STEREOSPECIFIC DEOXYGENATION OF EPOXIDES TO OLEFINS

Henry N.C.Wong*, Charles C.M.Fok, and Timothy Wong

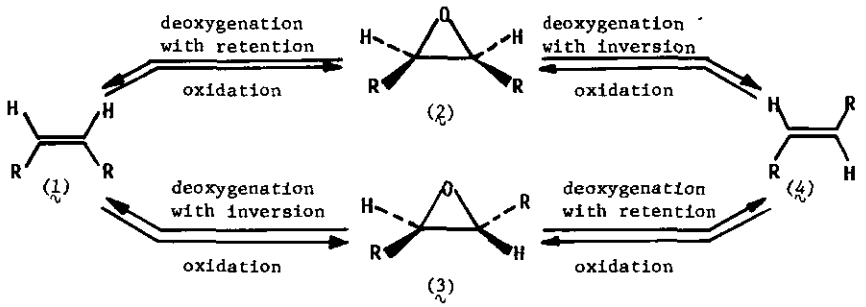
Department of Chemistry, The Chinese University of Hong Kong,
Shatin, New Territories, Hong Kong

Abstract - Various methods for stereospecific deoxygenation of epoxides to olefins are presented. The mechanisms involved in these transformations will also be discussed.

Introduction

Deoxygenation of epoxides to olefins has aroused great interest. In the past three decades, chemists have shown great enthusiasm to methods which are able to increase the yields as well as to control the stereochemistry of these reactions, so that they may become more feasible. Subsequently, a great many improvements in the stereospecificity of these reactions have been recorded.

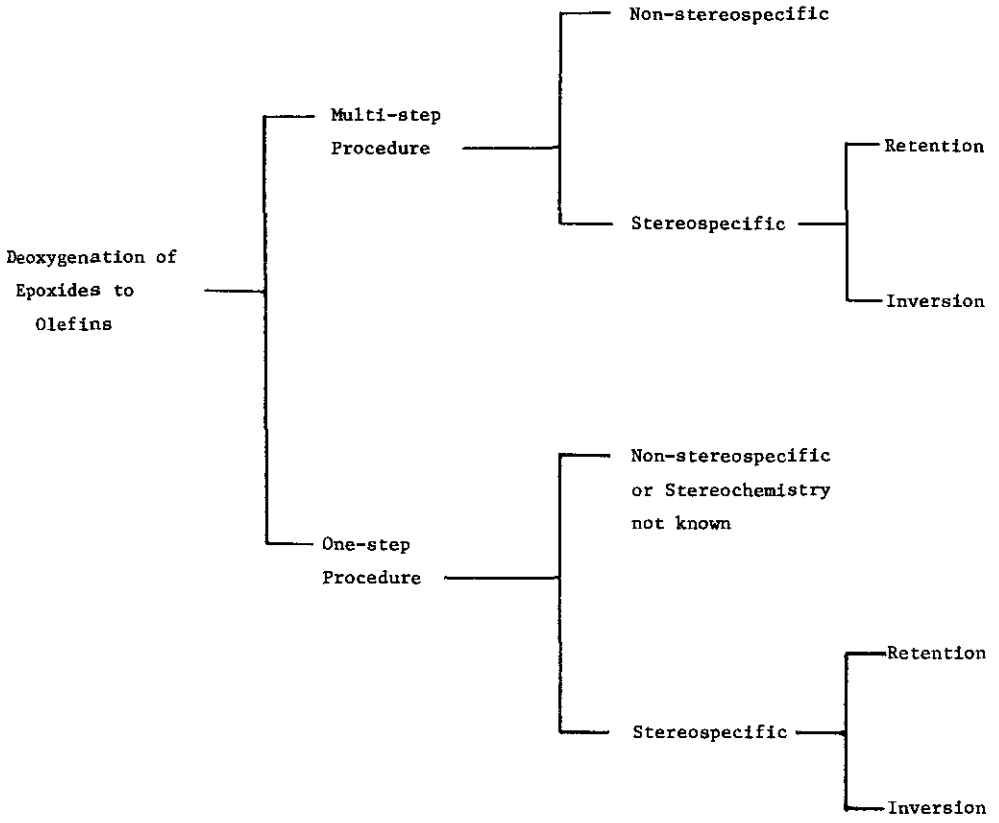
Deoxygenation of epoxides to olefins remains as one of the most important transformations in organic synthesis, because structure elucidation of complex organic molecules, as well as inversion of the geometry of carbon-carbon double bonds can be accomplished.[1] To this connection, cis-olefin (1) and trans-olefin (4) can undergo epoxidation to cis-epoxide (2) and trans-epoxide (3) respectively. When appropiate deoxygenation reagent is employed, cis-epoxide (2) and trans-epoxide (3) can be converted to the corresponding trans-olefin (4) and cis-olefin (1) respectively.[1]



Furthermore, a number of reagents have been found to possess ability of deoxygenation cis-epoxide (2) and trans-epoxide (3) to accordingly cis-olefin (1) and trans-olefin (4). The term "retention" is used to describe the geometry of this conversion, which is extremely useful in the structure elucidation of complex natural products containing epoxide linkage.

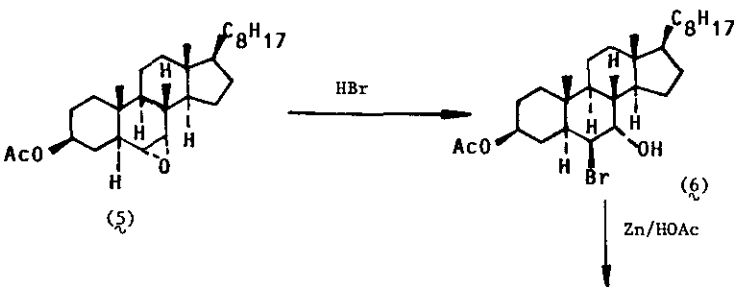
In the following text, we would briefly review some of the multi-step procedures which can produce olefins from epoxides stereospecifically or non-stereospecifically. Then some reagents which are capable of deoxygenating epoxides to olefins non-stereospecifically will be given in Table 4. Finally, the reagents and their mechanisms for the one-step epoxide stereospecific deoxygenation to olefin will be discussed in details. Table 1 shows the brief layout of this review.

Table 1

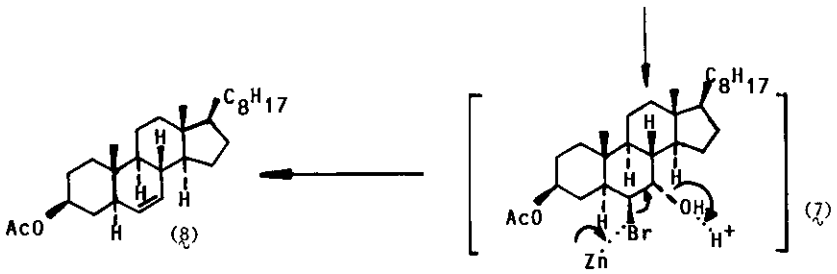


Multi-step Deoxygenation

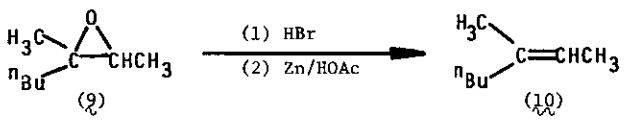
Classically, deoxygenation of epoxides to olefins can be realized by multi-step procedures. All the conversions discussed here involve opening of the epoxides as the initial step. For example, the steroidal epoxide (5) can be cleaved by treatment with HBr. The resulting bromohydrin (6) is converted to the olefin (8), presumably via the intermediate (7).[2] However, the non-stereospecific manner of zinc reduction has been established by the conversion of 2,3-epoxy-3-methylheptane (9)



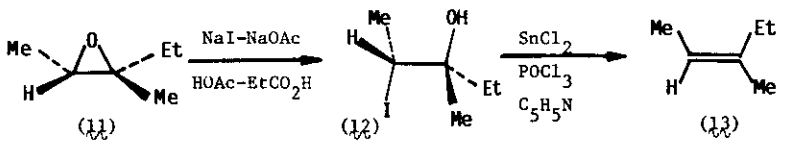
(5) (6)



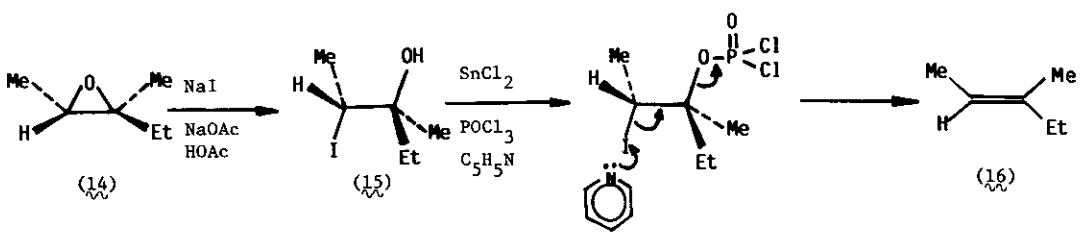
to 3-methylhept-2-ene (10).[3]



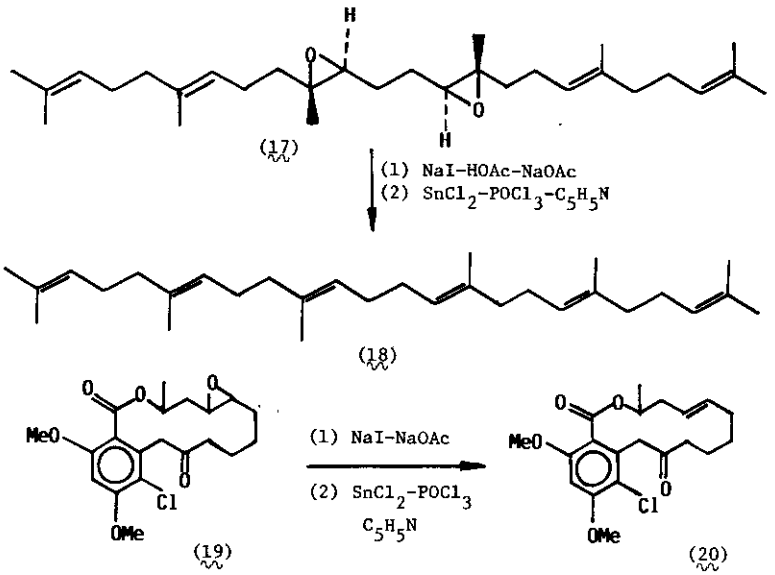
On the other hand, when epoxide (11) is treated with sodium iodide, iodohydrin (12) is furnished stereospecifically in 97% yield.[3] Deoxygenation of (12) to (13) can be accomplished in 83% yield by $SnCl_2$-$POCl_3$-C_5H_5N.[3]



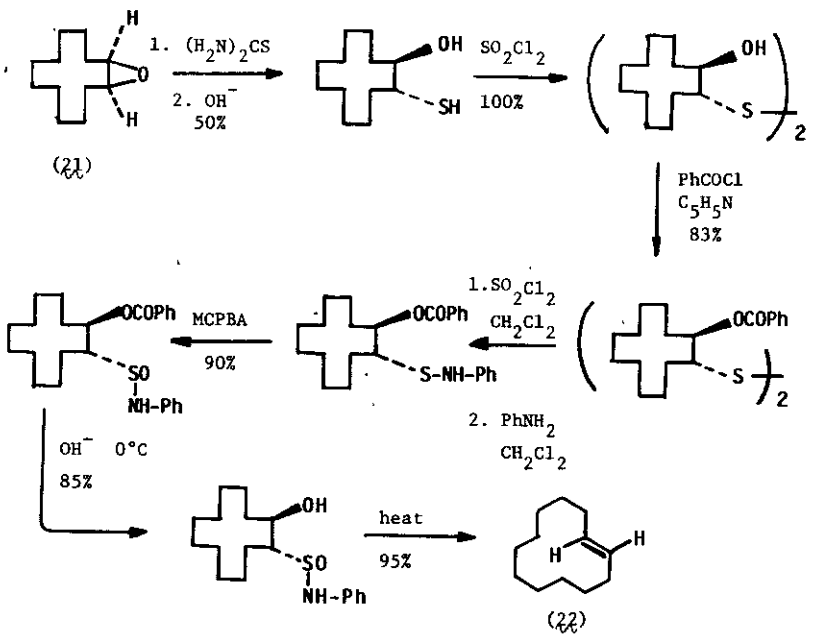
Moreover, (13) is produced stereospecifically with retention of configuration.[3] Likewise, (14) is converted to (16) via (15).[3]



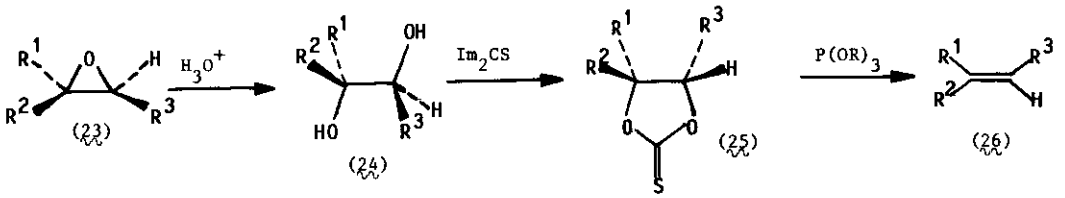
Application of this procedure to more complex molecules has been successful. Thus, the diepoxide (17) can be converted to squalene (18).[4] Likewise, epoxide (19) is converted to (20) with retention of configuration.[5]



Stereospecific transformation of cis-epoxide to a trans-olefin was reported by Corey and Durst.[6] Thus, cis-epoxide (21) can be converted to trans-olefin (22) via many steps.

