Tetrahedron. Vol. 29, pp. 4093 to 4097. Pergamon Press 1973. Printed in Great Britain

THE DEOXYGENATION IN THE CATALYTIC HYDROGENOLYSIS OF STYRENE OXIDES

S. Mitsui, S. Imaizumi, M. Hisashige[a] and Y. Sugi[b]
Department of Applied Science, Faculty of Engineering, Tohoku University, Sendai 980, Japan

(*Received in Japan* 18 *July* 1973; *Received in the UK for publication* 31 *August* 1973)

Abstract—In order to obtain information on deoxygenation in the hydrogenolysis of epoxides, a series of substituted styrene oxides were hydrogenolysed using Raney Ni, Pd and Pt as catalysts. Over Raney Ni, these styrene oxides gave ethylbenzenes (30–50%) as well as 2-phenylethanols. The ethylbenzenes were proved to be produced *via* the corresponding styrenes. These deoxygenations can be explained by the previously proposed mechanism involving the radical cleavage reaction. The hydrogenolyses over Pd gave selectively 2-phenylethanols. Over PtO_2, the deoxygenations were less than 10% except 3,4-dichlorostyrene oxide (V) which gave 3,4-dichloroethylbenzene in 75% yield. However, the significant deoxygenations were observed in all hydrogenolyses over Pt-black. The ethylbenzenes were proved to be produced directly from the corresponding styrene oxides, but not from 1-phenylethanols as proposed by Park and Fuchs. These deoxygenations are considered to occur *via* styrenes by *trans*-β-elimination. The difference in behaviour over Pt catalysts can be ascribed to the alkaline substances contained in the catalyst. The significant deoxygenation in the hydrogenolysis of V over PtO_2 can be explained by the effect of a trace of HCl produced from the substrate and/or products.

Deoxygenations have often been observed in the hydrogenolysis of epoxides.[1-6] Park and Fuchs[2] reported that the hydrogenolysis of *p*-bromo- and 3,4-dichlorostyrene oxides over a PtO_2 gave 1-phenylethanols as well as 2-phenylethanols, and the 1-phenylethanols underwent the subsequent hydrogenolysis to the corresponding ethylbenzenes. However, styrene oxide and its *p*-methyl derivative were hydrogenolysed selectively to 2-phenylethanol.[2] The authors considered from these results that the direction of ring-opening of epoxides by hydrogen was determined by the electronic effects of the substituents. On the other hand, we have described that more than 50% phenylcyclohexane was produced *via* 1-phenylcyclohexene in the Raney Ni catalysed hydrogenolysis of 1-phenyl-7-oxabicyclo [4.1.0]heptane, and proposed a possible mechanism.[1] In this work we studied the hydrogenolysis of a series of styrene oxides (I–VI) in order to obtain more detailed information on the deoxygenation.

RESULTS AND DISCUSSION

Raney Ni *catalyst.* The data in Table 1 summarize the hydrogenolysis of a series of styrene oxides (I–VI) over Raney Ni. These styrene oxides gave ethylbenzenes (30–50%) as well as 2-phenylethanols, and scarcely any effect of substituents was observed. No 1-phenylethanols could be detected during the reactions in all cases. The competitive hydrogenation of an equimolecular mixture of styrene oxide (I) and 1-phenylethanol also indicates that the amount of the latter compound was constant until I was consumed. Table 2 shows the dependence of the conversion on the deoxygenation in the hydrogenolysis of I. The deoxygenated products, ethylbenzene and styrene, were obtained significantly at an early stage of the reaction, and ethylbenzene was formed *via* styrene. The production of 2-phenylethanol increased as the reaction proceeded. A similar trend was also observed in the hydrogenolysis of p-methylstyrene oxide (II). These results eliminate the possibility that 1-phenylethanols are intermediates of ethylbenzenes, and indicate clearly that the deoxygenation of styrene oxides over Raney Ni proceeds *via* corresponding styrenes. The hydrogenolysis of optically active α-methylstyrene oxide (VI) occurred with the slightly predominant retention of configuration.[7] These deoxygenations can be explained by a previously proposed mechanism as shown in Scheme 1.[1]

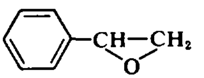
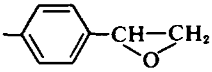
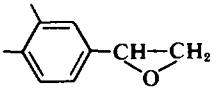
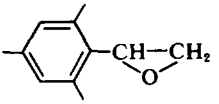
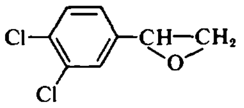
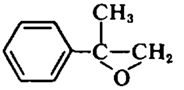
The strong adsorption of oxygen and phenyl groups increases the strain in the epoxy-ring, and the styrene oxide **1** will form the radical **2** as well as the π-benzyl complex **3**.[1] The radical **2** will yield competitively the styrene **4** and the complex **3**. The significant deoxygenation in an early stage of the reaction indicates that the epoxide will tend to cleave into the radical over fresh and active Raney Ni. As the reaction proceeds, the production of the radical will decrease because of aging of the catalyst. This consideration is supported by the fact that the deoxygenation increases by increasing the

---

[a] Present address: Denki Kagaku Co. Ltd., Ichihara-shi, Chiba-ken 290.

