


## SELECTIVE CATALYZED-REARRANGEMENT OF TERMINAL EPOXIDES TO METHYL KETONES

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### Summary



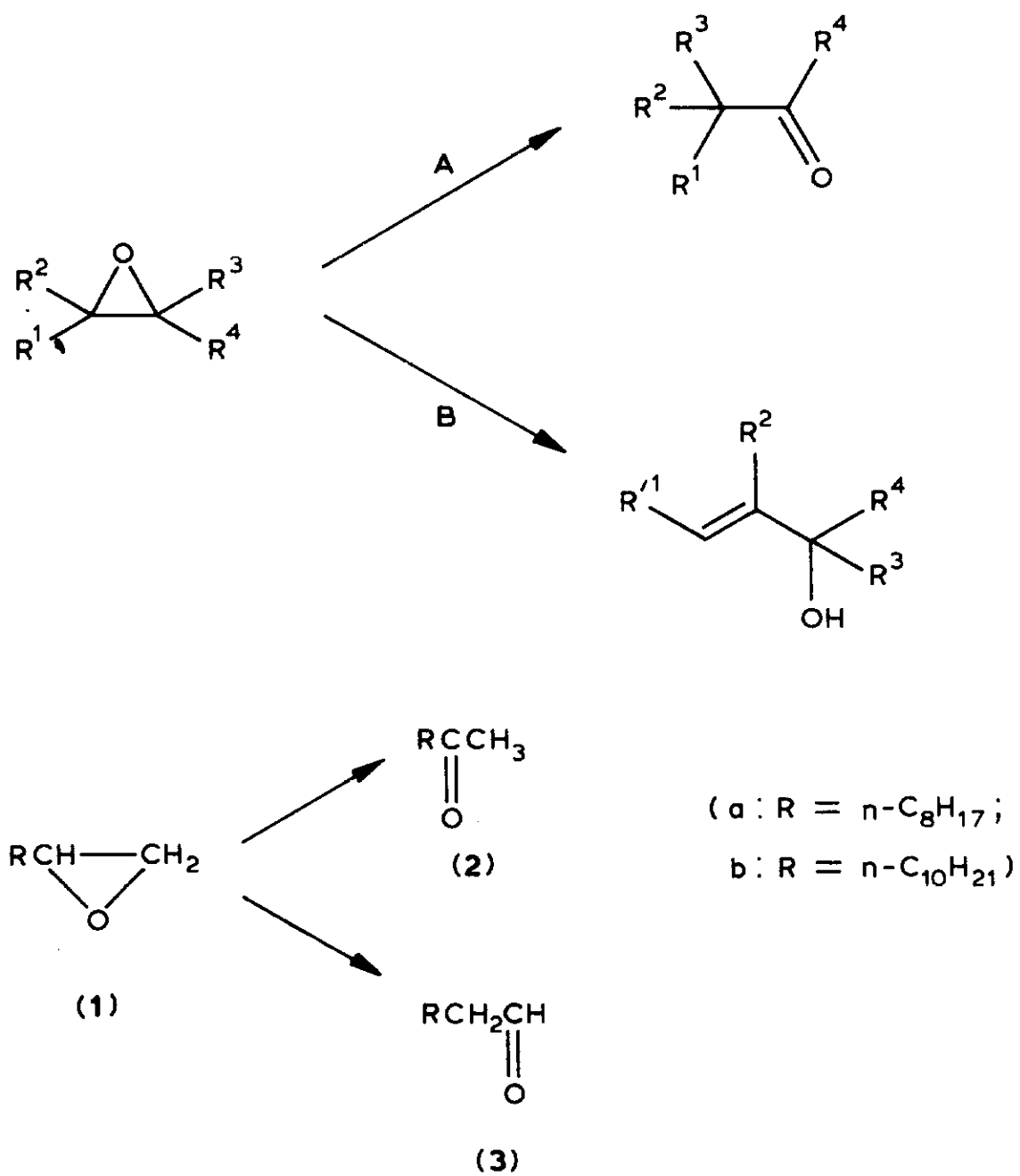
Terminal epoxides of the type RCH-CH<sub>2</sub> have been selectively converted into methyl ketones by various catalysts. Some lanthanide derivatives, MnI<sub>2</sub>, and Co<sub>2</sub>(CO)<sub>8</sub> gave the best results. The rearrangement of internal epoxides into ketones is much slower, allowing specific transformation of terminal epoxides. The scope of the reaction and tentative mechanisms are discussed.

