BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 746—749 (1969)

Deoxygenation of Styrene Oxide by Zinc Metal and Lewis Acid

Sotaro Miyano, Mitsuhiko Hida and Harukichi Hashimoto

Department of Synthetic Chemistry, The University of Tokyo, Hongo, Tokyo

(Received June 13, 1968)

Styrene oxide was deoxygenated to styrene in 83% yield by zinc metal and zinc chloride in aqueous ether. Under the same reaction conditions phenyl glycidyl ether gave only 2.8% of phenyl allyl ether, and propylene oxide did not give propylene. Effects of the reaction variables on the deoxygenation of styrene oxide were investigated. The yield of styrene was varied with metal halide in anhydrous THF in the following order; $ZnI_2 > ZnCl_2 \sim ZnBr_2 > AlCl_3 > SnCl_4 > FeCl_3 > NaI \gg MgBr_2$. Styrene was formed from styrene oxide by zinc metal and zinc chloride in *ca.* 50% yield in THF, acetone, acetic acid, and aqueous ethanol, but not in anhydrous benzene. The yield of styrene increased almost proportionally with the increase of the molar ratio of zinc chloride to styrene oxide up to 1 : 1. 2-Phenyl-2-chloroethanol gave styrene when treated with zinc metal in the presence or absence of zinc chloride, but 1-phenyl-2-chloroethanol did not. Possible reaction paths of the deoxygenation of styrene oxide by zinc metal and metal halide were discussed.

It is well known that 1,2-epoxides give halohydrins, rearrange to carbonyl compounds, or polymerize to polyethers when treated with Lewis acids.[1] On the other hand, in the course of the investigation of the reaction of zinc-methylene complex with epoxides,[2] we found that styrene oxide is deoxygenated to styrene by zinc metal and Lewis acid. In this paper, we report further investigation of the reaction.

Experimental

Materials. *Epoxides.* Commercial styrene oxide (bp 80°C/16 mmHg). Propylene oxide (Mitsui Chem. Co.) was refluxed and distilled over KOH (bp 34°C). Phenyl glycidyl ether was obtained by conventional method[4] (bp 118—118.3°C/11 mmHg; lit. bp 114—118°C/12 mmHg).

Metal Halides. Anhydrous magnesium bromide was prepared from magnesium turnings and bromine in THF or ether.[5] Anhydrous stannous chloride was prepared by dehydration of $SnCl_2 \cdot 2H_2O$ with acetic anhydride.[6] Zinc halides were either prepared from zinc dust and hydrogen halides, or were of commercial reagent grade.

Styrene Chlorohydrins. 2-Phenyl-2-chloroethanol was obtained by adding HCl gas to styrene oxide in chloroform[7] (bp 97—98.5°C/2.5 mmHg; lit. bp 97—99°C/1.2 mmHg). 1-Phenyl-2-chloroethanol was obtained by the addition of hypochlorite to styrene[8] (bp 106—109°C/7.5 mmHg; lit. bp 110—111°C/6 mmHg).

All solvents were purified as usual before use. Zinc-copper couple was prepared by LeGoff's method[9] and washed several times with the solvent used in the reaction.

Reaction of Styrene Oxide with Zinc Chloride and Zinc-Copper Couple. The reaction was carried out in a 100 m*l*, three necked reaction flask equipped with a dropping funnel, thermometer and reflux condenser topped with calcium chloride drying tube.

Freshly prepared zinc-copper couple obtained from 0.12 g-atom of zinc and 0.5 g of $Cu(OAc)_2 \cdot H_2O$ were mixed with 0.051 mol of zinc chloride and 30 m*l* of THF in a reaction flask. Into the mixture, styrene oxide (0.050 mol) dissolved in 20 m*l* of THF was added for 1 hr at 34—35°C with stirring. After the addition had been completed, reaction was continued for another 5 hr at 35°C with stirring. Then the flask was chilled in ice-water, and the amount of styrene was determined by g.l.c. with *t*-butylbenzene as an internal standard. The reaction mixture was treated as reported previously.[3] Styrene was isolated by distillation and identified by elemental analysis and IR spectrum; bp 58°C/39 mmHg (Found: C, 91.21; H, 7.85%). From the result of g.l.c. analysis the minimum amount of the reacted styrene oxide seemed to be determined, because

---

[1] F. Johnson, "Friedel-Crafts and Related Reactions," Vol. IV, ed. by G. A. Olah, Interscience Publishers, New York-London-Sydney (1965), p. 33.