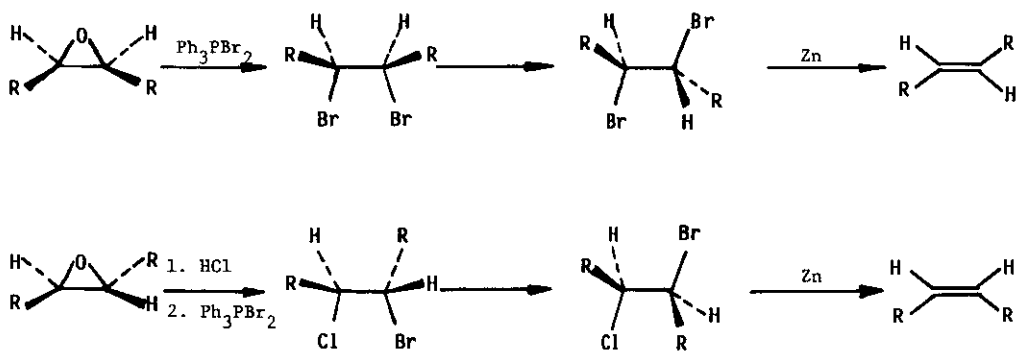


Inversion of configuration has also been observed when epoxide (23) is hydrolyzed stereospecifically to the diol (24) which is then treated with thionocarbonyldiimidazole (Im_2CS) to give the thionocarbonate (25). Trialkyl phosphite has been found to be effective in converting (25) to the olefin (26).[7]



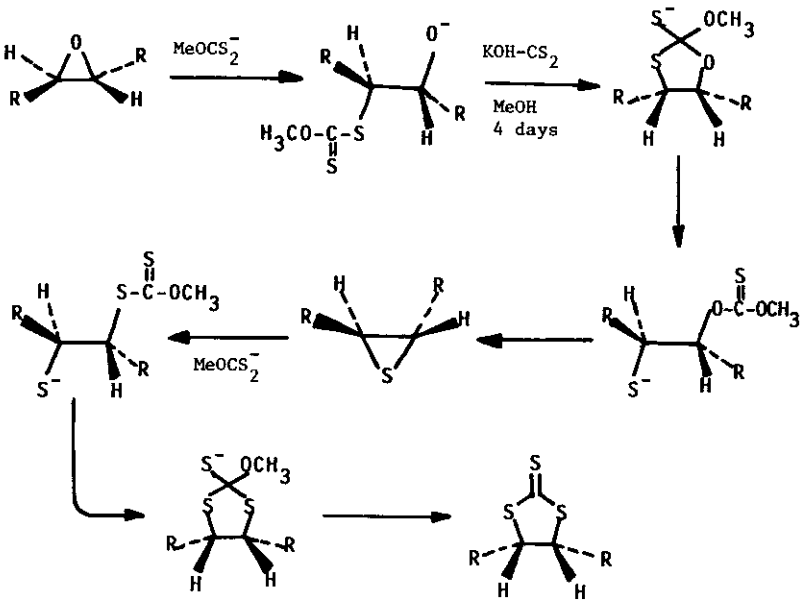
Isaacs and Kirkpatrick found out that treatment of epoxides with triphenylphosphine in carbon tetrachloride gave cis-1,2-dichloroalkane.[8] Therefore, cis-epoxide gives erythro dibromide with triphenylphosphine dibromide in benzene. On the other hand, trans-epoxides can be treated with hydrochloric acid to give chlorohydrin, which is further converted into threo-bromochloride by adding triphenylphosphine dibromide to replace the hydroxyl group. Zinc reduction can be performed in resulting anti-elimination at 0-5°C in DMF.[8] The overall result of this deoxygenation gives inverted olefin.(Scheme 1)

Scheme 1



Treatment of epoxides with potassium methyl xanthate affords trithiocarbonate with inverted configuration. The possible mechanism involves a trans opening of the epoxide ring and a trans closing of the episulfide ring. The intermediate episulfide is then attacked by a second molecule of xanthate with inversion. Since the closing of the trithiocarbonate ring does not involve the breaking of bonds at the asymmetric centers, the trithiocarbonate of inverted configuration should be obtained.[9] (Scheme 2)

Scheme 2

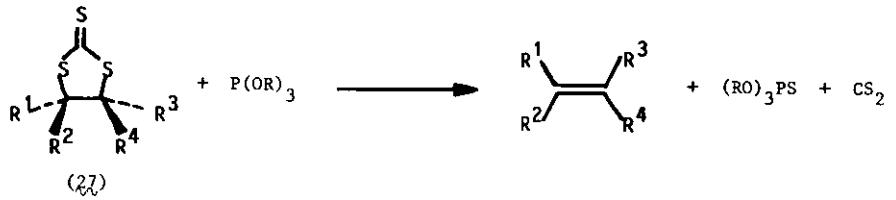


The final product, trithiocarbonate, can simultaneously precipitate in methanol solution.(Table 2)

Table 2

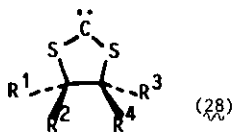
Epoxide	Stereochemistry	Yield (%)
R = Me	trans	53
R = Me	cis	72
R = Ph	trans	18
R = Ph	cis	67

Corey and co-workers reported that treatment of the trithiocarbonate (27) with an effective sulfur-removing reagent e.g. triisooctylphosphite would furnish olefin. Moreover, specific cis-elimination is observed.[10]



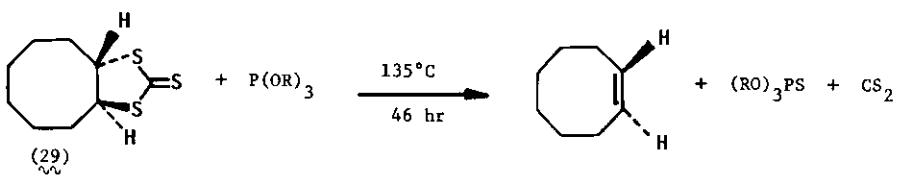
(27)

The reaction might undergo through formation of a carbene (28) which is unstable relative to olefin and carbon disulfide.



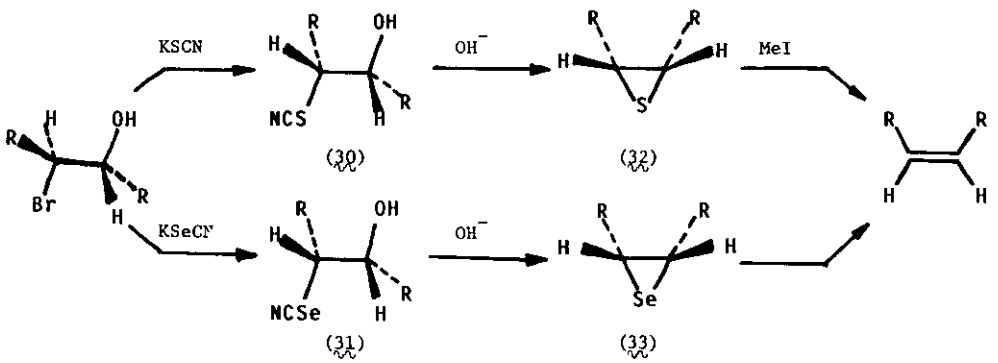
(28)

The trans-thiocarbonate (29) is converted to trans-cyclooctene with 99% stereospecificity in 99% yield by heating with triisooctyl phosphite at 135°C for 46 h.



(29)

Van Ende and Krief[11] discovered that treatment of bromohydrin with fourfold excess of potassium sulfocyanate or potassium selenocyanate in DMF at 60°C for 2 days produced the β-hydroxysulfocyanate (30) or the β-hydroxyselenocyanate (31) in high yields. When β-hydroxysulfocyanate (30) was further treated with potassium carbonate, a thiirane (32) was yielded in 70%. Compound (32) is then transformed to olefin with inverted configuration in 70% yield.[11]

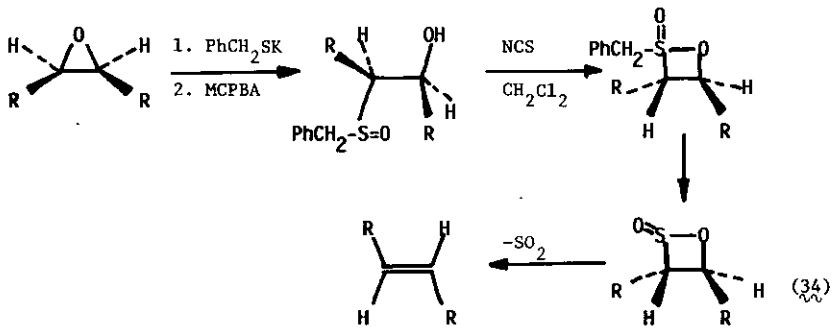


(30) (31) (32) (33)

When β-hydroxyselenocyanate (31) is subjected to similar treatment with base, an olefin would form directly in 40-58% yield. This phenomenon can be explained by analogy with sulfur via the formation of a selenirane (33) which is not stable and would expel smoothly the selenium atom leading to an olefin.

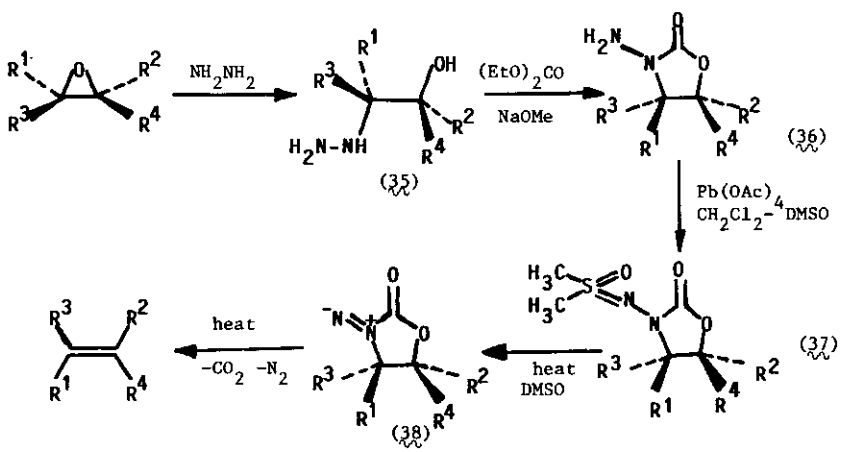
Hence epoxide can be converted into bromohydrin easily, which subsequently can be further eliminated to olefin with inversion of configuration. The stereospecificity is higher than 80%.[11]

Reduction of epoxides can be effected by reaction with potassium benzyl sulfide and oxidation of the product β-hydroxysulfinyl derivatives. β-Hydroxysulfinyls apparently do not eliminate directly, but further oxidation of which with NBS, NCS or SO_2Cl_2 in CH_2Cl_2 would produce olefins with inverted configuration.[12] The reaction, which has been depicted as proceeding through β-sulfines (34), succeeds best with highly-substituted epoxides. The yields of these reactions are fair (~45%) but the stereospecificity is good (>99%).