### Introduction

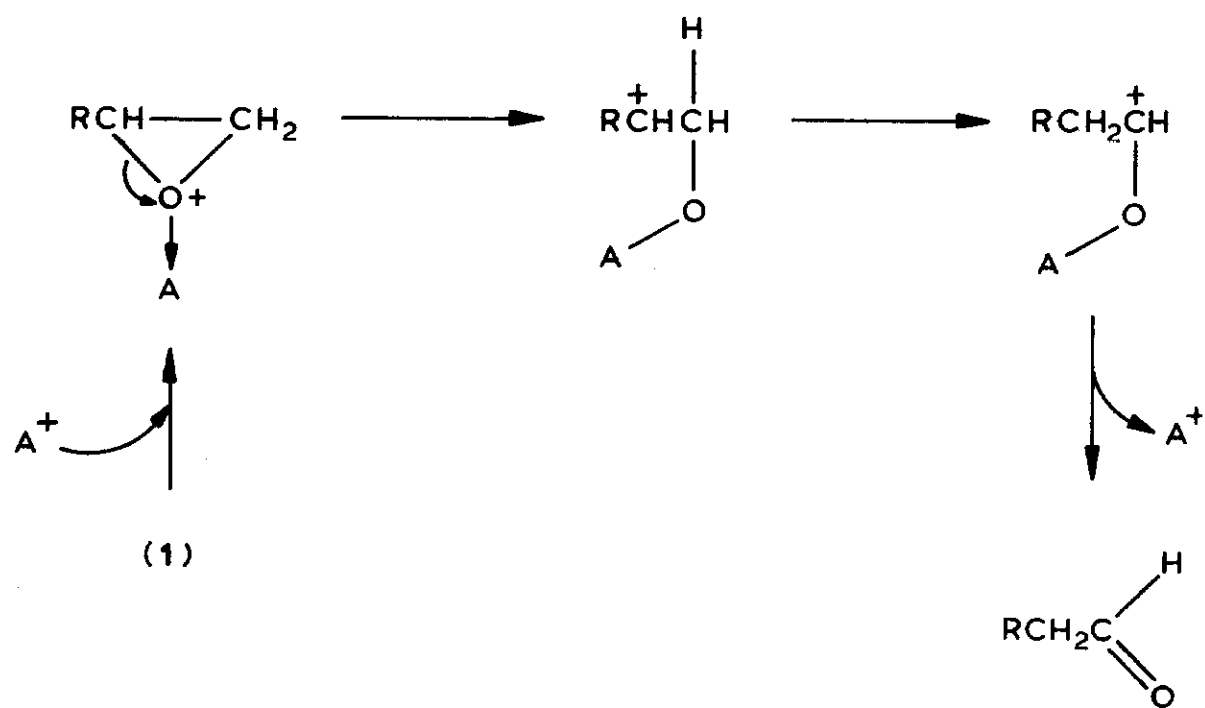
Rearrangement of epoxides is a well-documented reaction and leading references can be found in several reviews or articles [1–4]. The main product is a carbonyl compound (ketone or aldehyde) (route A, Scheme 1) when the reaction is initiated by an acid, usually a Lewis acid or an electrogenerated acid [5]. In presence of a base such a lithium amide route B is preferred, leading to an allylic alcohol. Epoxide isomerization can also occur when a functional group is vicinal to the epoxide, giving rise to a rich chemistry, especially if there is participation by the functional group. We were interested in reactions of type A in which the starting material is a terminal epoxide in an alkane chain. We tried to develop general methods for selectively rearranging an epoxide to the isomeric ketone and avoiding aldehyde formation (Scheme 1). Satisfactory control of this transformation would be helpful in some synthetic schemes and allow a two-steps conversion of a terminal olefin into a methyl ketone. A literature search has shown that there is no general solution to the problem. Acid-catalyzed rearrangement gives mainly or exclusively the aldehyde. We describe below our approaches to catalytic isomerization of epoxides **1** to ketones **2**.

### Catalysts for isomerization of epoxides

The classical mechanism which accounts for aldehyde formation from epoxide **1** is depicted in Scheme 2, where A<sup>+</sup> represents H<sup>+</sup> or a Lewis acid. The opening of the



SCHEME 1



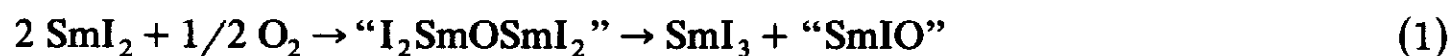
SCHEME 2

oxirane ring proceeds through formation of the more stable carbocation. In order to avoid this type of bond rupture we looked for mildly acidic catalysts. 1,2-Epoxydecane was chosen as the model terminal epoxide.

#### *Lanthanide catalysts*

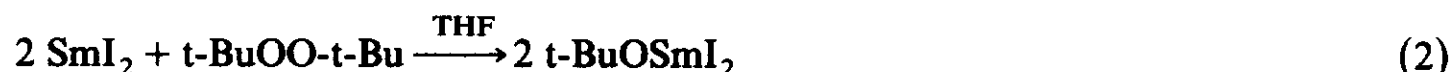
The investigation was prompted by some observations during our work on deoxygenation of epoxides by diiodosamarium [6]. It was found that terminal epoxides gave methyl ketones as a by-product, which arose as a consequence of the catalytic effect of  $\text{Sm}^{3+}$  species which accumulate during the reduction. The samarium agent ( $2 \text{SmI}_2$ ) is transformed to " $\text{I}_2\text{SmOSmI}_2$ " which slowly decomposes into a mixture of  $\text{SmI}_3$  and "SmIO".

We examined the activity of  $\text{SmI}_3$  (0.1 mol.equiv.) towards epoxide **1a** in THF. After 20 h at room temperature only traces of ketone **2a** were detected and no aldehyde **3a**; the only product was 1-iodo-2-hydroxy decane (20%).  $\text{Sm}_2\text{O}_3$  and  $\text{Sm}(\text{i-PrO})_3$  also showed no catalytic activity. We then tried "SmIO" as catalyst under the same conditions; it was readily obtained by the oxidation of  $\text{SmI}_2$  in THF:



Some 80% of  $\text{SmI}_3$  separated out, and the remaining solution was used as such. A good yield (80%) of 2-decanone **2a** was now obtained and a 90% yield of **2a** could be obtained by refluxing the THF solution for 20 h. Clearly the catalytic activity for the epoxide isomerization arises from the presence of SmIO, and  $\text{SmI}_3$  is unnecessary. Since SmIO is formed in deoxygenation of epoxide [6] by  $\text{SmI}_2$ , we expected the latter to catalyze the isomerization. Use of catalytic amounts of  $\text{SmI}_2$  gave satisfactory yields of methyl ketone (Table 1, entries 5,16). We then sought  $\text{Sm}^{\text{III}}$  catalysts showing some similarities to SmIO. We considered that SmIO might behave as a catalyst because of the simultaneous presence of some Lewis acidity, some basicity (in the SmO moiety), and the nucleophilic character of  $\text{I}^-$ . We thus decided to prepare various iodolanthanides alcoholates.

The very simple method devised for preparation of  $\text{t-BuOSmI}_2$  [7] is shown in the following equation:



The reaction was carried out at room temperature under nitrogen; the product was not isolated but various titrations were consistent with the formula  $\text{t-BuOSmI}_2$  [7]. The effect of this compound on the isomerization of epoxydecane **1a** was examined. The rearrangement to ketone **2a** occurs cleanly (20 h at r.t.) in 90% yield, and no aldehyde was detected. Thus  $\text{t-BuOSmI}_2$  appears to be an excellent catalyst for the ketone formation from terminal epoxides, and this was confirmed by the smooth transformation of 1-phenyl-2,3-epoxypropane into ketone (82% yield). More vigorous conditions are necessary for rearrangement of internal epoxides into ketones (4 h reflux in THF). Good yields were observed with *cis*-epoxycyclooctane and *trans*-5,6-epoxydecane (entries 10,8, Table 1). The different reactivities of terminal and internal epoxides result in almost exclusively rearrangement of the terminal species when a 1:1 mixture of the two epoxides is kept at 40°C for 2 h (entry 9, Table 1).