[2] To be published. For the previous work, see Ref. 3.

[3] a) S. Miyano, M. Hida and H. Hashimoto, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **69**, 2134 (1966). b) H. Hashimoto, M. Hida and S. Miyano, *J. Organometal. Chem.*, **10**, 518 (1967). c) S. Miyano, M. Hida and H. Hashimoto, *ibid.*, **12**, 263 (1968).

[4] K. Furukawa and R. Oda, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **55**, 673 (1952).

[5] H. O. House, *J. Am. Chem. Soc.*, **77**, 3070 (1955).

[6] J. W. W. Williams, "Organic Syntheses," Coll. Vol. III, p. 627 (1955).

[7] G. Berti, F. Bottari, P. L. Ferrarini and B. Macchia, *J. Org. Chem.*, **30**, 4091 (1965).

[8] W. S. Emerson, *J. Am. Chem. Soc.*, **67**, 516 (1945).

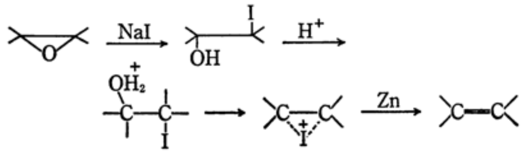
[9] E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).

styrene oxide showed all the same retention time on g.l.c. (DOP diasolid column) as phenylacetaldehyde, which may be present in the reaction mixture as the result of rearrangement of styrene oxide.

Reaction of Propylene Oxide with Zinc Metal and Zinc Iodide in Aqueous Ether. Aqueous solution of 57% HI (HI; 0.20 mol, H_2O; 1.09 mol) was added to the zinc dust (0.588 mol) covered with 100 m*l* of ether with stirring. After the evolution of gas subsided, propylene oxide (0.20 mol) dissolved in 50 m*l* of ether was dropped to the stirred suspension for 1 hr under gentle reflux (34—35°C). The reaction was continued for another 5 hr at 35°C. Gas evolved during the reaction was introduced with nitrogen into an another flask containing bromine - CCl_4 solution, in which propylene was converted into 1,2-dibromopropane. The dibromide was isolated by distillation, and confirmed by NMR and IR spectra. The yield was determined by g.l.c.

Results and Discussion

Reaction of Epoxides with Zinc Metal and Zinc Halides. Table 1 shows the results of the reaction of styrene oxide, propylene oxide and phenyl glycidyl ether with zinc metal and zinc halide in THF or aqueous ether. Styrene oxide was deoxygenated to styrene in high yields. Propylene oxide gave no propylene, but afforded a 4 : 1 mixture of 1-chloro-2-propanol and 2-chloro-1-propanol (bp 80.5—80.6°C/164 mmHg, 56% based on propylene oxide) (No. 5). When propylene oxide was treated with zinc iodide and zinc, propylene was obtained only in the low yield, but 1-iodo-2-propanol was also isolated in 48% yield based on propylene oxide; bp 76°C/22 mHg (No. 7). On the other hand, propylene was obtained in good yield in the presence of sodium iodide, zinc dust and sodium acetate in aqueous acetic acid, as described by Cornforth *et al.*[10] (No. 9). They reported the deoxygenation of alkylene oxides to alkenes by zinc metal and sodium iodide in acetic acid, and suggested the following reaction mechanism:



However, in our case, at least in anhydrous THF, the above protonation and dehydration mechanism may not be responsible for the styrene formation from styrene oxide with zinc metal and zinc halides (*vide infra*).