(34)

Kim and White[13] reported that when epoxide reacts with hydrazine, the resulting β-hydroxyalkylhydrazine (35) is able to cyclize to 3-amino-2-oxazolidone (36) with diethyl carbonate. Oxidation of (36) to sulfoximine (37) is accomplished with lead tetraacetate in CH_2Cl_2 and DMSO. The crystalline sulfoximine decomposes smoothly at 110-130°C in DMSO via diazene (38), producing olefin with inverted stereochemistry (Table 3).[13]



(35) (36) (37) (38)

Table 3 Conversion of epoxides to 3-amino-2-oxazolidones (36), sulfoximine (37) and olefins

R^1	R^2	R^3	R^4	Yield of (36)	Yield of (37)	Yield of olefin	Total yield
H	H	H	H	60%	68%	92%	38%
Me	H	H	H	63%	58%	91%	33%
Ph	H	H	H	16%	78%	94%	12%
Ph	H	H	Ph	31%	79%	97%	24%
$-(CH_2)_6-$		H	H	21%	68%	61%	9%
Me	Et	H	H	46%	67%	81%	25%
Et	Me	H	H	46%	67%	81%	25%
Ph	Ph	H	H	28%	-	91%	25%

As illustrated by the aforementioned examples, it appears that although some of the multi-step procedures are highly efficient and stereospecific, too many transformations would by all means decrease the total yield of an overall conversion. In order to realize the one-step stereospecific deoxygenation of epoxide to olefin, chemists have developed quite a number of reagents which can give either non-stereospecific or stereospecific results.

Non-stereospecific One-step Deoxygenation

Huge number of reagents are known to effect one-step deoxygenation of epoxides to olefins. Those reagents which lack stereocontrol or whose stereochemical nature has not been investigated are tabulated in Table 4.

Table 4 One step non-stereospecific deoxygenation of epoxides to olefins

Reagents	Solvents	References
$CrCl_2$	HOAc-HCl	14
$Cr(OAc)_2$	CH_3COCH_3-H_2O	14,15
$Cr(ClO_4)_2$-$H_2NCH_2CH_2NH_2$	DMF	16,17
Zn-NaI-NaOAc	HOAc	9
$(EtO)_3P$, 150-174°C, pressure	-	18
Ph_3P or $^nBu_3P$, m-ClC_6H_4CHO	-	19
Zn	HOAc	20
Zn-Cu	EtOH	17
Mg(Hg)-$MgBr_2$	THF	21
Li	THF	22
Ti, V, Cr, Co, Ni	-	23
$(\eta$-$C_6H_6)_2Ti$	THF	24
$Fe(CO)_5$	$Me_2NCONMe_2$ or Me_2NCOCH_3	25
Ph_3P-I_2	CH_2Cl_2	26
P_2I_4	C_5H_5N-Et_2O or CH_2Cl_2	27
SmI_2 or YbI_2	^tBuOH-THF	28
$FeCl_3$-^nBuLi	THF	29
$TiCl_3$-$LiAlH_4$	THF	30

Table 4 cont.

Reagents	Solvents	References
$NbCl_5$-$NaAlH_4$	THF-C_6H_6	31
$(\eta\text{-}C_5H_5)_2MoCl_2$-Na(Hg)	C_6H_6 or Et_2O or THF	32
$(\eta\text{-}C_5H_5)_2WCl_2$-Na(Hg)	C_6H_6 or Et_2O or THF	32
$(\eta\text{-}C_5H_5)_2TiCl_2$-Na(Hg)	C_6H_6 or Et_2O or THF	32
$(\eta\text{-}C_5H_5)_2ZrCl_2$-Na(Hg)	C_6H_6 or Et_2O or THF	32
$(\eta\text{-}C_5H_5)_2MoO$-Na(Hg)	C_6H_6 or Et_2O or THF	32
$(\eta\text{-}C_5H_5)_2WO$-Na(hg)	C_6H_6 or Et_2O or THF	32

One-step Stereospecific Deoxygenation with Retention of Configuration

In the last decades, organic chemists devoted great efforts to discover new methods and reagents for deoxygenation of epoxides to olefins. A lot of reagents have been reported for this interesting reaction in order to control the stereochemistry of olefinic products and to increase yield as well as to shorten the reaction time.[1] We will discuss in details those reagents which are able to deoxygenate epoxides to alkenes stereospecifically or with high stereoselectivity. In this section, we will concentrate on those reagents which are capable of preserving the configuration of the epoxides.

1. Low-valent Tungsten[33]

Sharpless prepared several tungsten reagents which were used to convert epoxides to olefins. Some of the tungsten reagents [(39),(40) and (41)] are prepared by *in situ* reduction of WCl_6 with alkyllithium in THF for small and medium scale deoxygenation. The other solid tungsten reagents [(43) and (44)] are easily prepared by reduction. Thus, the stoichiometric use of this reagent has been established.(Scheme 3)

Scheme 3

$$WCl_6 + 2RLi \xrightarrow{THF} (39)$$

$$WCl_6 + 3RLi \xrightarrow{THF} (40)$$

$$WCl_6 + 4RLi \xrightarrow{THF} (41)$$

$$WCl_6 + 2Li \text{ dispersion} \xrightarrow{THF} (42)$$

$$WCl_6 + 3LiI \xrightarrow[\text{in vacuo, no solvent}]{130^\circ} (43)$$

$$WCl_6 + 2LiI \xrightarrow[\text{in vacuo, no solvent}]{130^\circ} (44)$$

$$WCl_6 + 2KI \xrightarrow[\text{in vacuo, no solvent}]{130^\circ} (45)$$

$$(45) + 2LiCl \xrightarrow{THF} (46)$$

In using the reagent (39) to deoxygenate mono- and disubstituted epoxides in smaller rings, chlorohydrins are formed as by-products. The production of by-products can be suppressed by using the less acidic reagents (40), (41) or (43).

Sharpless and his co-workers used experimental evidence to show that chlorohydrins could not be the intermediate in such reaction. The explanation is that under the usual reaction conditions chlorohydrins are reduced much more slowly (and with complete loss of stereochemistry) than the corresponding epoxides. The controls are set up by adding excess diisopropylethylamine to take up the HCl presumed to be formed upon alcoholysis of the tungsten reagent by the chlorohydrin. Under mild conditions, iodohydrins are rapidly and stereospecifically reduced, suggesting that the sluggishness of the reduction of chlorohydrins cannot be attributed to rate-determining formation of the reduction of the alkoxytungsten intermediate.

However, the obtained chlorohydrin due to the use of reagent (39) can be converted to olefin by refluxing the reaction mixture.

Tungsten reagents show high stereospecificity in deoxygenating the isomeric cyclodecene oxides, but only limited stereospecificity is observed for reduction of acyclic di- and tri-substituted epoxides.

Reagent (43) shows high stereospecificity even with acyclic epoxides. This is suggested to be due to the presence of unreacted lithium iodide used in the preparation of reagent (43). Stereospecific reductions are also obtained by adding lithium iodide to reagent (40). Iodohydrin has been detected in the reaction. Thus, with the added iodide, the reaction does not require separation of iodohydrins but gives olefins *in situ*. The experimental results are tabulated in Table 5.

Table 5

Epoxides of	Yield of olefins (%)	% Retention	Tungsten Reagent	Reaction time/h	Reaction temp./°C
1-dodecene	80	-	(39)	42	reflux
1-dodecene	55	-	(40)	3	r.t.
cis-4-octene	86	66	(40)	2	r.t.
cis-4-octene	61	80	(40)	1	-10
cis-4-octene	61	93	(43)	2	r.t.
trans-4-octene	93	70	(40)	2	r.t.
trans-4-octene	84	>98	(43)	2	r.t.
trans-4-octene	97	>98	(40) + 2LiI	0.3	r.t.
4-ethylcyclohexene	75	-	(39)	3	reflux
4-ethylcyclohexene	65	-	(40)	3	r.t.
4-ethylcyclohexene	47	-	(41)	3	r.t.
cis-cyclododecene	89	94	(39)	2	0
cis-cyclododecene	88	96	(39)	2.5	-10
cis-cyclododecene	70	98	(39)	2	-22
trans-cyclododecene	98	95	(39)	2	r.t.
trans-cyclododecene	97	95	(44)	2.7	r.t.
trans-cyclododecene	98	95	(42)	2	r.t.
trans-cyclododecene	98	95	(44)	2	r.t.
cyclooctene	89	-	(39)	3	-5
cis-stilbene	80	-	(39)	<0.3	0
trans-stilbene	86	-	(39)	<0.3	r.t.
2,6-dimethyl-8-methoxy-1-octene	83	-	(39)	0.3	r.t.
gernaniol methyl ether	37	72	(39)	1	0
stigmasterol acetate	83	-	(40)	0.1	r.t.

2. Triphenylphosphine selenide[34]

Clive and Denyer reported that triphenylphosphine selenide and trifluoroacetic acid constituted an effective mild reagent for the deoxygenation of epoxides. The reaction proceeds rapidly at room temperature to give olefins with retention of configuration. The experimental procedure involves the addition of one equivalent of trifluoroacetic acid in CH_2Cl_2 to a solution of epoxide and an excess amount (2-3 equiv.) of triphenylphosphine selenide in the same solvent. The reaction route is expected to go through episelenide (47) which decomposes to give alkene. The mechanism is shown in Scheme 4. The experimental results are summarized in Table 6.[34]

Scheme 4

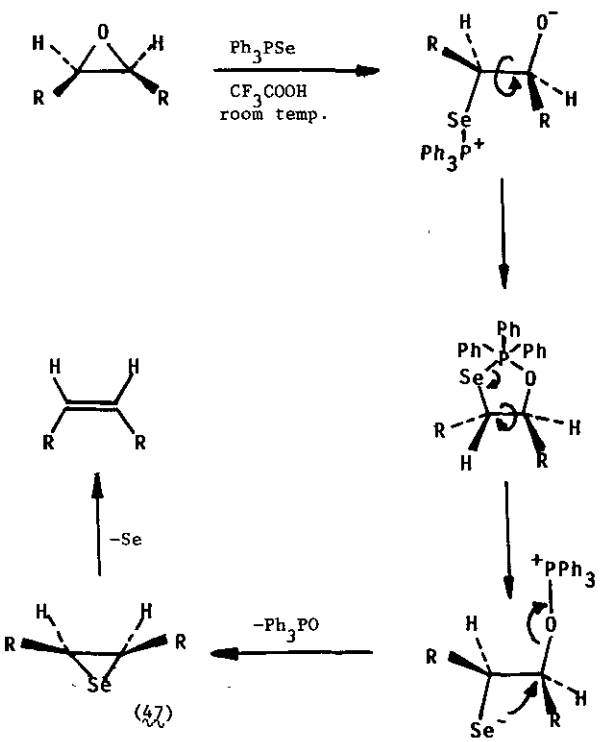


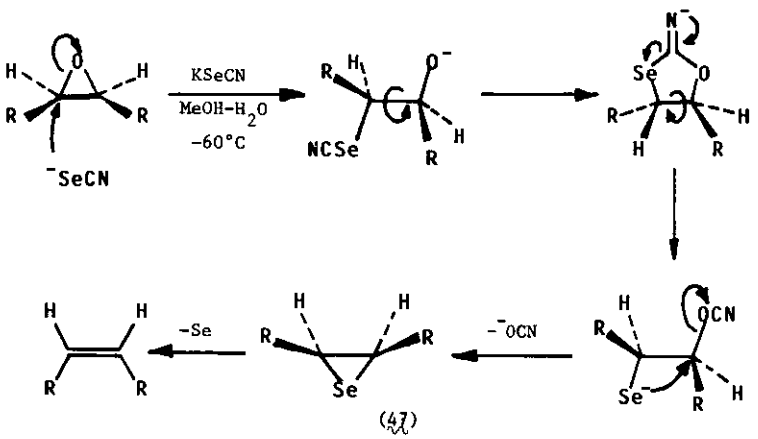
Table 6

Epoxides of	Yield of olefins (%)
1-octene	71
cis-2-octene	73
trans-2-octene	68
cis-stilbene	71
cyclohexene	53

3. Potassium selenocyanate[35]

In neutral or slightly alkaline solution,epoxides can be deoxygenated to olefins with methanolic solution of potassium selenocyanate. The reaction undergoes a minimum of two half-rotations about the carbon-carbon bond which is originally present in the epoxide system as in Scheme 5.