Cerium is the most available lanthanide, and so it was of interest to examine the

TABLE 1  
EPOXIDE REARRANGEMENTS CATALYZED BY LANTHANIDE DERIVATIVES

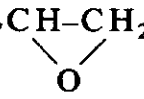
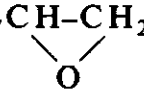
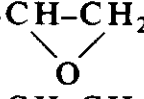
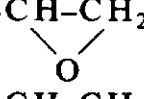
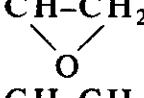

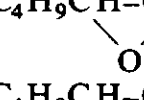
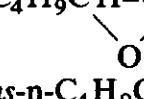
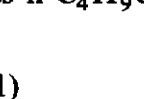
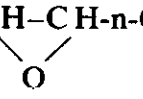
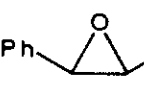

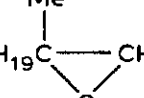
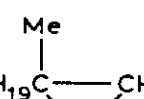
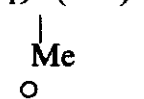
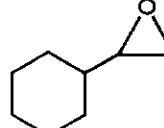
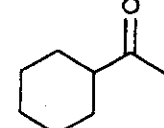
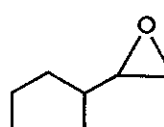
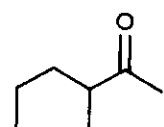
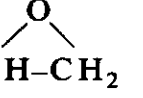
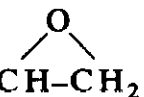
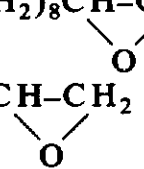
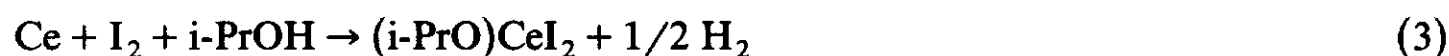
Epoxide <sup>a</sup>	Catalyst (0.1 mol eq)	Products	(Yield (%)) <sup>b</sup>
1 $n\text{-C}_8\text{H}_{17}\text{CH}-\text{CH}_2$ (1a) 	SmIO	$n\text{-C}_8\text{H}_{17}\text{C}(\text{O})(\text{CH}_3)$	(85)
2 $n\text{-C}_8\text{H}_{17}\text{CH}-\text{CH}_2$ (1a) 	SmIO <sup>c</sup>	$n\text{-C}_8\text{H}_{17}\text{C}(\text{O})(\text{CH}_3)$	(90)
3 $n\text{-C}_8\text{H}_{17}\text{CH}-\text{CH}_2$ (1a) 	t-BuOSmI <sub>2</sub>	$n\text{-C}_8\text{H}_{17}\text{C}(\text{O})(\text{CH}_3)$	(90)
4 $n\text{-C}_8\text{H}_{17}\text{CH}-\text{CH}_2$ (1a) 	t-BuOSmI <sub>2</sub> <sup>d</sup>	$n\text{-C}_8\text{H}_{17}\text{C}(\text{O})(\text{CH}_3)$	(80)
5 $n\text{-C}_8\text{H}_{17}\text{CH}-\text{CH}_2$ (1a) 	SmI <sub>2</sub>	$n\text{-C}_8\text{H}_{17}\text{C}(\text{O})(\text{CH}_3)$	(80)
6 $n\text{-C}_8\text{H}_{17}\text{CH}-\text{CH}_2$ (1a) 	CeI <sub>2</sub> (O-i-Pr) <sup>d</sup>	$n\text{-C}_8\text{H}_{17}\text{C}(\text{O})(\text{CH}_3)$	(80)
7 <i>trans</i> - $n\text{-C}_4\text{H}_9\text{CH}-\text{CH}-n\text{-C}_4\text{H}_9$ 	SmIO <sup>e</sup>	$n\text{-C}_4\text{H}_9\text{CO}-n\text{-C}_5\text{H}_{11}$	(90)
8 <i>trans</i> - $n\text{-C}_4\text{H}_9\text{CH}-\text{CH}-n\text{-C}_4\text{H}_9$ 	t-BuOSmI <sub>2</sub> <sup>f</sup>	$n\text{-C}_4\text{H}_9\text{CO}-n\text{-C}_5\text{H}_{11}$	(78)
9 1a + <i>trans</i> - $n\text{-C}_4\text{H}_9\text{CH}-\text{CH}-n\text{-C}_4\text{H}_9$ 	t-BuOSmI <sub>2</sub> <sup>d</sup>	$n\text{-C}_8\text{H}_{17}\text{COCH}_3$  $n\text{-C}_4\text{H}_9\text{CO}-n\text{-C}_5\text{H}_{11}$ <i>trans</i> - $n\text{-C}_4\text{H}_9\text{CH}-\text{CH}-n\text{-C}_4\text{H}_9$ 	(49)  (3) (47)
10 Epoxycyclooctane	t-BuOSmI <sub>2</sub> <sup>f</sup>	cyclooctanone	(83)
11 Epoxycyclooctane	SmIO	no reaction	
12 <i>trans</i> Ph  Ph	SmIO <sup>e</sup>	PhCOCH <sub>2</sub> Ph	(85)
13 <i>trans</i> Ph  Ph	t-BuOSmI <sub>2</sub> <sup>f</sup>	PhCOCH <sub>2</sub> Ph	(58) epoxide (30)
14 $n\text{-C}_9\text{H}_{19}\text{C}(\text{Me})-\text{CH}_2$ 	SmIO	no reaction apart $n\text{-C}_9\text{H}_{19}\text{C}(\text{OH})\text{CH}_2\text{I}$	(10)
15 $n\text{-C}_9\text{H}_{19}\text{C}(\text{Me})-\text{CH}_2$ 	t-BuOSmI <sub>2</sub> <sup>e</sup>	$n\text{-C}_9\text{H}_{19}\text{C}(\text{OH})\text{CH}_2\text{I}$ 	
16 	SmI <sub>2</sub>	 (45),	epoxide (35)
17 	t-BuOSmI <sub>2</sub>	 (55),	epoxide (35)
18 PhCH <sub>2</sub> CH-CH <sub>2</sub> 	t-BuOSmI <sub>2</sub>	PhCH <sub>2</sub> COCH <sub>3</sub>	(82)