Deoxygenation of Styrene Oxide. *Effect of Metal Halides.* All metal halides except anhydrous magnesium bromide in combination with zinc-copper couple gave fairly good yield of styrene from styrene oxide (Table 2). The inactivity of anhydrous magnesium bromide for styrene formation has not yet been understood clearly. Even sodium iodide gave styrene in a lower yield, but the addition of zinc acetate improved the yield of styrene. In the latter case, it seems that the resultant zinc iodide was an active catalyst. Lower yield of styrene in anhydrous THF compared with that in

TABLE 1. REACTION OF EPOXIDES WITH ZINC METAL AND ZINC HALIDE[a)]

No.	Epoxide[b)]		Reaction condition		Zn	Olefin (%)[c)]	Solvent[d)]
1	SO	0.025	$ZnCl_2$ H_2O	0.014 0.107	0.073	83	E 50(m*l*)
2		0.050	$ZnCl_2$	0.051	0.12[e)]	51	T 50
3		0.051	$ZnCl_2$	0.051	—	0	T 50
4		0.050			0.12[e)]	1.7	T 50
5	PO	0.020	$ZnCl_2$ H_2O	0.10 0.76	0.49	0	E 150
6		0.10	$ZnCl_2$	0.10	0.51[e)]	1.1	T 100
7		0.20	ZnI_2 H_2O	0.10 1.1	0.49	6.5	E 150
8		0.10	ZnI_2	0.10	0.51[e)]	6.4	T 100
9		0.20	NaI NaOAc H_2O	0.35 0.21 0.40	0.78	74	A 100
10	PGE	0.10	$ZnCl_2$ H_2O	0.051 0.38	0.26	2.8	E 200

a) 35°C, 6 hr.
b) SO: styrene oxide, PO: propylene oxide, PGE: phenyl glycidyl ether.
c) Based on epoxide used.
d) E; ether, T; THF, A; acetic acid.
e) Zinc-copper couple was used.

---

[10] J. W. Cornforth, R. H. Cornforth and K. K. Mathew, *J. Chem. Soc.*, **1959**, 112.

TABLE 2. EFFECT OF METAL HALIDE ON DEOXYGENATION OF STYRENE OXIDE[a]

Halide	$PhCH=CH_2$(%)	Minimum conversion of SO (%)
$ZnCl_2$	51	82
$ZnBr_2$	47	82
$ZnBr_2$[b]	51	
$ZnBr_2$[c]	49	98
ZnI_2	67	97
$MgBr_2$	0.9	73
$MgBr_2 \cdot 3H_2O$	72	100
$FeCl_3$	17	95
$AlCl_3$	40	100
$SnCl_4$	32	77
NaI	13	73
NaI $Zn(OAc)_2$[d]	30	79

a) Styrene oxide: 0.050 mol, solvent: THF 50m*l*, halide: 0.050 mol, Zn-Cu: 0.12 mol, 35°C, 6 hr.

b) The reaction was carried out in the scale of twice.

c) $ZnBr_2$ was prepared from zinc duct and bromine *in situ*. Reaction was carried out for 3 hr at 60°C.

d) 0.025 mol.

aqueous ether may be due to side reactions such as rearrangement to phenylacetaldehyde.[1]

Effect of Reagent Molar Ratio. The effect of the amount of zinc chloride on the styrene yield was shown in Fig. 1. No styrene was obtained when styrene oxide was treated only with zinc chloride, or only with zinc metal. The presence of both zinc metal and metal halides is necessary for styrene formation.

