

Selective Isomerization of Aryl Substituted Epoxides to Aldehydes Via Iron Lewis Acid Catalysis

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Received 14 January 1998; revised 5 February 1998; accepted 11 February 1998

Abstract: The iron Lewis acid $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{THF})]^+\text{BF}_4^-$ (**2**) catalyzes the ring opening isomerization of aryl substituted epoxides (**1**) to aldehydes (**3**) in excellent yield. © 1998 Elsevier Science Ltd. All rights reserved.

Epoxides are cyclic ethers that are highly reactive compounds known to undergo ring opening reactions. Ring opening can create various functional groups such as alcohols, diols, aldehydes, alkanes, alkenes, and ketones. The conversion of the ring to various groups is relatively straightforward, except for the isomerization of epoxides to aldehydes. There are few efficient procedures in the literature for this isomerization,¹ and in most cases it is not selective; often producing a mixture of aldehydes and ketones². Recently, transition metals have been used as effective catalysts for the rearrangement of epoxides to carbonyl compounds³. However, this rearrangement by transition metals is also not selective, producing a mixture of aldehydes and ketones along with alkenes.³ As far as we know, there is no efficient procedure in the literature for the transition metal catalyzed rearrangement of aryl substituted epoxides to aldehydes. Here, we wish to report the first selective isomerization reaction of aryl epoxides to aldehydes by a transition metal catalyst.

We found by treating the aryl epoxides (**1**) with 10 mole% of iron Lewis acid (**2**) the corresponding aldehyde (**3**) was obtained in excellent yield (Scheme 1). Various aryl substituted epoxides were used and reacted for different time periods to test the catalytic activity of the iron Lewis acid as well as the selectivity of this reaction. These results are summarized in Table 1. In the presence of the iron Lewis acid, *cis*-stilbene oxide **1a** gave a high yield of 93% aldehyde **3a**⁴ in 3 h. However, *trans*-stilbene oxide **1b** required 12 h to give a yield of 91% of **3b**. Styrene oxide **1c**, was reacted for an even longer period of time to give an excellent yield, 86% of aldehyde **3c**⁵ in 20 h. For aryl substitution, we used *trans*-4-chlorostilbene oxide **1d**, which was reacted for 72 h and the yield of aldehyde **3d**⁶ turned out to be 95%. Similarly, a mixture of *cis* and *trans*-4-methylstilbene oxide^{7a,b} **1e** also gave a yield of 95% of aldehyde **3e**⁸ in 16 h.

The Lewis acid $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{THF})]^+\text{BF}_4^-$, was prepared by protonation of the known methyl complex⁹ at -78°C in THF, which, in turn, was easily synthesized in two steps in high yield from the commercially available iron dimer¹⁰. In a typical reaction, the catalyst was dissolved in 5–6 ml of freshly distilled dichloromethane in a round bottom side-armed flask under nitrogen. The appropriate amount of epoxide was added and the mixture was allowed to stir at room temperature for 3 to 72 h. To terminate the reaction, 5–6 ml of diethyl ether was added and the mixture was then

passed through a plug of silica to remove the catalyst. The solvent was removed by rotatory evaporation. The aldehydes were identified by comparison of spectral data with those of authentic samples.^{4,5,6,8}