TABLE 1 (continued)

Epoxide <sup>a</sup>	Catalyst (0.1 mol eq)	Products	(Yield (%)) <sup>b</sup>
19 	SmI <sub>2</sub>	PhCH <sub>2</sub> COCH <sub>3</sub> (55),	epoxide (20)
20 CH <sub>3</sub> CH(OH)(CH <sub>2</sub> ) <sub>8</sub> CH-CH <sub>2</sub>	t-BuOSmI <sub>2</sub>	no reaction	
21 	t-BuOSmI <sub>2</sub>	no reaction	

<sup>a</sup> Reaction performed in THF for 20 h at room temperature unless otherwise stated. <sup>b</sup> Isolated yields, except for entries 8,12,15,16,18 (NMR and GLC measurements). <sup>c</sup> Reflux 20 h. <sup>d</sup> 2 h, 40°C. <sup>e</sup> 48 h, 60°C. <sup>f</sup> 4 h, 60°C.

activity of an iodocerium alcoholate. We found that (i-PrO)CeI<sub>2</sub> can be readily made from cerium metal according to eq. 3:



This alcoholate was used as a catalyst for the rearrangement of 1,2-epoxydecane under the conditions indicated in Table 1 (entry 6). It gave the results similar to those obtained with t-BuOSmI<sub>2</sub>. i-PrOAlI<sub>2</sub> was also examined as a catalyst, but it showed no activity, thus demonstrating the importance of the lanthanide cation.



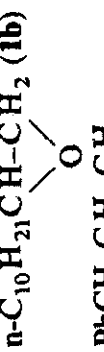

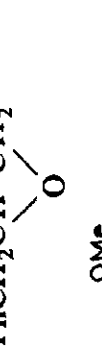
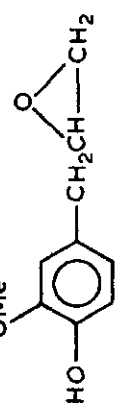
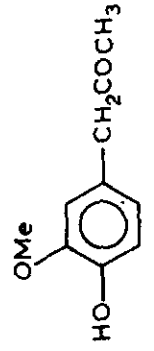
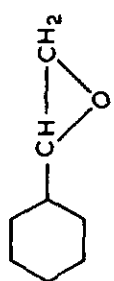
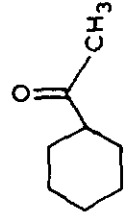
#### Transition-metal catalysts

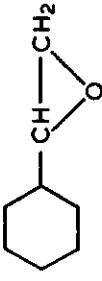
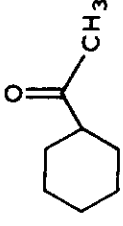

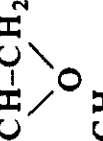
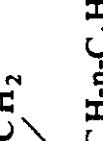


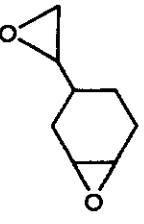
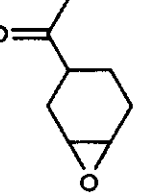
In order to find alternative catalysts to lanthanides we tested various metal derivatives, including some transition-metal salts or complexes. The compounds CoBr<sub>2</sub>, (Co(CO)<sub>3</sub>PPh<sub>3</sub>)<sub>2</sub>, Mn<sub>2</sub>(CO)<sub>10</sub>, Mn(OAc)<sub>2</sub>, (i-PrO)<sub>4</sub>Ti + NaI, AlI<sub>3</sub>, and MnCl<sub>2</sub> were all found to show no catalytic activity. However, MnI<sub>2</sub> was found to catalyze isomerization of terminal epoxides when the reaction was carried out in acetone, in THF or without a solvent; 80% rearrangement took place, to give ketone and aldehyde in ratios which depended on the conditions (see Table 2). The MnI<sub>2</sub> appears to be less reactive than but as selective as t-BuOSmI<sub>2</sub> for formation of ketone when the reaction is performed without solvent, but the selectivity falls when a solvent such as THF or acetone is used (entry 2, Table 2).

During our investigations a report by Eisenmann [8] came to our attention in which it was briefly reported that Co<sub>2</sub>(CO)<sub>8</sub> in methanol catalyzes rearrangement of epoxypropane, 1,2-epoxybutane, 2,3-epoxybutane and epoxycyclohexane to the corresponding ketones. For examination of the effect of this catalyst with 1,2-epoxydodecane **1b** we used the following conditions: 5% mol. equiv. of catalyst, heating 24 h at 40°C. Ketone **2b** was isolated in 70% yield, free from the isomeric aldehyde. This catalytic system under these conditions did not cause rearrangement of internal epoxides such as 4,5-epoxydecane or epoxycyclohexane. In one case, with 2-methyl-1,2-epoxyundecane, we observed deoxygenation of the epoxide, but in very low yield; Co<sub>2</sub>(CO)<sub>8</sub> is known to be a deoxygenation agent for epoxides [15] but when the reaction was carried out in methanol and rearrangement was possible, we found that deoxygenation did not occur.

(Continued on p. 456)

TABLE 2  
EPOXIDE REARRANGEMENTS CATALYZED BY SOME TRANSITION METAL DERIVATIVES

	Epoxide	Catalyst <sup>a</sup> (mol eq.)	Products	(Yield (%)) <sup>b</sup>
1		MnI <sub>2</sub> (0.1)	n-C <sub>10</sub> H <sub>21</sub> COCH <sub>3</sub>	(80)
2		MnI <sub>2</sub> (0.1) in THF	n-C <sub>10</sub> H <sub>21</sub> COCH <sub>3</sub> (80) + n-C <sub>11</sub> H <sub>23</sub> CHO	(3)
3		Co <sub>2</sub> (CO) <sub>8</sub> (0.04)	n-C <sub>10</sub> H <sub>21</sub> COCH <sub>3</sub>	(71)
4		MnI <sub>2</sub> (0.06) <sup>c</sup>	PhCH <sub>2</sub> COCH <sub>3</sub>	(58)
5		Co <sub>2</sub> (CO) <sub>8</sub> (0.05)	PhCH <sub>2</sub> COCH <sub>3</sub>	(92)
6		Co <sub>2</sub> (CO) <sub>8</sub> (0.2)		(50)
7		MnI <sub>2</sub> (0.06) <sup>d</sup>		(51)