[b] Present address: National Chemical Laboratory for Industry, Mita, Meguro-ku, Tokyo 153. The correspondences should be addressed to this author.

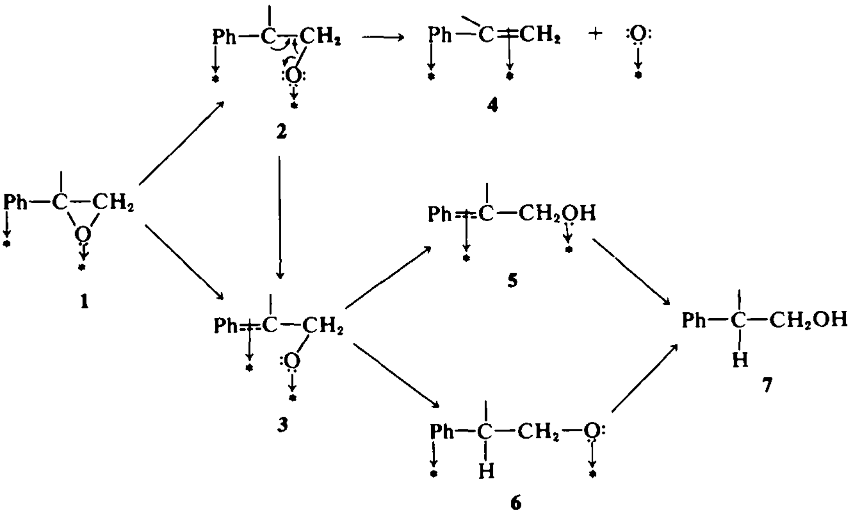
Table 1. The hydrogenolysis of styrene oxides over Raney Ni

Substrate	Catalyst[a] (g)	Products (%) Ethyl-benzene	Products (%) 2-Phenyl-ethanol
 (I)	0·05	23	77
	0·4	35	65
	1·0	56	44
	0·4[b]	7	93
	0·4[c]	12	88
 (II)	0·4	39	61
	0·4e[c]	13	87
 (III)	0·4	35	65
 (IV)	0·4	40	60
 (V)	0·4	50	50
 (VI)	0·4	36	64

Substrate: 4 mmole. EtOH: 10 ml. Under 1 atm and 25°.
[a] Wet weight with EtOH. [b] Under 100 atm. [c] NaOH (1 mmole) was added.

amount of Raney Ni as shown in Table 1. Moreover, the formation of ethylbenzene under 100 atm by hydrogen was lower than that under 1 atm; the hydrogen addition to the radical or the nucleophilic reaction becomes dominant rather than the formation of styrene as the hydrogen pressure increases.

The addition of sodium hydroxide to the reaction decreases the formation of ethylbenzenes, as shown in Table 1. The hydrogenolysis of optically



Scheme 1

Table 2. Dependence of the conversion on the deoxygenation in the hydrogenolysis of styrene oxide (I) over Raney Ni

Conversion (%)	Products (%)		
	Ethylbenzene	Styrene	2-Phenylethanol
5	20	40	40
20	25	25	50
40	20	6	74
95	25	—	75

Substrate: 4 mmole. EtOH: 10 ml. Raney Ni 0·4 g (wet weight with EtOH).

active VI proceeded with predominant inversion of configuration in the presence of sodium hydroxide.[7] The presence of sodium hydroxide on the catalyst surface will decrease the adsorptivity of the epoxy-oxygen, and promote the "SN 2" process, and, consequently, result in the decreased deoxygenation.

Pd catalyst. The hydrogenolysis of styrene oxides (I–VI) yielded selectively 2-phenylethanols; scarcely any deoxygenation was observed. Optically active VI was hydrogenolysed predominantly to configurationally inverted 2-phenylpropanol.[7] This result indicates that the hydrogenolysis of these styrene oxides also proceeds predominantly *via* "SN 2" process as shown in Scheme 2. However, the hydrogenolysis of 2-phenylpropane-1,2-diol, which involves the same π-benzyl complex **11**, gave 2-phenylpropane (24%) as well as 2-phenylpropanol.[8] Similar phenomena were observed in the hydrogenolysis of 1-phenyl-7-oxabicyclo- [4.1.0] heptane[1] and 1-phenylcyclohexane-1,2-diol.[9] Smith and Roth[10] have described that a benzyl carbon metal bond will not achieve the maximum overlap because of π-complexing of phenyl to the surface, and the result of this effect is to increase the rate of the hydrogen addition to the complex. These facts indicate that the π-benzyl complex **9** will yield the alkoxide anion **10** rather than the π-benzyl complex **11**.