Scheme 1: Isomerization of epoxides to aryl substituted aldehydes

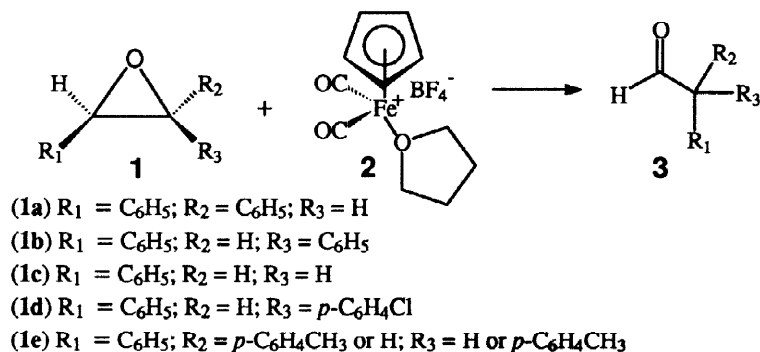


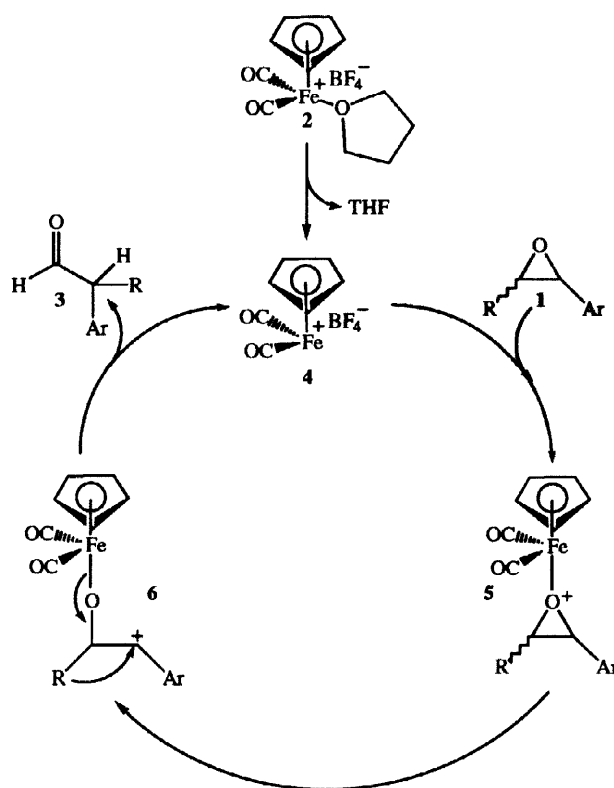
Table 1: Yields of aldehydes from reactions of aryl substituted epoxides catalyzed by the iron Lewis acid $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{THF})]^+\text{BF}_4^-$, **2**.^a

Entry	Structure	Time (hr)	Aldehyde	Yield (%)
1		3		93
2		3		40
3		12		91
4		20		86
5		72		95
6		16		95

^aReactions were carried out at RT with 10 mole% catalyst.

Although we have not yet studied the mechanism of this highly selective isomerization, a plausible one is outlined in Scheme 2. In this proposed cycle, the iron Lewis acid **2** dissociates from THF to form the active catalyst **4**. No reaction in THF strongly suggests an initial dissociation of the THF ligand to form **4** as a key step in the catalytic cycle. After this dissociation, the oxygen atom of the epoxide binds to the metal center to form **5**. At this stage in the cycle, ring opening occurs forming a more stable benzylic carbonium ion **6**¹¹, which undergoes R group migration to form aldehyde **3** and regenerates the active catalyst **4**. The steric difficulty of *trans*-stilbene oxide binding to the iron to form **5** may be the reason for its decreased reactivity compared to *cis*-epoxide. The slow aptitude of migration of a hydrogen versus the phenyl group as observed by others^{2b} may be accounted for by the low reactivity of styrene oxide.¹² Slow migration of the electron-poor aryl group in the carbonium ion **6** and weak binding to the Lewis acid may also be accounted for by the low reactivity of *trans*-4-chlorostilbene oxide in the isomerization reaction.

Scheme 2: Proposed catalytic cycle of the iron Lewis acid with epoxides to produce aldehydes



$\text{Ar} = \text{Ph}$ or $p\text{-PhCH}_3$

In summary, we have demonstrated that the iron Lewis acid selectively catalyzes the isomerization of aryl epoxides to aldehydes in excellent yield. These results provide the first example of a metal-catalyzed rearrangement of aryl epoxides to aldehydes. The Lewis acid is relatively inexpensive, easy to synthesize, and stable for an indefinite period of time in a refrigerated area, making a new efficient synthesis of diaryl-substituted aldehydes available.