8		$\text{Co}_2(\text{CO})_8$ (0.08) <sup>e</sup>		(79)
9	Epoxyoctane	$\text{MnI}_2$ (0.1) <sup>f</sup>	no reaction	
10	Epoxyhexane	$\text{Co}_2(\text{CO})_8$ (0.05)	no reaction	
11	$\text{CH}_3\text{CHOH}(\text{CH}_2)_8\text{CH}-\text{CH}_2$ 	$\text{MnI}_2$ (0.1)	$\text{CH}_3\text{CHOH}(\text{CH}_2)_8\text{COCH}_3$	(59)
12	$\text{CH}_3\text{CHOH}(\text{CH}_2)_8\text{CH}-\text{CH}_2$ 	$\text{Co}_2(\text{CO})_8$ (0.05) <sup>g</sup>	$\text{CH}_3\text{CHOH}(\text{CH}_2)_8\text{COCH}_3$	(75)
13	$\text{CH}_3\text{C}(\text{CH}_2)_8\text{CH}-\text{CH}_2$ 	$\text{Co}_2(\text{CO})_8$ (0.05)	$\text{CH}_3\text{CO}(\text{CH}_2)_8\text{COCH}_3$ (50)	epox. (20)
14	<i>trans</i> - $\text{n-C}_4\text{H}_9\text{CH}-\text{CH-n-C}_4\text{H}_9$ 	$\text{MnI}_2$ (0.09) <sup>h</sup>	$\text{n-C}_4\text{H}_9\text{COCH}_2\text{-n-C}_4\text{H}_9$	(80)
15	<i>trans</i> - $\text{n-C}_4\text{H}_9\text{CH}-\text{CH-n-C}_4\text{H}_9$ 	$\text{Co}_2(\text{CO})_8$ (0.09) <sup>h</sup>	no reaction	
16		$\text{Co}_2(\text{CO})_8$ (0.05) <sup>e</sup>		diketones (9)

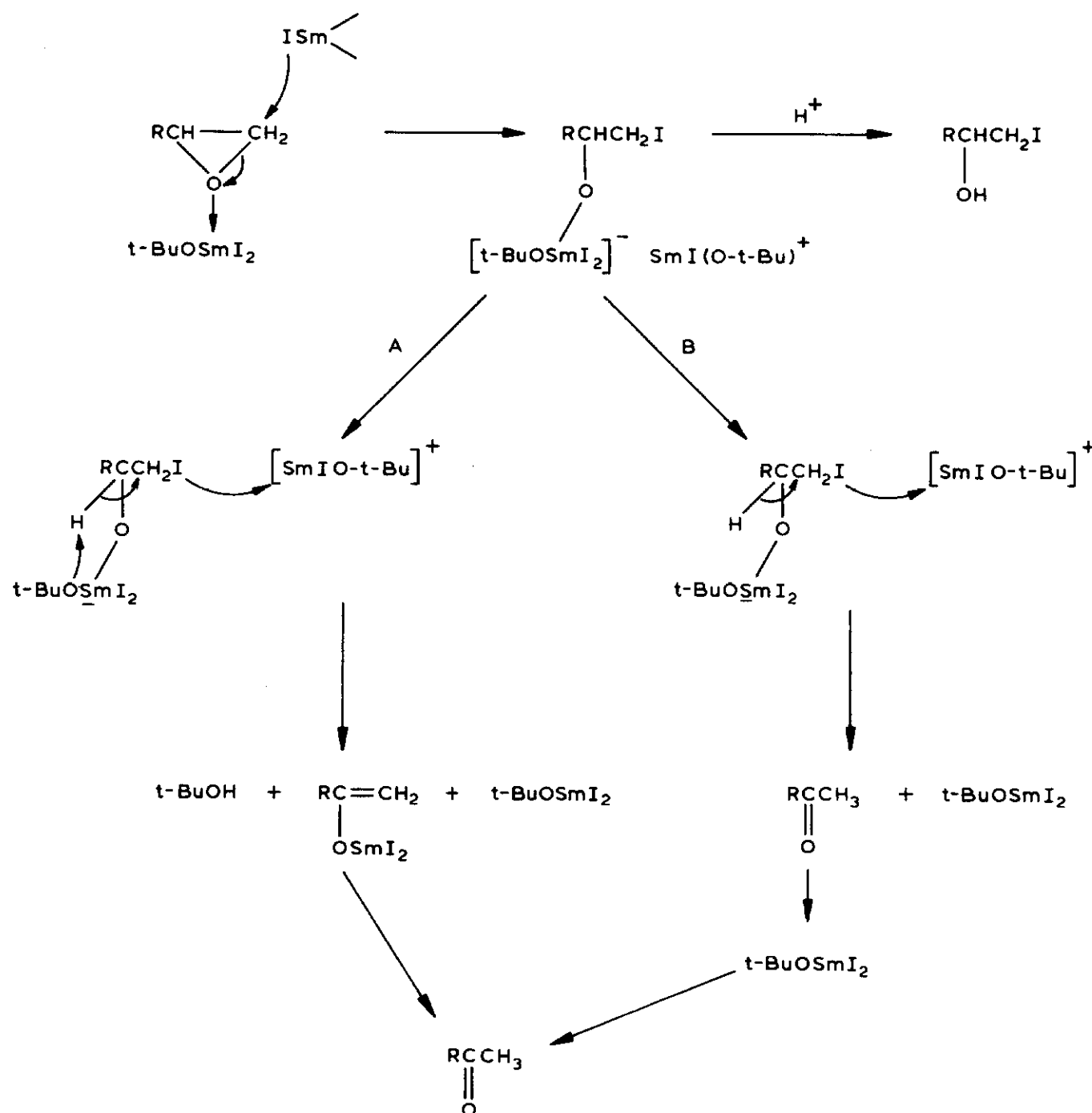
<sup>a</sup> Reaction conditions were as follows: In case of  $\text{MnI}_2$ , 2 h at 70°C with no solvent. In case of  $\text{Co}_2(\text{CO})_8$ , 24 h at 40°C in methanol. <sup>b</sup> Isolated yields. <sup>c</sup> 24 h. <sup>d</sup> 1.3 h, 80°C. <sup>e</sup> 4 days. <sup>f</sup> 12 h. <sup>g</sup> 35 h. <sup>h</sup> 3 h. <sup>i</sup> NMR measurement.

