2934 (vs), 2874 (s), 1730 (vs), 1360 (vs), 1249 (vs), 1094 (s), and 1060 (m) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.36 (s, 3H), 2.52(s.br, OH), 3.94 (dd, 2H), 4.30 (t, 1H). ^{13}C-NMR ($CDCl_3$): δ 25.59, 63.61, 69.05, 197.00.

4.4.6. Oxidation of 2-propen-1-ol

After continuous extraction with Et_2O for 7 days, the ether layer was dried over anhydrous $MgSO_4$ and evaporated. GC analysis indicated that four products were formed in a 1.1:1.0:6.7:1.5 ratio. The first two products were identified as 1-hydroxy acetone and 3-hydroxy propanal. ^{1}H-NMR ($CDCl_3$) for 1-hydroxy acetone: $\delta = 2.35$ (s, 3H), and 4.07 (s, 2H) ppm. ^{1}H-NMR ($CDCl_3$) for the 2,4-dinitrophenylhydazone derivative of 3-hydroxy-propanal: δ 2.71 (td, 2H), 3.98 (t, 2H), 7.63 (t, 1H), 7.96 (d, 1H), 8.30 (dd, 1H), 9.11 (d, 1H), 11.06 (s.br, 1H).

The third product was collected by preparative GC and characterized as 3-chloro-1,2-propanediol. ^{1}H-NMR ($CDCl_3$): δ 2.35 (s.br, 2OH), 3.62 (dd, 2H), 3.71 (dd, 2H), and 3.93 (m, 1H) ppm. ^{13}C-NMR ($CDCl_3$): δ 46.2, 63.6, 71.6. Using a 0.3 molar ratio Eu(hfc)$_3$, the ee of 3-chloro-1,2-propanediol was found to be 50%.

The fourth fraction was collected by preparative GC and found to be a mixture of 3-chloro-1,2-propanediol and a second product. ^{1}H-NMR ($CDCl_3$) for the mixture: δ 2.35 (s.br) 3.62 (dd), 3.68 (d), 3.74 (d), 3.92 (m), and 5.16 (m) ppm. ^{13}C-NMR ($CDCl_3$) for the mixture: δ 42.4, 46.2, 63.7, 71.6, 71.7. The second product was identified as 2-chloro-1,3-propanediol.

4.4.7. Oxidation of allylphenyl ether

The products were extracted with CH_2Cl_2 (3×50 ml). GLC analysis indicated two products were formed, which were collected by preparative GLC. ^{1}H-NMR indicated the first product was 1-phenoxy acetone. The second product was 1-phenoxy-3-chloro-2-propanol. ^{1}H-NMR ($CDCl_3$): δ 2.54 (d, OH), 3.72–3.76 (dd, 1H), 3.77–3.82 (dd, 1H), 4.07–4.10 (dd, 2H), 4.23 (m, 1H), 6.91 (d, 2H), 7.00 (t, 1H), 7.30 (m, 2H). ^{13}C-NMR ($CDCl_3$): δ 46.03, 68.55, 69.96, 114.58, 121.42, 129.51, 158.12.

In run 12 the chlorohydrin product was determined to have an (*R*) configuration by analysis of its MTPA ester, while in run 13 it had an (*S*) configuration.

4.4.8. Oxidation of allyl-α-naphthyl ether

The work-up was identical to that used in the previous reaction. A 0.20 g sample of the crude product was charged on a silica gel column. The column was eluted first with 20% CH_2Cl_2–petroleum ether to afford a yellowish-brown product, which was identified as 1-naphthoxy acetone. ^{1}H-NMR ($CDCl_3$): δ 2.29 (s, 3H), 4.65 (s, 2H), 6.75 (d, 1H), 7.25–7.43 (m, 4H), 7.73 (t, 1H), 8.25 (t, 1H). ^{13}C-NMR ($CDCl_3$): δ 26.8, 73.1, 120.5, 121.7, 125.5, 126.6, 127.6, 128.5, 133.8, 137.0, 149.6, 205.7. Next the column was eluted with CH_2Cl_2 to give a light-yellow product which was identified as 1-naphthoxy-3-chloro-2-propanol. ^{1}H-NMR ($CDCl_3$): δ 2.08 (d, OH), 2.87 (dd, 1H), 3.24 (dd, 1H), 4.26 (d, 2H), 4.35 (m, 1H), 7.13 (d, 1H), 7.39 (d, 1H), 7.44 (m, 3H), 7.74 (dd, 1H), 8.18 (dd, 1H). ^{13}C-NMR ($CDCl_3$): δ 33.90, 63.44, 70.02, 112.89, 120.58, 121.43, 125.38, 125.85, 127.34, 127.93, 133.27, 148.67.

4.4.9. Recovery of bimetallic catalyst from reaction mixtures

The bimetallic catalyst could be readily recovered from final reaction mixtures by adding LiBr and working the reaction mixture up as usual. After the organic products have been eluted from the chromatographic column, the bimetallic catalyst was recovered using 10% ethyl acetate in CH_2Cl_2. The ^{1}H- and ^{13}C-NMRs were identical to an authentic sample.

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