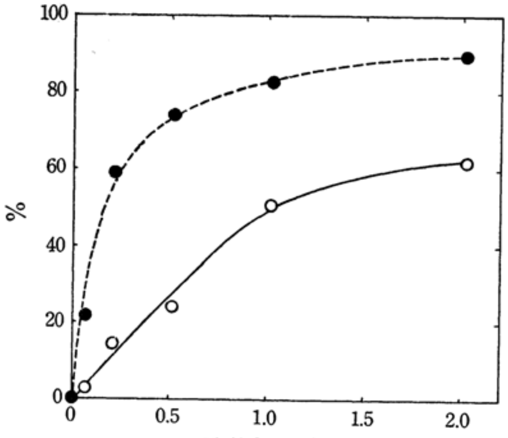


Fig. 1. Effect of the molar ratio of zinc chloride to styrene oxide.
Styrene oxide: 0.050 mol, solvent: THF 50 *ml*, 35°C, 6 hr.
○ Styrene yield.
● Minimum conversion of styrene oxide.

Solvent Effect. Styrene oxide was deoxygenated to styrene by zinc-copper couple and zinc chloride even in protic solvents such as acetic acid and aqueous ethanol, but was not in anhydrous benzene (Table 3). These results may indicate the ionic character of this styrene formation reaction (*vide infra*).

TABLE 3. SOLVENT EFFECTS FOR THE DEOXYGENATION OF STYRENE OXIDE[a]

$PhCH=CH_2$ (%)	Minimum conversion of SO (%)	Solvent
51	82	THF
57	89	acetone
0	42	PhH
55	100	aq. EtOH
43	79	AcOH

a) Styrene oxide: 0.050 mol, Zu-Cu: 0.12 mol, $ZnCl_2$: 0.050 mol, solvent: 50 m*l*, 35°C, 6 hr.

Reducing Reagents Other than Zinc Metal. Zinc metal can be replaced by triphenylphosphine[11] or magnesium metal, though the yield of styrene was reduced. However, stannous chloride was not effective (Table 4). Magnesium metal was used in the form of turnings, and triphenylphosphine may form acid-base complex with zinc chloride as suggested by Wittig and Haag.[11] These factors may partly be responsible for the lower yield of styrene.

TABLE 4. REDUCING REAGENTS FOR THE DEOXYGENATION OF STYRENE OXIDE[a]

Reducing reagent		$PhCH=CH_2$ (%)	Minimum conversion of SO (%)
Zn-Cu	0.12	51	82
Mg	0.12	16	93
Ph_3P	0.16	38	97
$SnCl_2$	0.060	2.1	47

a) Styrene oxide: 0.050 mol, $ZnCl_2$: 0.050 mol, THF 50 m*l*, 35°C, 6 hr.

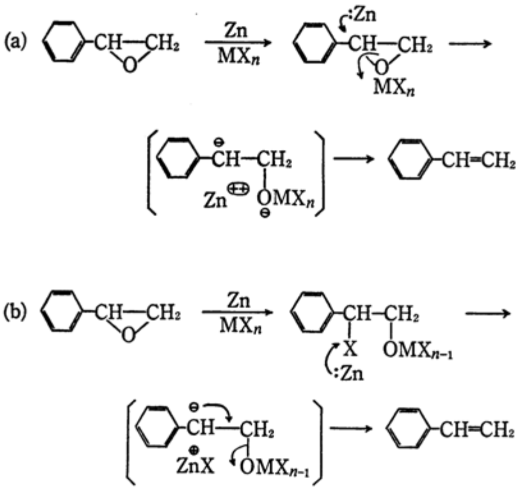
Reaction of Styrene Chlorohydrins and Mechanistic Consideration of Deoxygenation of Styrene Oxide. Reactions of 1-phenyl-2-chloroethanol and 2-phenyl-2-chloroethanol with zinc metal in the presence or absence of zinc chloride were compared with those of styrene oxide (Table 5). Though zinc can not eliminate hypochlorite from alkyl chlorohydrins[10,12] except from those of

---

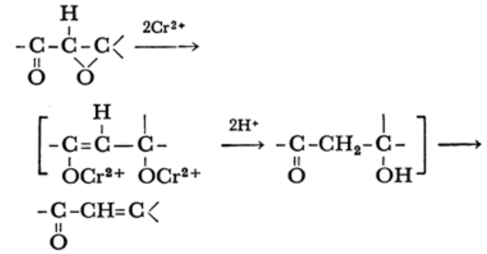
11) G. Wittig and H. Haag, *Chem. Ber.*, **88**, 1654 (1955).