## Discussion

Our investigation, which was not exhaustive, showed that several types of catalysts can promote the conversion of a terminal epoxide of type 1 into a methyl ketone.

### Lanthanide catalysts

The compounds  $\text{SmIO}$  and  $t\text{-BuOSmI}_2$  are effective because a basic center is present (oxygen of a  $\text{Sm-O}$  bond) as well as a soft nucleophile ( $\text{I}^-$ ) and  $\text{Sm(OR)}_3$  or  $\text{SmI}_3$  alone show no catalytic activity. Taking into account the Lewis acidity of trivalent lanthanides the mechanisms shown in Scheme 3 can be considered. The two mechanisms have in common nucleophilic ring opening by iodide after mild epoxide activation by complexation to samarium. This explains the regioselectivity of the attack and the much lower reactivity of internal epoxides. In route A the rearrangement leads to a samarium enolate after a proton abstraction, while in route B the ketone is obtained directly by a hydride shift. The fact that 1,2-epoxy-2-methylundecane is not rearranged (entry 14, Table 1) favours mechanism A.



SCHEME 3

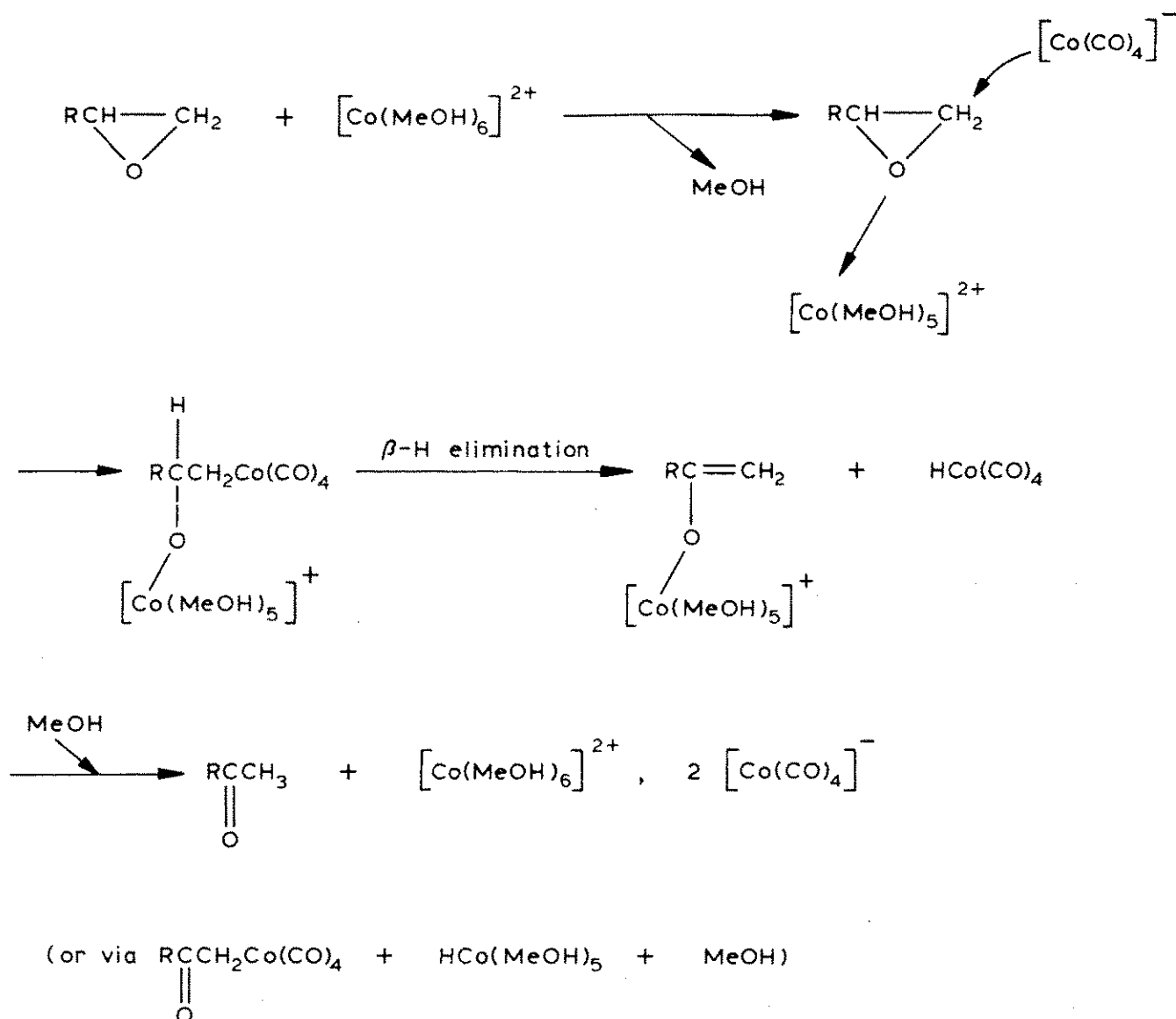


### Dihalogenomanganese

The iodide  $MnI_2$  shows catalytic activity for formation of methyl ketone. No trace of aldehyde is detected when reaction is performed without a solvent (entries 1, 4 and 7, Table 2), while in THF solution about 10% of aldehyde was observed. Some internal epoxides give ketones (entry 14, Table 2), or do not rearrange at all (entry 9, Table 2). A by-product of all the reactions is an iodohydrin (5–10%). There are many similarities to the lanthanide catalysts. It is very probable that the reaction starts as in Scheme 3 by ring opening of epoxide by iodide in a  $S_N2$ -like process. We have not enough information to discuss the mode of formation of the transient iodoalcoholate.  $MnBr_2$  is not active, presumably because the ring opening does not occur.