Scheme 5



(47)

This reaction proceeds faster at higher temperatures. But it fails in the aprotic solvents, such as DMSO and DMF even at high temperatures. The reaction rate is second-order in epoxide and selenocyanate. Experimentally, the reaction time and temperature are typically 18 hr and 65°C, respectively. The solvent used can be methanol-water (v/v 10:1). The results are shown in Table 7.[35]

Table 7

Epoxides of	Yield of olefins (%)	Reaction temp/°C	Reaction time/h
methyl cis-9-octadecenoate	100	58	18
methyl trans-9-octadecenoate	98	65	18
trans-stilbene	100	65	2.5
cyclohexene	100	25	72
1-methylcyclohexene	62	25	72
cycloheptene	34	58	72

4. 3-Methyl-2-selenoxobenzothiazole[36]

It was reported that even at low temperature (-15°C), epoxides reacted with 3-methyl-2-selenoxobenzothiazole (48) in CH_2Cl_2 to give olefins with retention of configuration. The reaction might proceed through two Walden inversions in order to maintain same configuration as the starting epoxide. The recovered selenium can be reused. The reaction scheme and experimental results are shown in Scheme 6 and Table 8 respectively.[36]

Scheme 6

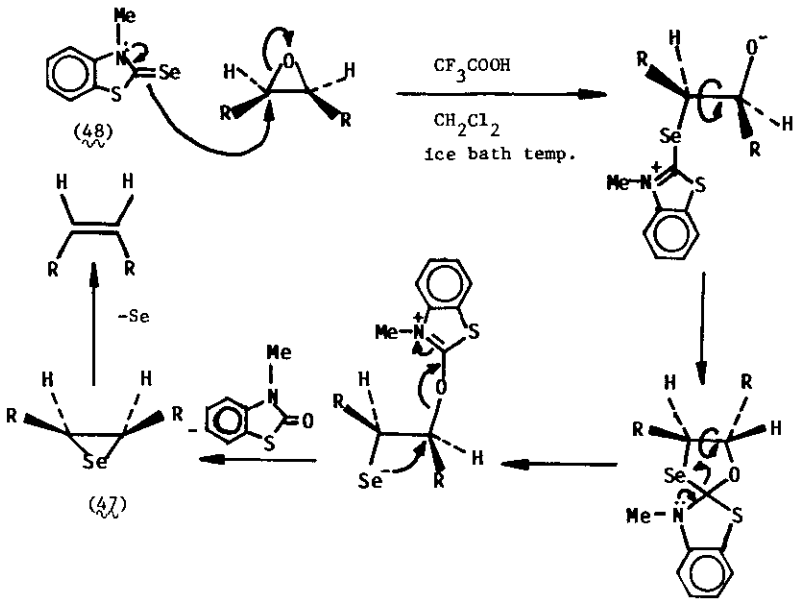


Table 8

Epoxides of	Yield of olefins (%)
cyclohexene	100
styrene	90
vinyl chloride	100
cis-stilbene	97
trans-stilbene	95

5. Alkali metal O,O-diethylphosphorotelluroates[37]

Clive and Menchen discovered that alkali metal O,O-diethylphosphorotelluroates (49) are highly effective reagent for the stereospecific deoxygenation of epoxides. These reagents can by made by stirring elemental tellurium with one equivalent of dimethyl phosphite salt $(EtO)_2PO_2^- M^+$ in anhydrous ethanol (or THF). After evaporation, a white crystalline solid is left and can be readily destroyed in atmosphere. Thus, the tellurium salt (49) should be prepared and used under nitrogen. Although these reagents can be prepared in THF, they fail to deoxygenate epoxides in the same solvent. Instead, ethanol is used for this propose. These reagents possess the property to react with methyl iodide to give ester (50).

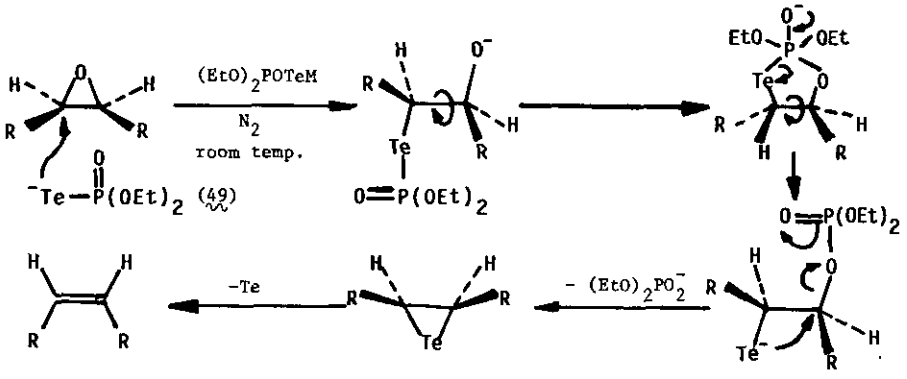
$$(EtO)_2PO\text{-}Te^- M^+ \quad (49) \quad + \quad CH_3I \longrightarrow (EtO)_2PO\text{-}TeCH_3 \quad (50) \quad (M = Li,Na,K)$$

Early work on these reagents showed that elemental tellurium powder dissolved quickly in sodium diethylphosphite-ethanol solution. Deoxygenation of terminal epoxides proceeded rapidly, but sodium diethylphosphite did not react with epoxides at a comparable rate.

Thus, the experimental procedures have been modified to the level of a catalytic process. Small amount of tellurium and terminal epoxide are stirred in ethanol under nitrogen. To this mixture, an ethanolic solution of sodium diethylphosphite is added slowly. The tellurium is dissolved to liberate the active species, salt (49) which deoxygenates the epoxide to olefin. During the reaction, tellurium is liberated and is able to combine with the sodium diethylphosphite to regenerate salt (49) for further reaction with epoxide.

The sodium diethylphosphite tellurium should be added in small amount everytime, the tellurium alternatively dissolves and precipitates. But, when the phosphite solution is injected more rapidly, the reaction mixture stays clear until all epoxide has been deoxygenated and at about that stage the metal deposits. This is used to indicate the rough end-point of the reaction. The reaction scheme is shown in Scheme 7.

Scheme 7



The tellurium salt (49) can discriminate between different kinds of epoxide and the reactivity of these salts depends on the counter cations of the salts. Amongst the three alkali tellurium salts, the lithium dimethyl phosphite is the most reactive reagent. The following observations have been obtained from experimental results.

(i) Terminal epoxides are deoxygenately more rapidly than the other substituted epoxides

(ii) Z-Geometrical isomer is more reactive than the E-geometrical isomer

(iii) The deoxygenation reaction is stereospecific and the stereochemistry of the epoxide is retented. This means that a Z-epoxide would produce a Z-olefin.

(iv) Cyclohexene oxide is deoxygenated more easily than cyclopentene oxide.

Formation of a cyclic intermediate (51) accounts for the slowness of reaction involving cyclopentene oxide because the intermediate of such compound is suspected to be geometrically unfavorable. This means that the intermolecular transfer of phosphorus from tellurium to oxygen is unfavorable.

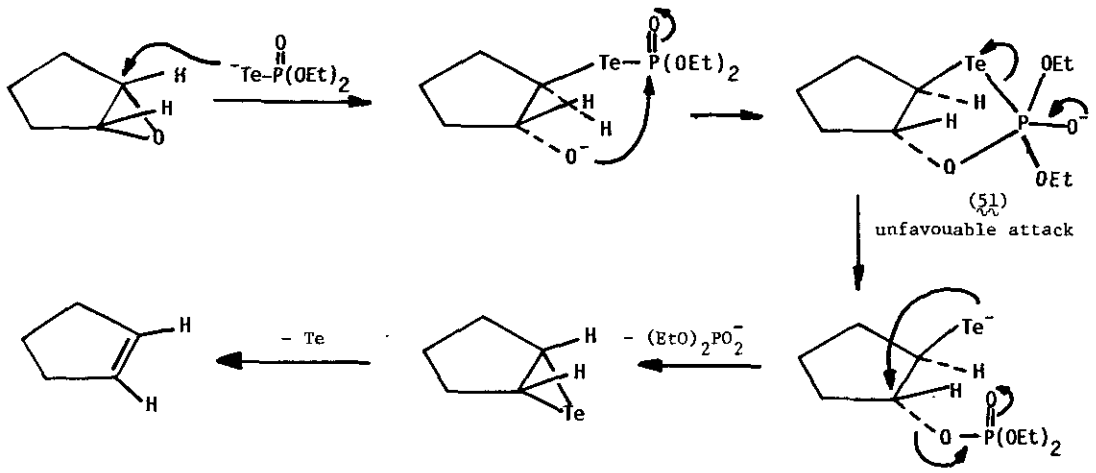


Table 9 is a collection of experimental results obtained employing these reagents to the deoxygenation of epoxides to olefins.

Table 9

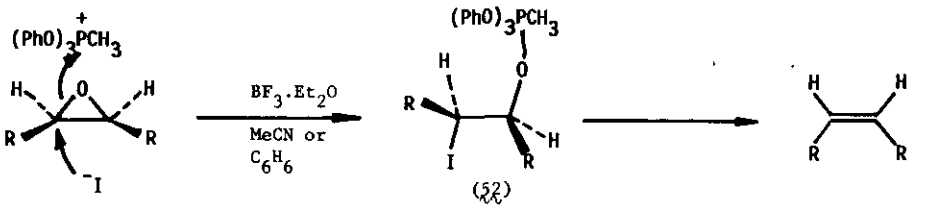
Epoxides	Olefins	Reagent (49)	Yields (%)
1-octene oxide	1-octene	$(EtO)_2PONa$ + Te	72
1-decene oxide	1-decene	$(EtO)_2PONa$ + Te	70
1-eicosene oxide	1-eicosene	$(EtO)_2PONa$ + Te	91
cis,trans-dodeca-4,8-diene dioxide	cis,trans-dodeca-4,8-diene	$(EtO)_2POTeLi$	6.6
	cis,trans-dodeca-4,8-diene-4,5-oxide		5.2
	cis,trans-dodeca-4,8-diene-8,9-oxide		46.8
cyclohexene oxide	cyclohexene	$(EtO)_2PONa$ + Te	88
2β,3β-oxido-5α-cholestane	5α-cholest-2-ene	$(EtO)_2POLi$ + Te	90
limonene dioxide	limonene-1,2-oxide	$(EtO)_2PONa$ + Te	76
3-methoxy-estra-1,3,5,16-tetraene-16,17-oxide	3-methoxy-estra-1,3,5,16-tetraene	$(EtO)_2POLi$ + Te	39

6. Methyltriphenylphosphonium iodide (MTPI)[38,39]

At room temperature for one to two hours and in the presence of boron trifluoride etherate in CH_3CN, MTPI can readily deoxygenate mono-, di-, and tri-substituted epoxides stereospecifically to olefins with retention of configuration.

The reaction of MTPI and epoxide is suspected to go via the presumable intermediate (52) as shown in Scheme 8.

Scheme 8



The suggested intermediate (52) is a phosphorylated iodohydrin which undergoes anti-elimination to give the stereospecific olefin.

The reactivity of the iodide ion on the deoxygenation reaction using MTPI has been investigated by using the following experiments. When sodium iodide is used instead of MTPI, epoxides are partly transformed into iodohydrins without the formation of olefins. However, this deoxygenation could be more effective by applying potassium iodide complexed with crown ether to an extent less than the deoxygenation with MTPI. The aforementioned observation shows that the reactivity of the iodide ion is important for the deoxygenation. Moreover, MTPI is considered to be a more effective method than the method using the "naked" iodide ion generated from potassium iodide and crown ether. The related experimental results are summarized in Table 10.