12) D. V. Banthorpe, "Elimination Reactions," ed. by E. D. Hughes, Elsevier Pub. Co., Amsterdam-London-New York (1963). p. 136.

special steroidal series,[13] benzylic chloride in 2-phenyl-2-chloroethanol was active enough to give styrene. It may be noticeable that the dechlorohydrination of *erythro*-1,2-diphenyl-2-chloroethanol by zinc dust in acetic acid is well known as the synthetic method of *trans*-stilbene.[14] From these facts the following two reaction paths seem to be probable for the formation of styrene from styrene oxide by zinc metal and metal halides.



Path (a) shows a concerted electron transfer from zinc to benzylic carbon, followed by an elimination of $OMXn^{-2}$. Path (b) shows the formation of metal salt of 2-phenyl-2-haloethanol as an intermediate. The formation of organozinc intermediate is excluded since no phenethyl alcohol was formed even in acetic acid. Several authors suggested the formation of transient carbanion in the elimination of hypobromite from boromohydrins by zinc metal.[15] Cole and Julian showed that α,β-epoxy ketones and styrene oxide are deoxygenated to olefins by chromous chloride in acetic acid.[16] They suggested the direct attack of chromous ion to α,β-epoxy ketones as follows:



Though they did not mention the mechanism of styrene formation from styrene oxide by chromous chloride, the above two reaction paths (a and b) may be plausible also.[17] Kharasch *et al.* suggested radical chain mechanism for the propylene formation from propylene oxide or two isomers of propylene chlorohydrins by Grignard reagent in the presence of transition metal halide.[18] But styrene was not formed from 2-phenyl-2-chloroethanol by phenylmagnesium bromide in the presence of zinc chloride in THF (Table 5). Further investigation seems to be necessary for the detailed discussion of the reaction of epoxides with zinc metal and metal halide.

TABLE 5. COMPARISON OF THE REACTION OF STYRENE OXIDE AND STYRENE CHLOROHYDRINS[a)]

Ph-	$\times 10^{-2}$	Reaction condition	$\times 10^{-2}$	Solvent	PhCH=CH$_2$ (%)
$-CH-CH_2$ \O/	2.5	Zn ZnCl$_2$ H$_2$O	7.3 1.4 11	E 50 m*l*	83
	5.0	Zn-Cu ZnCl$_2$	12 5.1	T 50	51
	5.0	Zn-Cu	12	T 50	1.7
$-CH-CH_2$ Cl OH	1.6	Zn ZnCl$_2$ H$_2$O	4.6 0.75 5.6	E 30	58
	1.7	Zn H$_2$O	4.6 6.2	E 30	3.6
	1.6	PhMgBr ZnCl$_2$	2.7 1.6	T 30	0
$-CH-CH_2$ OH Cl	1.5	Zn-Cu	6.1	E 30	1.1

a) 35°C, 6 hr.

This work was partly supported by a grant from the Ministry of Education.

---

[13] S. Mori, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **70**, 257 (1949).

[14] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston (1964), p. 219.

[15] a) D. R. James, R. W. Rees and C. W. Shoppee, *J. Chem. Soc.*, **1955**, 1370. b) H. O. House and E. S. Ro, *J. Am. Chem. Soc.*, **80**, 182 (1958). c) S. J. Cristol and L. E. Rademacher, *ibid.*, **81**, 1600 (1959).

[16] W. Cole and L. Julian, *J. Org. Chem.*, **19**, 131 (1954).

[17] Chromous chloride was prepared by the reduction of chromic chloride by zinc metal, and zinc chloride or chromic chloride seems to act as Lewis acid.

[18] M. S. Kharasch, L. Biritz, W. Nudenberg, A. Bhattacharya and N. C. Yang, *J. Am. Chem. Soc.*, **83**, 3229 (1961).