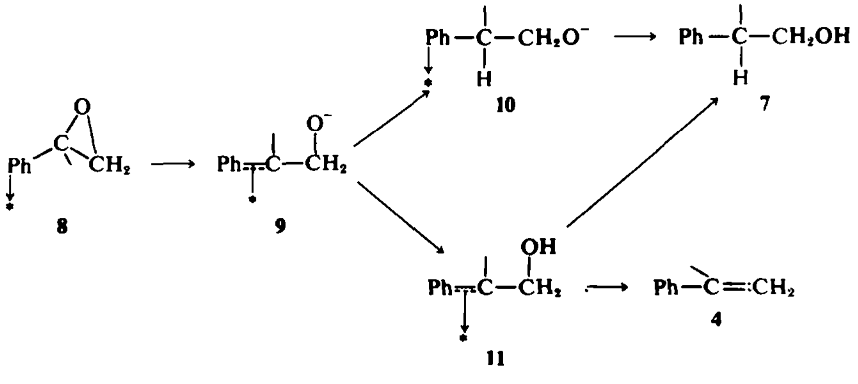
Pt catalysts. Table 3 shows the hydrogenolysis of styrene oxides (I–VI) over Pt catalysts. The deoxygenations over PtO_2 were less than 10% except the case of 3,4-dichlorostyrene oxide (V), which gave 3,4-dichloroethylbenzene in 75% yield. However, significant deoxygenations were observed in all hydrogenolyses over Pt-black.[c] In these cases, no 1-phenylethanols were obtained.

Part and Fuchs[2] stated that V gave 1-(3,4-dichlorophenyl)ethanol as well as 2-(3,4-dichlorophenyl)ethanol over PtO_2, and 3,4-dichloroethylbenzene was produced by the subsequent hydrogenolysis of the former product. Table 4 shows the dependence of the conversion on the deoxygenation in the hydrogenolysis of V over PtO_2. The selective production of 3,4-

Table 3. The hydrogenolysis of styrene oxides over Pt catalysts

Substrate	Catalyst	Products (%)	
		Ethylbenzene	2-Phenylethanol
I	PtO_2	8	92
	Pt-black	44	56
II	PtO_2	6	94
	Pt-black	50	50
III	PtO_2	4	96
	Pt-black	41	59
IV	PtO_2	15	85
	Pt-black	27	73
V	PtO_2	75	25
	Pt-black	73	27
VI	PtO_2	6	94
	Pt-black	58	42

Substrate: 4 mmole. EtOH: 10 ml. Catalyst: PtO_2, 50 mg. Pt-black, 50 mg (as PtO_2).



SCHEME 2

---

[c] This catalyst was prepared by the reduction of PtO_2 with hydrogen, and washed well with water to remove alkaline substances.

Table 4. Dependence of the conversion on the deoxygenation in the hydrogenolysis of 3,4-dichlorostyrene oxide (V) over PtO_2

	Products (%)	
Conversion (%)	3,4-Dichloroethylbenzene	2-(3,4-Dichlorophenyl)ethanol
16	100	—
30	65	35
75	52	48

V: 3 mmole. PtO_2: 4 mg. EtOH: 10 ml.

dichloroethylbenzene was observed at an early stage of the reaction. 2-(3,4-Dichlorophenyl)ethanol increased as the reaction proceeded, and no 1-(3,4-dichlorophenyl) ethanol was detected during the reaction. There is also a possibility that no 1-(3,4-dichlorophenyl) ethanol could be detected because of its rapid hydrogenolysis. However, the competitive hydrogenation of an equimolecular mixture of V and 1-(3,4-cichlorophenyl)ethanol over PtO_2 indicates that the amount of the latter compound was constant until V was consumed. These facts eliminate the possibility of the deoxygenation *via* 1-(3,4-dichlorophenyl)ethanol.