Table 10

Epoxides of	Yield of Olefins by using MTPI (%)	KI-crown ether (%)
1-decene	60	54
methyl cis-9-octadecenoate	95	85
methyl trans-9-octadecenoate	99	94
methyl cis-13-doeicosenoate	86	46
methyl trans-13-doeicosenoate	99	71
2,6-dimethyl-8-methoxy-1-octene	74	31
2-androsten-17-one	99	78
5-cholestene	91	53
4-cholesten-3-one	99	44

7. Diphosphorus tetraiodide[26,40]

In the presence of dry ether (or CCl_4) and pyridine, or if required, at reflux under nitrogen, epoxides can be efficiently converted to the olefins with diphosphorus tetraiodide. The diphosphorus tetraiodide can be easily prepared by disproportionation of phosphorus triiodide and potassium iodide in dry ether.

Arylepoxides, vinylepoxides and α,β-epoxycarbonyl compounds are deoxygenated smoothly in ether at room temperature, while the reaction of simple alkyl epoxides is sluggish under the same conditions and heating is required in CCl_4 for completion.

There are several advantages in employing this reagent for the deoxygenation. There are neither observable rearrangement of epoxides into carbonyl compound nor saturation of the double bond when this reagent is used. The reagent does not attack cyclopropane ring. The simultaneous formation of non-terminal alkenes can be avoided during the deoxygenation of terminal epoxides. Moreover, the reaction would proceed rapidly, cleanly and mildly.

Conventionally, vinylphosphates can be synthesized by treating 1-alkyl-1-hydroxyethylphosphates with thionyl chloride where isomeric product other than the vinyl product is produced. But, newer and more satisfactory method for the synthesis of these vinyl derivatives of phosphorus compounds can be aided by the use of diphosphorus tetraiodide.

The synthetic route is the initial conversion of p-toluenesulfonate to diphenyl-vinylphosphine oxide (53) which is then converted to the target, vinyl derivatives (54) of phosphorus compounds. The general equation and the experimental results are shown in Scheme 9 and Table 11 respectively.

Scheme 9

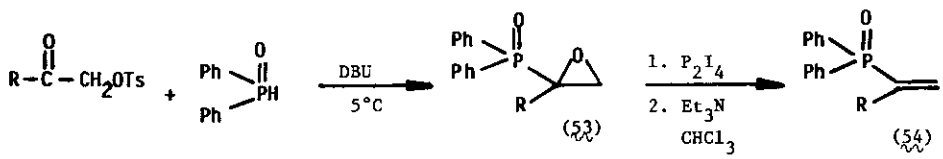
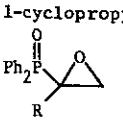
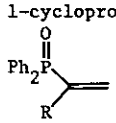
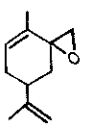
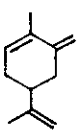


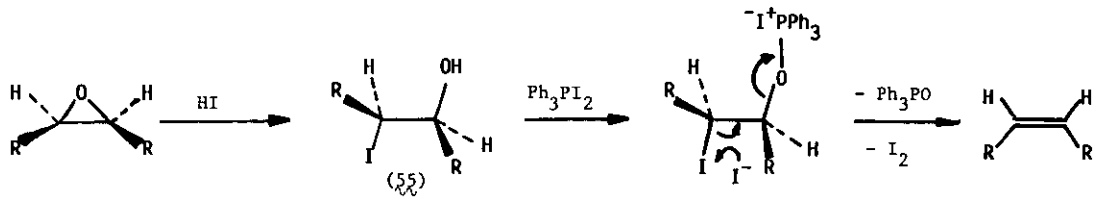
Table 11

Epoxides	Olefins	Yields (%)
5-phenylpenta-1,3-diene-1,2-oxide	5-phenylpenta-1,3-diene	42
isophorone oxide	isophorone	95
1-nonene oxide	1-nonene	92
trans-stilbene oxide	trans-stilbene	83
1,1-diphenylethene oxide	1,1-diphenylethene	70
1-p-tolyl-1-ethylethene oxide	1-p-tolyl-1-ethylethene	64
1-cyclopropyl-1-phenylethene oxide	1-cyclopropyl-1-phenylethene	54
		80(R = Ph) 70(R = Me) 76(R = Et) 70(R = C_6H_{11})
		64

8. Triphenylphosphine diiodide and triphenylphosphine hydriodide[41]

The iodohydrin (55) can be prepared by anti-opening of epoxide with hydrogne iodide. Subsequently, the iodohydrin (55) can be phosphorylated by triphenylphosphine diiodide wiich afterwards proceeds through an anti-elimination to provide the olefin stereospecifically with retention of configuration. The mechanism of this reaction is shown in Scheme 10.[41]

Scheme 10



Combining use of triphenylphosphine diiodide and triphenylphosphine hydriodide, epoxides can be deoxygenated to olefins. The conversion scheme and experimental results are shown in Scheme 11 and Table 12.

Scheme 11

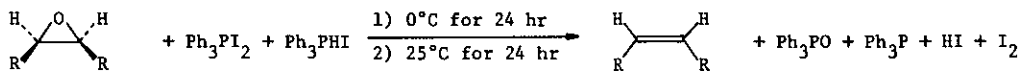


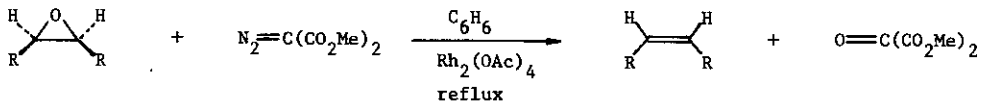
Table 12

Epoxides of	Stereospecificity (%)	Yield of Olefins (%)
1-eicosene	-	95
trans-3-octene	100	>95
trans-4-octene	100	>95
cis-4-octene	99	>95
cis-2-methyl-7-octadecene	>98	91
cis-7-dodecenyl acetate	>99	93
trans-4-tridecenyl acetate	>98	94
cis-9-tetradecenyl formate	100	93
3,7-dimethyl-7-octenyl formate	-	98

9. Dimethyl diazomalonate[42]

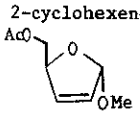
Dimethyl diazomalonate has been reported to deoxygenate epoxides to olefins with catalytic amount of binuclear rhodium (II) carboxylate. The reaction condition has been described to be mild and neutral. The experimental procedure involves the reflux of epoxide in benzene (or toluene) for a period of 30-45 min with dirhodium tetraacetate $Rh_2(OAc)_4$ as catalyst. The reaction can be summarized in Scheme 12.

Scheme 12



The mechanism has not been reported. The reaction products are olefins with retention of configuration. Different epoxides are used to react with dimethyl diazomalonate in the solvent with reflux. The results are shown in Table 13.

Table 13

Epoxides of	Solvents	Yield of Olefins (%)
cyclohexene	toluene	80
cis-cyclododecene	benzene	83
cis-cyclododecene/trans-cyclododecene	benzene	85
cis-2-hexene	benzene-d_6	82
trans-2-hexene	benzene-d_6	80
2,3-dimethyl-2-butene	toluene	60
propene	benzene	84
4-bromo-1-butene	toluene	84
3-acetoxy-cyclohexene	benzene	76
2-cyclohexenone	benzene	80
		82

10. Alkyl and homoalkylmanganese complexes[43]

Kauffmann and Bisling reported the use of alkyl and homoalkylmanganese complexes on the deoxygenation of olefins to epoxides. The results are listed in Table 14.
From Table 14, it is observed that the reagent Bu_3MnLi is more effective than MeMnCl in the deoxygenation of epoxides.

Table 14

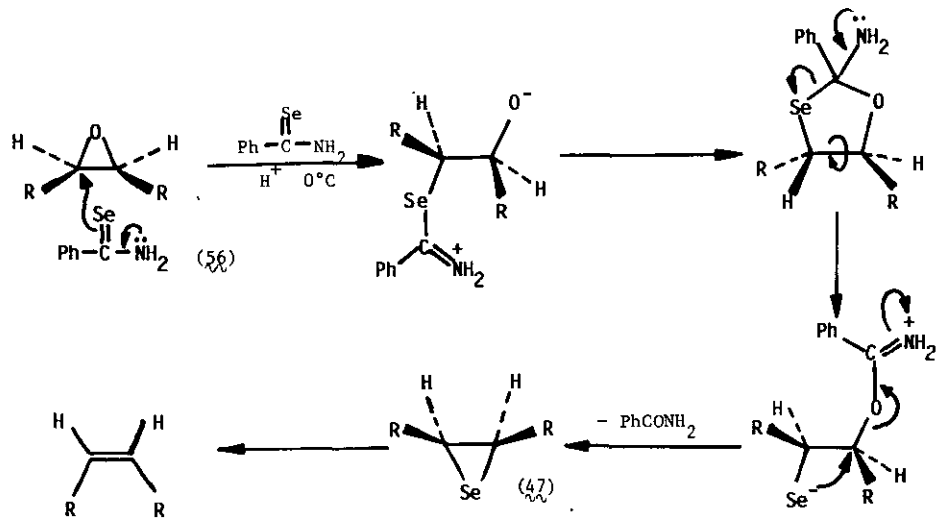
Epoxides of	Reagents	Yield of Olefins (%)	Z/E ratio
styrene	MeMnCl	63	-
trans-stilbene	MeMnCl	7	0/100
trans-stilbene	Bu_3MnLi	58	0/100
trans-stilbene	Bu_3MnLi[a]	66	0/100
cis-stilbene	Bu_3MnLi	16	6/94
cis-stilbene	Bu_3MnLi[b]	59	10/90
cyclohexene	MeMnCl	71	-
cyclododecene (epoxide Z/E = 95/5)	Bu_3MnLi[b]	65	94/6

a. 1 h at -30°C, then 2 h at 20°C
b. 1 h at -30°C, then 2 h at 60°C.

11. Selenocarboxamides[44]

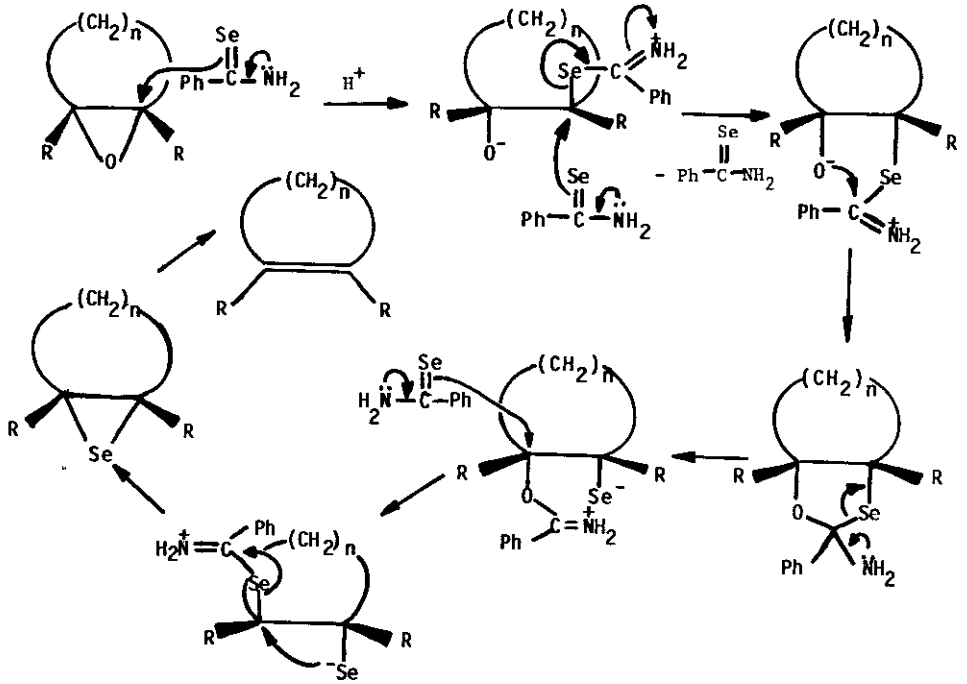
Sonoda and his coworkers discovered the use of arylselenocarboxamide (56) to the deoxygenation of epoxides stereospecifically to olefins with retention of configuration in the presence of catalytic amount of a strong acid. This reagent is known to be easily prepared by the reaction of nitriles with elemental selenium, carbon monoxide, and water. This reagent can reduce mono-, di-, and tri-substituted epoxides following the suggested mechanism shown in Scheme 13.