### The cobalt catalyst, $Co_2(CO)_8$

This catalyst was briefly studied by Eisenmann [8]. Since it was effective only in methanol, the latter author suggested the initial formation of 2  $[Co(CO)_4]^- [Co(MeOH)_6]^{2+}$ , which would account for the evolution of CO when the complex is dissolved in methanol. This species was later characterized [9]. Eisenmann suggested that  $[Co(MeOH)_6]^{2+}$  initiates the reaction by virtue of its Lewis acidity towards the epoxide oxygen. No explanation was offered for the regioselectivity of the rearrangement. We propose the mechanism shown in Scheme 4. The formation of methyl



SCHEME 4

ketone and the reactivity pattern for various epoxides can be readily accounted for in terms of nucleophilic opening of the epoxide by anion  $\text{Co}(\text{CO})_4^-$ . Similar stoichiometric reactions between epoxides and metal carbonyl anions are known, especially with iron [11]. The next step is a classical  $\beta$ -hydrogen elimination which leads to a cobalt enolate or to a  $\alpha$ -substituted ketone depending on the direction of elimination. More work is necessary to clarify the mechanism. We found that  $\text{Pd}(\text{PPh}_3)_4$ , recently used by Noyori for rearrangement of epoxy ketones or diepoxides into  $\beta$ -diketones [12,13] does not bring about rearrangement of the terminal epoxides.

The rhodium complex  $(\text{Rh}(\text{P}(\text{Me})_3)_3\text{Cl})$  was recently reported by Milstein to bring about smooth rearrangement of epoxides into methyl ketones [9,10]; the mechanism was considered to involve a *cis*-hydridoalkylrhodium complex, which could be isolated. A similar mechanism cannot operate in the  $\text{Co}_2(\text{CO})_8$ -catalyzed reaction.

### Concluding remarks

The lanthanide or transition-metal catalysts we have used appear to be very specific for the clean isomerization of  $\text{RCH}_2\text{CH}-\text{CH}_2$  to the corresponding methyl ketone. The rearrangement is slower for epoxides of type  $\text{RCH}(\text{R}')\text{CH}-\text{CH}_2$  and very slow for internal epoxides. 2,2-Disubstituted epoxides  $\text{R}(\text{R}')\text{C}-\text{CH}_2$  do not react. It is thus possible in principle to bring about selective rearrangement of terminal epoxides (see entry 9, Table 1 or entry 16, Table 2). The choice of catalyst will depend on the structural features and the nature of the functional groups in the molecule. For example  $t\text{-BuOSmI}_2$  or  $\text{SmI}_2$  are not suitable for some hydroxy or keto epoxides (entries 20,21, Table 1), while  $\text{Co}_2(\text{CO})_8$  or  $\text{MnI}_2$  give reasonable yields of rearranged products (entries 11–13, Table 2). In contrast,  $t\text{-BuOSmI}_2$  catalyzes the conversion of epoxycyclooctane to cyclooctanone, whereas  $\text{Co}_2(\text{CO})_8$  and  $\text{MnI}_2$  are inactive. We are currently exploring the effectiveness of the various catalysts with polyfunctionalized epoxides and investigating the mechanism of the reactions.

## Experimental section

### Apparatus

Infrared spectra were recorded on a Perkin–Elmer 237 spectrophotometer. Proton magnetic resonance spectra ( $^1\text{H}$  NMR) were recorded on a Perkin–Elmer model R32 spectrometer at 90 MHz. Chemical shifts in  $\text{CDCl}_3$  are reported in ppm relative to  $\text{Me}_4\text{Si}$  as an internal standard. Mass spectra were obtained with a GLC-MS Ribermag R10-10 instrument. Gas chromatographic analyses were carried out on Carlo Erba Fractovap 2150 or 4130, and integrations of peak area were performed with Delsi Icap 5 or Spectra Physics 4270 calculators. Silica gel (Merck 230–240 mesh; 0.040–0.063 mm) was used for flash chromatography.

### Solvents and reagents

The THF must be anhydrous and deoxygenated. It was carefully distilled under nitrogen from sodium benzophenone ketyl. Absolute methanol (Rhône-Poulenc) was

used without further purification. Commercial cerium powder (Labelcomat) was kept in oil and before use was cleaned with pentane in a dry box filled with nitrogen. Samarium powder (40 mesh; packed under argon) was purchased from Labelcomat.

$\text{SmI}_2$ ,  $t\text{-BuOSmI}_2$ ,  $i\text{-PrOCeI}_2$ ,  $(i\text{-PrO})_3\text{Sm}$ ,  $\text{SmI}_3$  were prepared as previously described [7,16]. Commercial  $\text{Sm}_2\text{O}_3$  (Rhône-Poulenc) was used.  $\text{SmIO}$  was prepared by oxidation of  $\text{SmI}_2$  with dry oxygen; 80% of the  $\text{SmI}_3$  formed separated out, and  $\text{SmIO}$  remains in solution along with 20% of  $\text{SmI}_3$ , as indicated by titrations [16]. This solution was used as the catalyst.

Commercially available samples of  $(i\text{-PrO})_4\text{Ti}$ ,  $\text{Co}_2\text{CO}_8$ , anhydrous  $\text{MnCl}_2$ , and  $\text{Mn}_2\text{CO}_{10}$ , were purified before use by distillation, sublimation or recrystallisation. Anhydrous  $\text{MnI}_2$  and  $[\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3]_2$  were prepared by published literature procedures [14,17].  $\text{CoBr}_2$  was obtained from the hexahydrate by drying at  $130^\circ\text{C}$ .

Epoxides were prepared by the standard method from the corresponding olefins and *m*-chloroperoxybenzoic acid. Olefins were commercial samples and were purified by distillation, except for 11-dodecene-2-ol, which was prepared by a Grignard reaction from 10-undecenal, and 11-dodecene-2-one which was obtained by Oppenauer oxidation [7] of the 11-dodecene-2-ol.

The purities of the epoxides were checked by GLC and NMR analysis. 4-Vinylcyclohexene dioxide was shown by GLC analysis to be a mixture of at least three diastereoisomers.

#### *Standard procedure for catalytic isomerization by lanthanide compounds*

A solution of 0.2 mmol of the lanthanide compound in 2.5 ml of THF was placed in a Schlenk tube under argon and a solution of 2 mmol of the epoxide in 2.5 ml of THF was added from a syringe. Stirring for 20 h at room temperature (unless otherwise stated) was followed by hydrolysis and standard work-up [6] to give a crude product, which was purified by distillation or flash chromatography and then analyzed by GLC and by  $^1\text{H}$  NMR spectroscopy and GLC/MS.