As shown in Table 3, the significant deoxygenations were observed over Pt-black in contrast with PtO_2. These differences are ascribed to the alkaline substances contained in the Pt catalyst. In order to confirm the possibility of this assumption, the effect of HCl and *o*-dichlorobenzene on the deoxygenation was studied as shown in Table 5. The hydrogenolysis of I over PtO_2 in the presence of a micro drop of conc HCl resulted in significant formation of ethylbenzene. The presence of *o*-dichlorobenzene in the reaction mixture also increased the deoxygenation of I; this can be ascribed to a trace of HCl formed by the hydrogenolysis of *o*-dichlorbenzene. These results suggest that a trace of alkaline substances in PtO_2 will hinder the deoxygenations of styrene oxides. The significant deoxygenation in the hydrogenolysis of V can be explained by the effect of a trace of HCl formed by the hydrogenolysis of the substrate and/or products;[d] the alkaline substances in PtO_2 will neutralize a trace of HCl.

Table 5. The effect of additive on the hydrogenolysis of styrene oxide (I) over PtO_2

	Products (%)	
Additive	Ethylbenzene	2-Phenylethanol
o-Dichlorobenzene (4 mmole)	62	38
Conc-HCl (a micro drop)	70	30
—	8	92

I: 4 mmole. PtO_2: 50 mg. EtOH: 10 ml.

The hydrogenolysis over Pt catalyst is complicated because of these alkaline substances. However, optically active VI was hydrogenlysed with predominant inversion of configuration not only over PtO_2 but also over Pt-black. Pt-black contains less alkaline substances than PtO_2, because alkaline substances are decreased by washing with water. These facts indicate that the hydrogenolysis of styrene oxides (I–VI) can be expected to occur *via* a "SN 2" process. The π-benzyl complex **9** yields the complex **11** as well as the alkoxide anion **10**. In the deoxygenation over Pt-black, the hydrogenolysis probably proceeds *via* **11**, and the styrene is produced by the *trans*-β-elimination.[9] Since alkaline substances stabilize the alkoxide anion, the hydrogenolysis over PtO_2 probably proceeds mainly *via* **10**.

The differences of Pd and Pt catalysts can be ascribed to the difference in the nature of the carbon–metal bond: this depends on this bond length, polarizability of this bond, and others. There is also a possibility that the bases in the catalyst affect the reaction. Further investigations are desirable.

EXPERIMENTAL

Materials. Styrene oxide was prepared by the procedure of Ogata and Sawaki.[11] α-Methylstyrene oxide and 2-phenylpropane-1,2-diol were obtained by the methods described previously.[7] Other styrene oxides were synthesized from corresponding phenacylbromides *via* their bromohyrins.[12]

Catalysts. Raney Ni was prepared by the W-4 method.[13] Platinum oxide (PtO_2) was purchased from Wako Junyaku Co. Ltd., Osaka, Japan. Platinum black (Pt-black) was obtained by the reduction of PtO_2 with H_2, and by washing well with H_2O. Pd, 5% on charcoal, was prepared by the procedure in the literature.[14]

Hydrogenolyses. The hydrogenolyses were conducted under 1 atm and 25°, using EtOH as solvent. The mixtures were analysed by a Hitachi F-6 or K-53 gas chromatograph equipped with a Carbowax Golay column and with a Flame Ionization Detector.

REFERENCES

[1] S. Mitsui, Y. Sugi, M. Fujimoto, and K. Yokoö, *Tetrahedron*

[2] G. J. Park, and R. Fuchs, *J. Org. Chem.* **22**, 93 (1957)

[3] D. R. Howton, and R. W. Kaiser, *Ibid.* **29**, 2420 (1964)

[4] D. Cornet, Y. Gault, and F. G. Gault, *Proc. 3rd Int. Congr. Catal., Amsterdam, 1964*, p. 1185 (1965)

---

[d] No dechlorinated products could be detected by gas chromatographic analyses.

[5] S. Nishimura, M. Shiota, and A. Mizuno, *Bull. Chem. Soc. Japan* **37**, 1207 (1964)
[6] H. Inamura, *Nippon Kagaku Zasshi* **88**, 648 (1967)
[7] Mitsui, and S. Imaizumi, *Ibid.* **86**, 219 (1965)
[8] S. Mitsui, and S. Imaizumi, *Ibid.* **86**, 232 (1965)
[9] S. Mitsui, M. Fujimoto, T. Sukegawa, and Y. Nagahisa, *Kogyo Kagaku Zasshi* **73**, 97 (1970)
[10] G. V. Smith, and J. A. Roth, *J. Am. Chem. Soc.* **88**, 3879 (1966)
[11] Y. Ogata, and Y. Sawaki, *Tetrahedron* **20**, 2065 (1964)
[12] F. Fuchs, *J. Am. Chem. Soc.* **78**, 5612 (1956)
[13] H. Adkins, and A. A. Pavlic, *Ibid.* **69**, 3039 (1947)
[14] E. Horning, *Organic Syntheses*, coll. Vol. III, 868 (1955)