Scheme 13

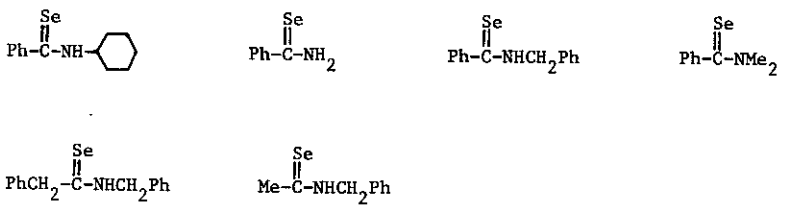


The reaction mechanism is similar to that of the deoxygenation using potassium selenocyanate and 3-methyl-2-selenoxobenzothiazole (48). Due to the fact that rotation of a carbon-carbon bond of a cyclic epoxide is restricted, an addition mechanism of *this reaction is proposed as shown in Scheme* 14.

Scheme 14



Other selenoamides, which can afford approximately 80% yield of olefins from epoxides, are shown as follows:



The results of deoxygenation employing the benzeneselenoamide (56) are summarized in Table 15.

Table 15

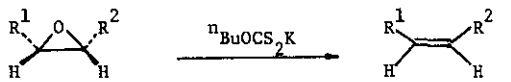
Epoxides of	Yield of Olefins (%)
1-octene	89
trans-2-octene	74
cis-2-octene	75
styrene	54

Table 15 (cont'd)

Epoxides of	Yield of Olefins (%)
cyclopentene	85
cyclohexene	84
1-methylcyclohexene	51
cyclododecene	82

12. Potassium ^{n}butyl xanthate[45]

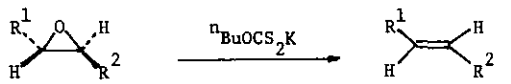
When potassium ^{n}butyl xanthate is employed to deoxygenate epoxides (57) and (58), olefins (59) and (60) can be isolated respectively in acceptable yields with retention of configuration. However, the mechanism of this reaction is expected to involve thiocarbonate formation and episulfide extrusion. Examples of the transformation are shown in Table 16.



(57) (59)

$R^1 = -(CH_2)_mMe$

$R^2 = -(CH_2)_nCO_2H$



(58) (60)

Table 16

Epoxides	m	n	Olefins	Yields (%)
(57)	10	4	(59)	45
(57)	7	7	(59)	50
(57)	7	11	(59)	48
(58)	10	4	(60)	48
(58)	7	7	(60)	40
(58)	7	11	(60)	45

13. Trifluoroacetyl iodide-sodium iodide[46,47]

It has been reported that trifluoroacetyl iodide can be generated in situ from trifluoroacetic anhydride and sodium iodide.[46] The combination of trifluoroacetyl iodide and excess sodium iodide formulates a highly efficient reagent system for the stereospecific deoxygenation of epoxides to olefins with retention of configuration. The mechanism of this transformation is shown in Scheme 15 and the results are tabulated in Table 17.[46] Two Walden inversions are responsible for retention of

configuration.

Scheme 15

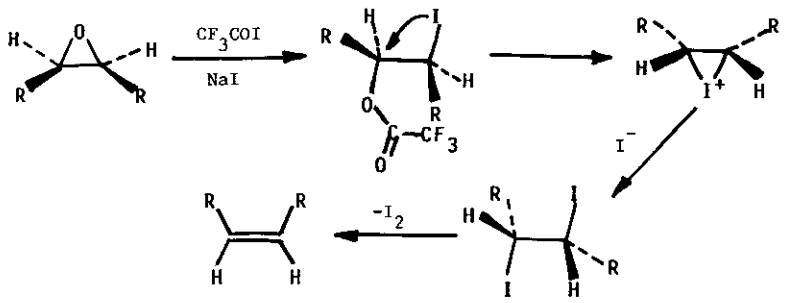
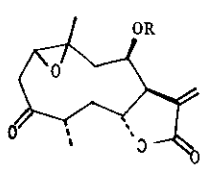
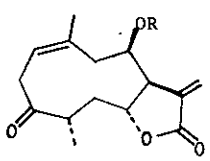


Table 17[46]

Epoxides of	Yield of Olefins (%)	Geometry Z/E
cyclohexene	77	-
1-decene	91	-
trans-5-decene (epoxide 93% trans)	95	4.5/95.5
cis-5-decene (epoxide 94% cis)	95	93/7
1-methyl-cis-7-octadecene (epoxide 97.5% cis)	90	91.7/2.3
1-methyl-trans-7-octadecene (epoxide 97.5% trans)	90	3/97

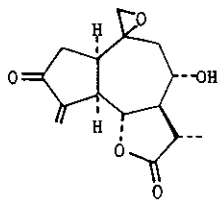
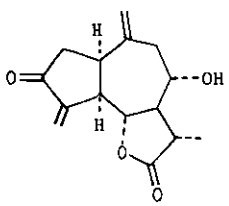
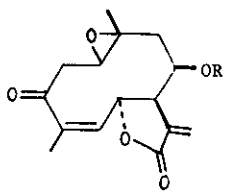
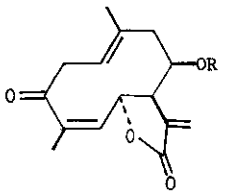
Recently, Sarma and Sharma[47] discovered that the combination of trifluoroacetic acid and sodium iodide can also smoothly effect deoxygenation of epoxides to olefins with retention of configuration.[47] The results are shown in Table 18.

Table 18[47]

Epoxides	Olefins	Yields (%)
5-cholestene-5α,6α-oxide	5-cholestene	90
5-cholesten-3β-ol-5α,6α-oxide	5-cholesten-3β-ol	90
trans-stilbene oxide	trans-stilbene	90
		60

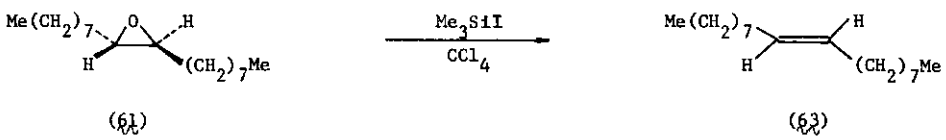
R = -CO-^{i}Pr

Table 18 (cont'd)

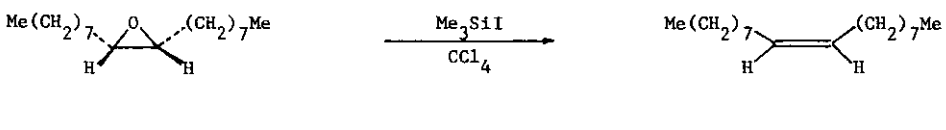
Epoxides	Olefins	Yields (%)
		20
 R = -CO-^{i}Pr		30

14. Trimethylsilyl iodide[48,49]

Trimethylsilyl iodide is able to deoxygenate (61) and (62) to (63) and (64) respectively.[48] However, in situ generation of trimethylsilyl iodide can be realized by reaction of trimethylsilyl chloride with sodium iodide. Thus, epoxides can be converted to alkenes with retention of config-



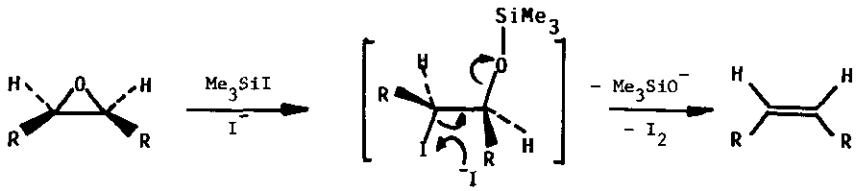
(61) (63)



(62) (64)

uration.[49] The mechanism of deoxygenation with trimethylsilyl iodide is shown in Scheme 16 and some of the results are listed in Table 19.[49] Anti-elimination of (65) would generate alkene with retention of configuration.

Scheme 16



(65)

Table 19

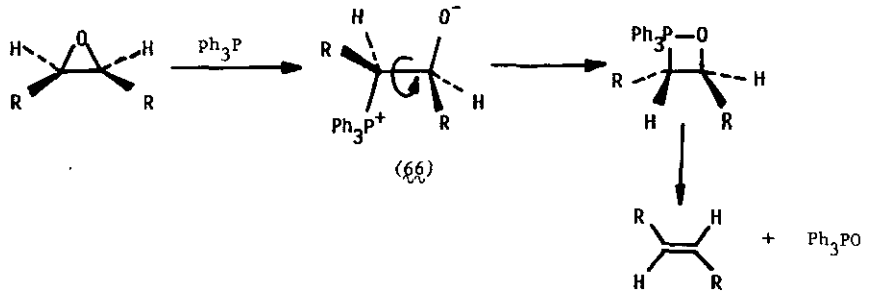
Epoxides	Olefins	Yields (%)
5α-cholest-2-ene-2α,3α-oxide	5α-cholest-2-ene	96
4-cholestene-4α,5α-oxide	4-cholestene	95
4-cholestene-4β,5β-oxide	4-cholestene	95
5-cholestene-5α,6α-oxide	5-cholestene	97
3-methyl-2-cholestene-2α,3α-oxide	3-methyl-2-cholestene	96
cis-4-^{t}butylcyclohexene oxide	cis-4-^{t}butylcyclohexene	94
trans-4-^{t}butylcyclohexene oxide	trans-4-^{t}butylcyclohexene	93
cyclohexene oxide	cyclohexene	94
cis-2,5-dimethyl-3-hexene oxide	cis-2,5-dimethyl-3-hexene	92
trans-2,5-dimethyl-3-hexene oxide	trans-2,5-dimethyl-3-hexene	95

One-step Stereospecific Deoxygenation with Inversion of Configuration

Reagents which are able to alter the configuration of epoxides are useful because olefin inversion is an important process in organic synthesis.[1] The following text will be a brief survey of those reagents which can effect deoxygenation with inversion of configuration.

1. Triphenylphosphine[50]

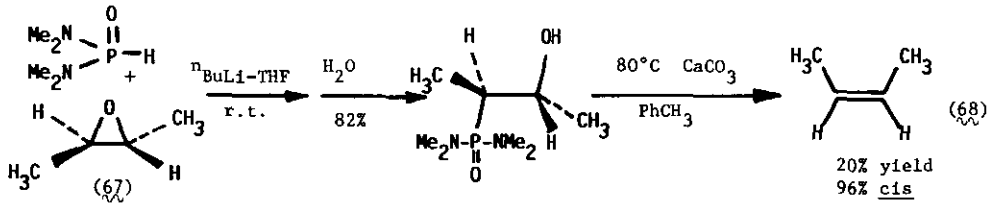
Wittig and Haag discovered that epoxide and triphenylphosphine reacted at 200°C to give 75% yield of the corresponding olefin. The reaction might go through the betaine intermediate (66) so that the product has an inverted stereochemistry.[50]



(66)

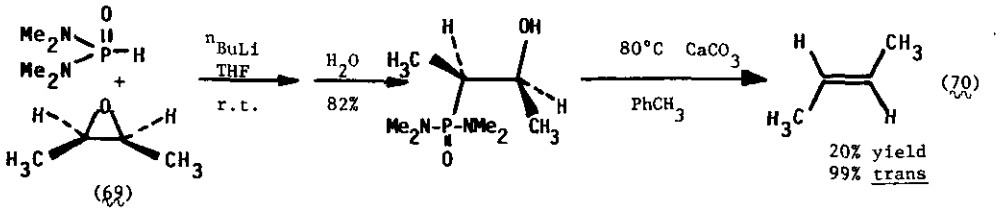
2. Bis(dimethylamino)phosphorous acid[51]

When trans-2-butene oxide (67) was treated with bis(dimethylamino)phosphorous acid in ^{n}butyllithium solution at room temperature for 72 h, and followed by thermal decomposition in toluene at 80°C, cis-2-butene (68) was yielded in 20% with stereospecificity of 96%. Similarly, cis-2-butene oxide (69) gave trans-2-butene (70) in good yield.