#### *Standard procedure for catalytic isomerization by $\text{Co}_2(\text{CO})_8$*

A solution of 0.11 mmol of  $\text{Co}_2(\text{CO})_8$  in 1 ml of methanol was placed in a Schlenk tube under nitrogen and kept at  $35^\circ\text{C}$ ; CO was rapidly evolved and the dark brown solution turned light pink. A solution of 2.6 mmol of the epoxide in 0.5 ml of methanol was then added from a syringe and the mixture was stirred at  $35^\circ\text{C}$  for 24 h (unless otherwise stated). The methanol was evaporated off and the residue purified by distillation or flash chromatography. The product was analyzed by GLC,  $^1\text{H}$  NMR spectroscopy and GLC/MS.

#### *Standard procedure for catalytic isomerization by $\text{MnI}_2$*

Freshly recrystallized  $\text{MnI}_2$  (0.19 mmol) was vacuum dried at  $80^\circ\text{C}$  for 2 h in a Schlenk tube, then the epoxide (3.34 mmol) was added from a syringe. The dark brown mixture was stirred under nitrogen at  $70^\circ\text{C}$  for 2 h, then the crude product was distilled and the distillate analyzed.

*11-Hydroxy-1,2-epoxydodecane.*  $^1\text{H}$  NMR: 3.8 (m)  $\text{CHOH}$ , 1H; 2.9 (m) epoxide, 1H; 2.75 (t) 1H, epoxide); 2.45 (q) 1H, epoxide; 2.0 (s) 1H, (OH); 1.3 (m) 16H,  $(\text{CH}_2)_8$ ; 1.15 (d) 3H,  $\text{CH}_3$ . IR (neat): 3380s, 860m  $\text{cm}^{-1}$ .

*11-Hydroxy-2-dodecanone.*  $^1\text{H}$  NMR: 2.1 (s) 3H,  $\text{COCH}_3$ ; 1.6 (m) 1H, OH; 1.28 (m) 12H,  $(\text{CH}_2)_6$ ; 1.16 (d) 3H,  $\text{CHOHCH}_3$ . IR (Nujol): 3320s, 3250s, 1700s  $\text{cm}^{-1}$ .

*11,12-Epoxy-2-dodecanone.*  $^1\text{H}$  NMR: 2.9 (m) 1H, epoxide; 2.75 (t) 1H, epoxide; 2.5–2.3 (m) 3H, 1H epoxide,  $\text{CH}_2\text{C}=\text{O}$ ; 2.15 (s) 3H,  $\text{CH}_3\text{C}=\text{O}$ ; 1.7–1.25 (m) 14H,  $(\text{CH}_2)_7$ . IR (neat): 1705s, 860m  $\text{cm}^{-1}$ .

*2,11-Dodecanedione.*  $^1\text{H}$  NMR: 2.4 (t) 4H,  $\text{CH}_2\text{CO}$ ; 2.13 (s) 6H,  $\text{CH}_3\text{C}=\text{O}$ ; 1.8–1.2 (m) 12H,  $(\text{CH}_2)_6$ .

*4-Vinylcyclohexene dioxide.*  $^1\text{H}$  NMR: 3.15 (m) 2H, cyclic epoxide; 2.7–2.6 (m) 2H, epoxide; 2.45 (m) 1H, epoxide; 2.2–1 CH,  $\text{CH}_2$ , cycle.

*3,4-Epoxyacetylcyclohexane.*  $^1\text{H}$  NMR: 3.2 (m) 2H, cyclic epoxide; 2.15 (s) 3H,  $\text{CH}_3\text{C}=\text{O}$ . IR: 1705  $\text{cm}^{-1}$ .

The product (mixture of 2 diastereoisomers) was hydrolyzed ( $\text{H}_2\text{O}$ ,  $\text{HClO}_4$  cat.) and benzoated with  $\text{PhCOCl}$  plus pyridine to yield the dibenzoates.

$^1\text{H}$  NMR: 8.3–7.9 (m) 4H ar. *ortho*; 7.7–7.3 (m) 6H, ar. *meta, para*); 5.35 (m) 2H,  $\text{COOCH}$ . IR: 3060w, 1715s, 1600m, 1585w, 1490w, 1450s, 1275s  $\text{cm}^{-1}$ .

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### References

- 1 R.E. Parker and N.S. Isaacs, *Chem. Rev.*, 59 (1959) 737.
- 2 R.J. Gritter, in S. Patai (Ed.), *Chemistry of Functional Groups*, Vol. 3, Wiley, New York, 1967, p. 400.
- 3 A.S. Rao, S.K. Paknikak and J.G. Kirtane, *Tetrahedron*, 39 (1983) 2323.
- 4 *Organic Reactions*, Vol. 29, Wiley, New York, 1983, p. 345.
- 5 (a) J. Delaunay, A. Lebouc, A. Tallec and J. Simonet, *J. Chem. Soc., Chem. Commun.*, (1982) 387; (b) K. Uneyama, A. Isimura, K. Fujii and S. Torii, *Tetrahedron Lett.*, (1983) 2857.
- 6 P. Girard, J.L. Namy and H.B. Kagan, *J. Am. Chem. Soc.*, 102 (1980) 2693.
- 7 J.L. Namy, J. Soupe, J. Collin and H.B. Kagan, *J. Org. Chem.*, 49 (1984) 2045.
- 8 J.L. Eisenmann, *J. Org. Chem.*, 27 (1962) 2706.
- 9 D. Milstein, O. Buchman and J. Blum, *J. Org. Chem.*, 42 (1977) 2299.
- 10 D. Milstein and J.C. Calabrese, *J. Am. Chem. Soc.*, 104 (1982) 3773.
- 11 M. Nitaya and M. Rosenblum, *J. Organomet. Chem.*, 136 (1977) C23.
- 12 M. Suzuki, Y. Oda and R. Noyori, *J. Am. Chem. Soc.*, 101 (1979) 1624.
- 13 M. Suzuki, A. Watanabe and R. Noyori, *J. Am. Chem. Soc.*, 102 (1980) 2095.
- 14 F. Ducelliez, *Bull. Soc. Chim. Fr.*, 13 (1913) 815.
- 15 P. Dowd and K. Kang, *J. Chem. Soc., Chem. Commun.*, (1977) 384.
- 16 J.L. Namy, P. Girard, H.B. Kagan and P. Caro, *Nouv. J. Chim.*, 5 (1981) 479.
- 17 A.R. Manning, *J. Chem. Soc. (A)*, (1968) 1135.