Acknowledgement: We gratefully thank the NIH for the partial support of this research.

References and Notes

1. (a) House, H. O. *J. Am. Chem. Soc.* **1955**, 77, 3070; 5083; *Org. Synth. Coll. Vol. IV*, 1963, 375. (b) Stork, G.; Colvin, E. *J. Am. Chem. Soc.* **1971**, 93, 2080. (c) Maruoka, K.; Nagahara, S.; Ooi, T.; Yamamoto, H. *Tetrahedron Lett.* **1989**, 30, 5607. (d) Yanagisawa, A.; Yasue, K. Yamamoto, H. *J. Chem. Soc. Chem. Commun.* **1994**, 2103.
2. (a) Crandall, J. K.; Apparau, M. *Org. React.* **1983**, 29, 345. (b) Smith, J. G. *Synthesis* **1984**, 629. (c) Larock, R. C. *Comprehensive Organic Transformations*. VCH, New York, **1989**, p 628. (d) Rickborn, B. in *Comprehensive Organic Synthesis*, ed. Trost, B. M.; Fleming, I; Pattenden, G. Pergamon, Oxford, 1991, vol. 3, p.733.
3. (a) Eisenmann, J. L. *J. Org. Chem.* **1962**, 27, 2706. (b) Milstein, D.; Buchman, O.; Blum, J. *Tetrahedron Lett.* **1974**, 2257; *J. Org. Chem.* **1977**, 42, 2299. (c) Alper, H.; Roches, D. D.; Durst, T.; Legault, R. *J. Org. Chem.* **1976**, 41, 3611. (d) Suzuki, M.; Oda, Y.; Noyori, R. *J. Am. Chem. Soc.* **1979**, 101, 1623. (e) Miyashita, A.; Shimada, T.; Sugawara, A.; Norhira, H. *Chem. Lett.* **1986**, 1323. (f) Vankar, Y. D.; Chaudhuri, N. C.; Singh, S. *P. Synth. Commun.* **1986**, 16, 1621.
4. (a) Fry, G. L.; Miraz, T. J. *Tetrahedron Lett.* **1979**, 847. (b) van Tamlene, E. E.; Gladysz, J. A. *J. Am. Chem. Soc.* **1974**, 96, 5290.
5. (a) Curtin, D. Y.; Kellom, D. B. *J. Am. Chem. Soc.* **1953**, 75, 6011. (b) Gurudutt, K. N.; Ravindranath, B. *Tetrahedron Lett.* **1980**, 1173.
6. Halterman, R. L.; McEvoy, M. A. *J. Am. Chem. Soc.* **1990**, 112, 6690.
7. (a) Tsujihara, K.; Furukawa, N.; Oae, K.; Oae, S. *Bull. Chem. Soc. Jpn.* **1969**, 42, 2631. (b) Yasumitsu T.; Bayomi S. M.; Sumoto, M. I. *Synthesis* **1977**, 693.
8. (a) Stork, G.; Jung, M. E. *J. Am. Chem. Soc.* **1974**, 96, 3682. (b) Olah, G. A.; Vankar, Y. O.; Arvanaghi, M. *Tetrahedron Lett.* **1979**, 3653.
9. Seitz, W. J.; Saha, A. K.; Hossain, M. M. *Organometallics* **1993**, 12, 2604.
10. King, R. B. *J. Inorg. Nucl. Chem.* **1963**, 25, 1296.
11. The benzylic carbonium ion was also suggested as an intermediate in other transition metal-catalyzed isomerization reactions: see ref. 3.
12. It is more likely that the stable benzylic carbonium ion **6** would form over the less stable methyl carbonium ion in the case of styrene oxide.