(67) (68)

20% yield
96% cis

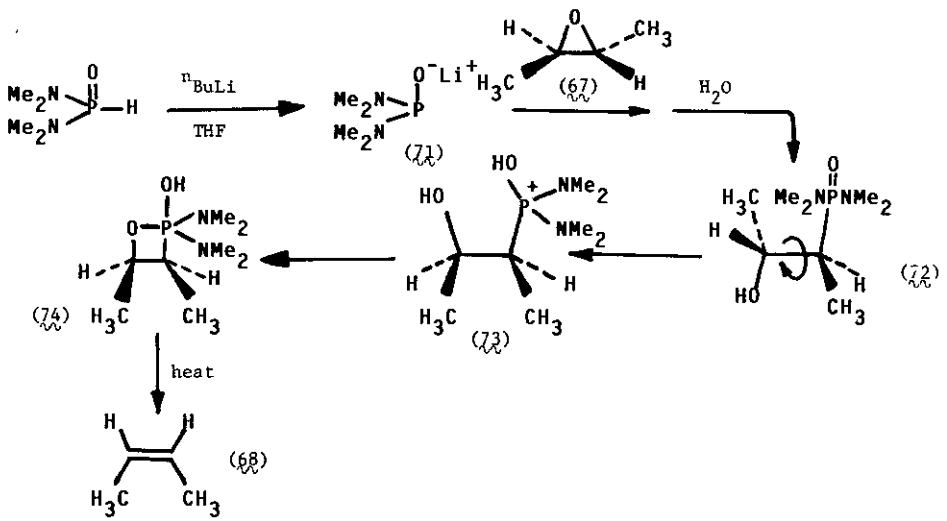


(69) (70)

20% yield
99% trans

The purpose of using calcium carbonate-silica gel is to neutralize the acidic phosphoric amide and to prevent isomerization of the olefinic products.
The mechanism is found to be Wittig-like, i.e. the reaction undergoes an SN_2 mechanism and is then followed by a cis-elimination pathway (Scheme 17).

Scheme 17



Normant[52] suggested that the diamidophosphite anion (71) was able to react with various alkyl halides to give the corresponding alkylphosphonodiamides, the products of P-alkylation. Such anion might react with a suitable epoxide to produce a β-hydroxyphosphonamide (72), which is further eliminated to produce an olefin, via consequently betaine (73) and oxaphosphetane (74).

3. Lithium diphenylphosphide[53]

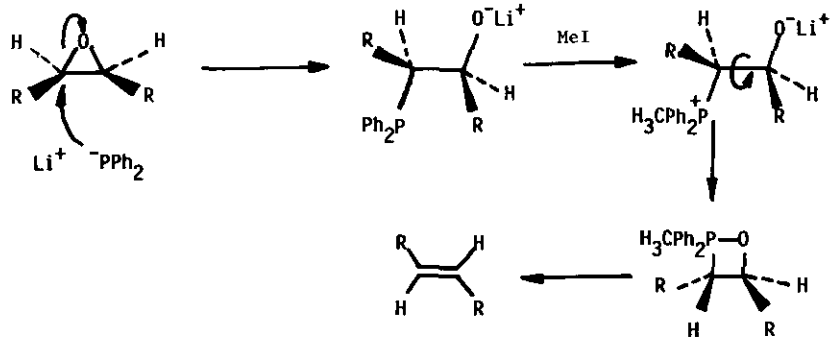
Vedejs and Fuchs developed the deoxygenation by using lithium diphenylphosphide (LDP), which can be conveniently prepared from chlorodiphenylphosphine and lithium wire or from chloro-diphenylphosphine and ^{n}butyllithium. The reagent is responsible for high yield deoxygenation of epoxides (Table 20).

Table 20

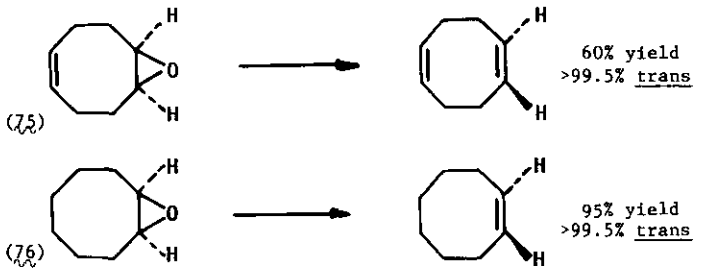
Epoxides	Olefins	Yield of Olefins (%)	Stereospecificity (%)
trans-stilbene oxide	cis-stilbene	95	>98
cis-stiblene oxide	trans-stilbene	95	>99
trans-2-octene oxide	cis-2-octene	77	>99.5
cis-2-octene oxide	trans-2-octene	75	>99.5

The mechanism of this transformation is a typical Wittig-like, phosphorus betaine formation, which is followed by elimination in mild reaction condition[53] (Scheme 18).

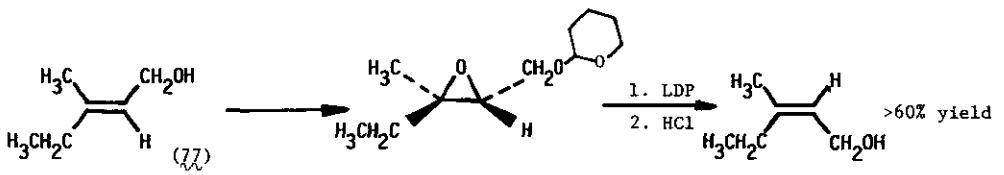
Scheme 18



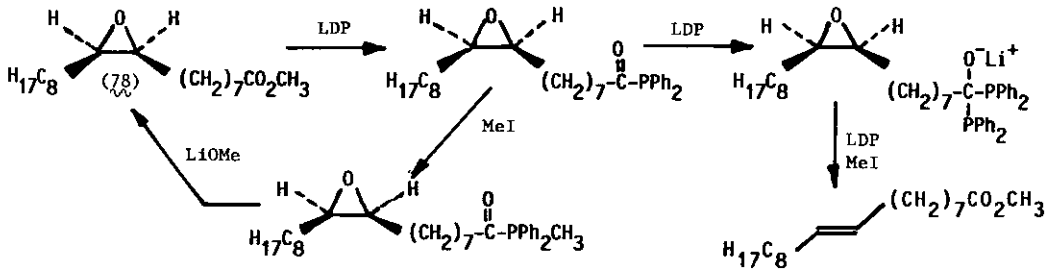
The mechanism may be supported by the fact that cycloocta-1,5-diene monoxide (75) gives low yield, while (76) gives high yield. Obviously, carbon-carbon single bond of (76) rotates freely but the carbon-carbon double bond of (75) is rigid. An angle strain is generated while forming betaine intermediate.



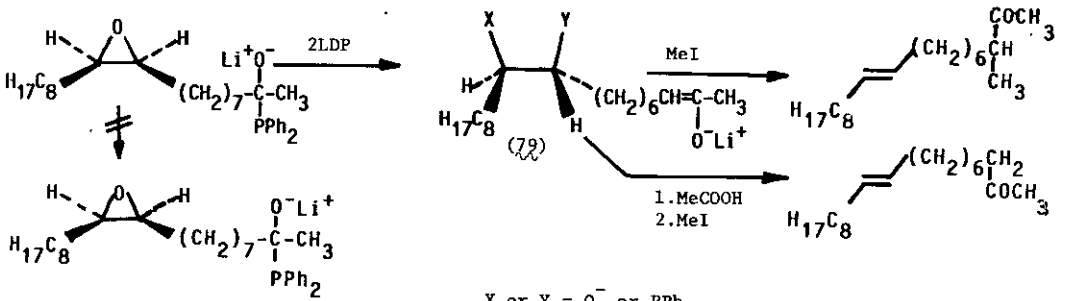
However, LDP is not useful for reduction of epoxides of alkene esters since it can attack the ester carbonyl functional group. Moreover, LDP is sensitive to steric hindrance. If the epoxide is bulky, the reaction proceeds very slowly and the yield is decreased. In addition, LDP is a strong base as well as a good nucleophile. To this connection, it should be noted that compounds with base sensitive groups should be protected. Thus, (77) is protected as acetal before it is subjected to oxidation and deoxygenation with inversion.



Moreover, reaction of (78) with 3 equivalents of LDP, followed by excess methyl iodide, afforded the inverted alkene ester in 40% yield. However, treatment of (78) with 1 equivalent (or 2 equivalents) of LDP and followed by methyl iodide resulted in 60% recovery of the starting epoxide and only trace amount of inverted alkene.

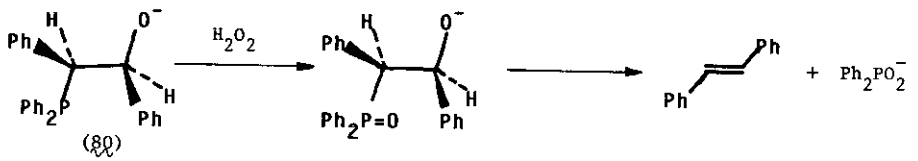


An enolate (79) was generated by the strong basicity of LDP. The undersired C-methylation could be avoided by carefully neutralizing the enolate with 1 equivalent of acetic acid prior to addition of methyl iodide. With this modification, the reaction gave the inverted ketoalkene in 85% yield.



X or Y = O^- or PPh_2

Furthermore, a modification[54] of this method involves hydrogen peroxide oxidation of the intermediate (80) so that the elimination by-product, a diphenylphosphinate salt, would become water-soluble which facilitates product isolation.



4. Hexamethyldisilane and potassium methoxide[55]

Reaction of cis and trans epoxides with hexamethyldisilane and potassium methoxide in anhydrous hexamethylphosphoric triamide (HMPT) at 65°C under argon for 3 h afforded the corresponding trans and cis olefins respectively (Table 21).

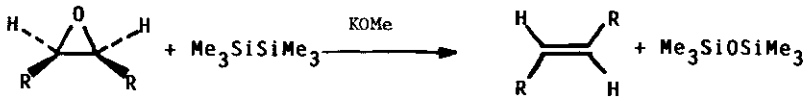
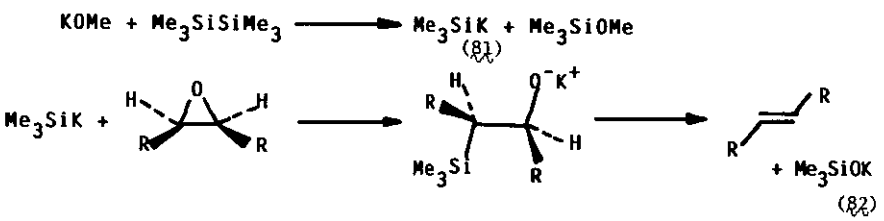


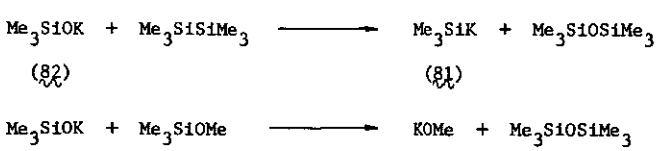
Table 21

Epoxides	Olefins	Yields (%)	Stereospecificity (%)
trans-3-hexene oxide	cis-3-hexene	99	>99
cis-3-hexene oxide	trans-3-hexene	86	>99
trans-4-octene oxide	cis-4-octene	96	>99
cis-4-octene oxide	trans-4-octene	93	>99
trans-2,5-dimethylhex-3-ene oxide	cis-2,5-dimethylhex-3-ene	93	98
cis-2,5-dimethylhex-3-ene oxide	trans-2,5-dimethylhex-3-ene	75	92
trans-3-methylpent-2-ene oxide	cis-3-methylpent-2-ene	91	>99
cis-3-methylpent-2-ene oxide	trans-3-methylpent-2-ene	99	>99

The reaction might be initiated by the reaction of potassium methoxide and hexamethyldisilane to form trimethylsilylpotassium (TMSK)(81) and trimethylmethoxysilane. Backside attack of TMSK (81) on the cis (or trans) epoxide generates the threo (or erythro) β-alkoxysilane respectively. Hudrlik and coworkers[56] have demonstrated that the base-induced elimination of β-hydroxysilane occurs stereospecifically in a cis manner. Thus, cis-elimination of the β-hydroxysilane provides the inverted olefin and potassium trimethylsilanolate (82).



Potassium trimethylsilanolate (82) from the deoxygenation step would further react with either hexamethyldisilane or trimethylmethoxysilane to form hexamethyldisiloxane and trimethylsilylpotassium or potassium methoxide.

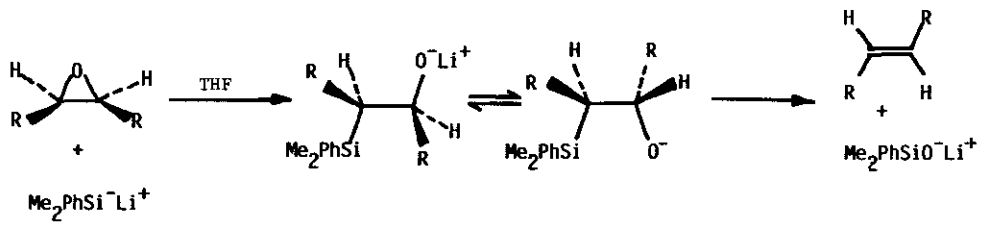


Although the entire role of HMPT is not yet known, it is believed that HMPT would complex with potassium cations and would participate in several steps of this reaction. Furthermore, the rate of elimination depends to some extent on the choice of metal cation, usually K >> Na >> Mg, which is apparently due to the affinity of the cation and alkoxy anion.

5. Dimethylphenylsilyl lithium[57]

Reetz and Plachky developed the same kind of Dervan and Shippey's reagent.[55] Also, they reported their experimental results almost simultaneously. Reetz and Plachky found out that dimethylphenylsilyl lithium reduced epoxides to inverted olefins. The reaction can be performed in THF at room temperature for 4 h and it might undergo the pathway as depicted in Scheme 19.

Scheme 19



Furthermore, they found out that dimethylphenylsilyl lithium could not be used to reduce epoxy-ester, since the strong nucleophile, dimethylphenylsilyl lithium, could attack the ester carbonyl group.
Their empirical data are summarized in Table 22.

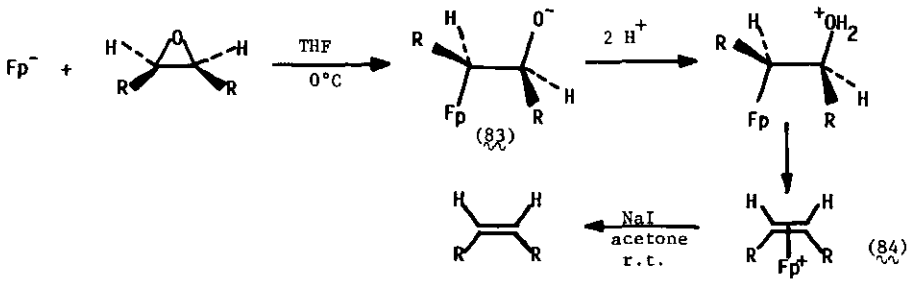
Table 22

Epoxides	Olefins	Yields (%)	Stereospecificity (%)
trans-stilbene oxide	cis-stilbene	75	97
cis-stilbene oxide	trans-stilbene	83	>99
1-pentene oxide	1-pentene	60	-
1-octene oxide	1-octene	64	-

6. Sodium (cyclopentadienyl)dicarbonylferrate[58]

Initially, Giering, Rosenblum and Tancrede developed the deoxygneation of epoxides to olefins with retention of configuration by using sodium (cyclopentadienyl)dicarbonylferrate $[C_5H_5Fe(CO)_2^-Na^+]$ $[Fp^-Na^+]$[58]. The sequence of reactions could be performed without isolation of intermediates. (Scheme 20)

Scheme 20

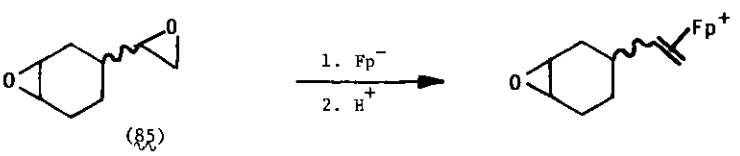


Treatment of epoxides at or below room temperature in THF solution of Fp^-Na^+ would result in the conversion to the alkoxides (83). Subsequent addition of 2 equivalents of fluoroboric acid or hexafluorophosphoric acid in situ would convert the alkoxides (83) instantaneously and in high yield to the olefin-iron complexes (84). (Table 23)

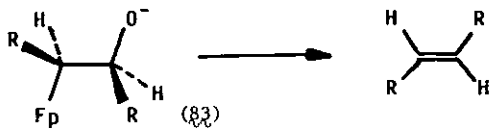
Table 23

Epoxides	Yields of Olefin-iron complexes (%)
ethylene oxide	90
propylene oxide	91
1-butene oxide	91
cis-2-butene oxide	64
trans-2-butene oxide	50
styrene oxide	62
trans-stilbene oxide	83
cis-stilbene oxide	82
cyclohexene oxide	66
butadiene oxide	91
acrolein oxide	90
trans-ethyl crotonate oxide	96
4-vinyl cyclohexene dioxide	50

The relative rates of reaction of the anion Fp^- with terminal and internal epoxides reflects the larger steric demand of this reagent. The reaction with terminal epoxides is essentially complete at room temperature within several minutes, however, several hours are required for complete consumption of cis or trans-stilbene, cyclohexene oxide and cis and trans-2-butene oxide. Thus, we can take advantage of these rate differences to selective conversion of 4-vinyl cyclohexene dioxide (85) to a mixture of stereoisomeric monoxide-iron complex.



Subsequently, Rosenblum, Saidi and Madhavarao improved this reaction to give inverted olefins by simply decomposing by heating the intermediate alkoxides (83).



Decomposition may be performed by the following methods:

Method A: refluxing (83) in THF solution for 1 h.

Method B: removal of solvent from solution in vacuo and heating the solid residue briefly at 130-150°C for 15 min.

Method C: passing solution of (83) through a heated tube at 240°C for ca. 3 sec.

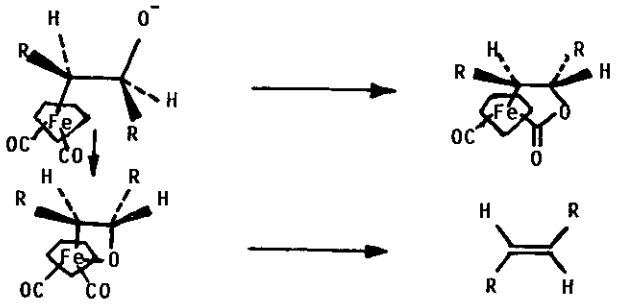
The results are depicted in Table 24.

Table 24

Epoxides	Olefins	Method	Yields(%)	Stereospecificity(%)
cis-stilbene oxide	trans-stilbene	A	96	99
trans-stilbene oxide	cis-stilbene	B	92	94
cis-2-butene oxide	trans-2-butene	B	86	99
trans-2-butene oxide	cis-2-butene	B	69	99
cis-2-pentene oxide	trans-2-pentene	B	61	99
trans-2-pentene oxide	cis-2-pentene	B	63	99
trans,trans-2,4-hexadiene monoxide	cis,trans-2,4-hexadiene	B	62	94 (cis,trans) 6 (trans, trans)
trans,trans-2,4-hexadiene dioxide	cis,cis-2,4-hexadiene	B	51	45 (cis,cis) 48 (cis,trans) 7 (trans, trans)
trans-3-penten-2-one oxide	cis-3-penten-2-one	B	54	85

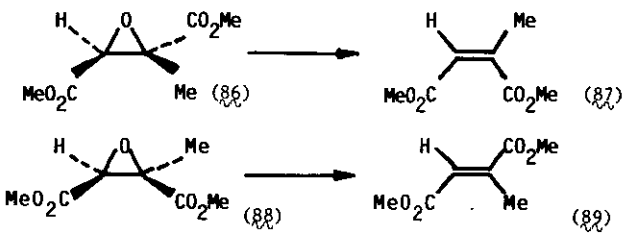
The detailed mechanism of this decomposition reaction has not been established, but it might involve cis-elimination, reminiscent of the thermal decomposition of betaines. It might proceed either by direct attack of the oxygen anion at the metal center or through initial addition to a carbonyl ligand. (Scheme 21)

Scheme 21



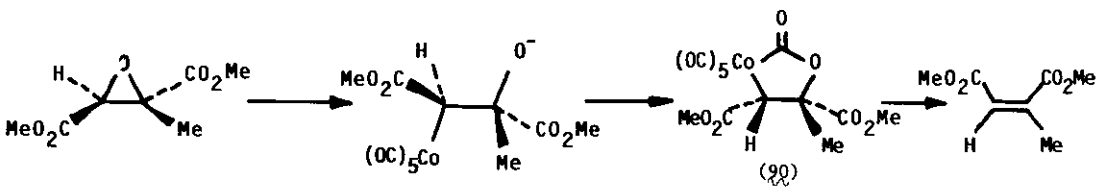
7. Octacarbonyldicobalt[59]

Octacarbonyldicobalt is capable of reducing epoxides stereospecifically to olefins with inverted configuration. This reagent can be used successfully on ester-bearing epoxides , while the other methods[53,57] meet with difficulties. Treatment of cis-dimethylepoxymethylsuccinate (86) with $Co_2(CO)_8$ for 18 h at room temperature gave 95% yield of dimethylmesaconate (87). Under the same conditions, trans-dimethylepoxymethylsuccinate (88) yielded 99% of dimethylcitroconate (89).[59]



Tentatively, the mechanism of this reaction has been suggested to undergo through a cobalt heterocycle intermediate (90) which leads to the product with inverted stereochemistry (Scheme 22).

Scheme 22



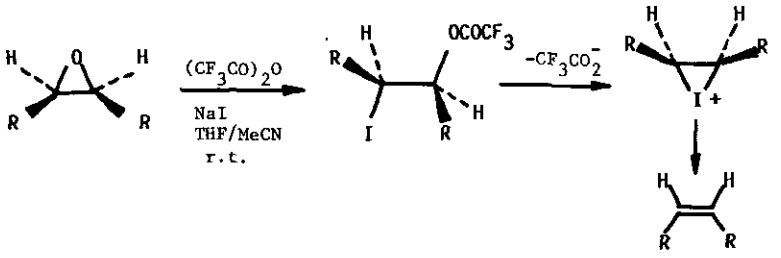
8. Lithium halides and trifluoroacetic anhydride[60,61]

Sonnet[60] reported that reaction of epoxides with trifluoroacetic anhydride (TFAA) and sodium iodide gave olefins with retention of configuration (Scheme 23).

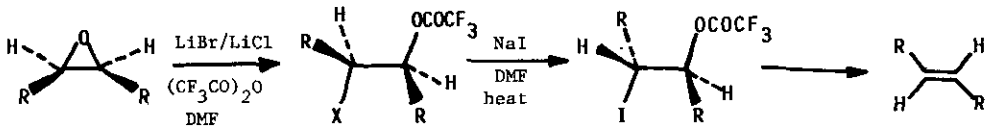
The reaction might first go through an SN_2 mechanism. Subsequently, the elimination would be aided by the participation of the iodine atom, so that an iodonium ion would form. Breaking down of the

iodonium ion gives olefin with retention of configuration (Scheme 23).

Scheme 23



Two years later, Sonnet[61] developed a reaction by heating vic-bromo-, or vic-chlorohydrin trifluoroacetates (91) with sodium iodide in DMF, from which olefins with inversion of stereochemistry would be produced, because a SN_2 displacement of bromide (or chloride) by iodide has occurred.



(91)

This reaction could proceed under the following methods:

Method A: TFAA/LiCl in DMF, room temperature, followed by NaI, 130°C, 24 h.

Method B: TFAA/LiBr in DMF, room temperature, followed by NaI, 90°C, 24 h.

The results of this transformation is summarized in Table 25. As a whole, yields are higher than 85%.

Table 25

Epoxides	Olefins	Methods	Stereospecificity (%)
cis-4-octene oxide	trans-4-octene	A	>99
trans-4-octene oxide	cis-4-octene	A	>99
cis-4-decene oxide	trans-4-decene	A	99
trans-5-decene oxide	cis-5-decene	A	95
cis-2-methyloctadec-7-ene oxide	trans-2-methyloctadec-7-ene	A	>99
trans-2-methyloctadec-7-ene oxide	cis-2-methyloctadec-7-ene	A	97
cis-4-octene	trans-4-octene	B	>99
cis-2-methyloctadec-7-ene oxide	trans-2-methyloctadec-7-ene	B	94
trans-2-methyloctadec-7-ene oxide	cis-2-methyloctadec-7-ene	B	99

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