Formation of 8-Membered Ring Compounds by the Reaction of Styrene Oxide with MoCl₅

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Styrene oxide reacted with group 5 and 6 metal halides in 1,2-dichloroethane to afford an 8-membered ring compound, 2,3,6,7-dibenzo-9-oxabicyclo[3,3,1]nona-2,6-diene. When the reaction was carried out in benzene instead of 1,2-dichloro-ethane as a solvent, unexpected new 8-membered ring product, tribenzobicyclo[3,3,2]decatriene, and 1,1,2-triphenylethane were obtained. The structures of the 8-membered ring compounds were confirmed by X-ray analysis.

Epoxide and other cyclic ethers are versatile starting material or intermediates in organic synthesis.¹ It is well known that when epoxide or other cyclic ethers are treated with metal halides, halohydrins are formed as main products (Eq 1).²

$$O(n + MXn \longrightarrow X^{(n)}OH^{(1)}$$

(n = 0, 1, 2,)

Recently, we have reported that group 5 and 6 metal halides were efficient catalysts for acylative C–O bond cleavage of cyclic and acyclic ethers.³ In the course of our further study, we found group 5 and 6 metal halides mediated unexpected ring-opening reaction of styrene oxide. We would like to report the formation of 8-membered ring compounds, 2,3,6,7-dibenzo-9-oxabicyclo[3.3.1]nona-2,6-diene⁴ and tribenzobicyclo[3.3.2]decatriene⁵ by the reaction of styrene oxide with MoCl₅ in 1,2-di-chloroethane and in benzene, respectively, along with the formation of 1,1,2-triphenylethane⁶ in benzene.



1:41% yield

A representative procedure for the formation of 8-membered ring compound is as follows: To a mixture of $MoCl_5$ (1 mmol) in 1,2-dichloroethane(or benzene) (5 mL), styrene oxide (1 mmol) was added, and the mixture was stirred at r.t. for 3 h. Then the reaction mixture was quenched with hydrochloric acid (3 N) and extracted with diethyl ether. The organic phase was treated as usual workup, flash column chromatography on silica gel eluting with a mixture of ether and hexane yielded the 8-membered ring compounds as pure compounds.

As shown in Eq 2, when styrene oxide reacted with 1 equiv. of MoCl₅, styrene oxide was completely consumed and 2,3,6,7dibenzo-9-oxabicyclo[3,3,1]nona-2,6-diene **1** was formed in 41% yield (isolated yield: 36%) with the formation of some undefined oligomer. The structure of 8-membered ring compound **1** was verified by X-ray crystallographic analysis and the crystal data were consistent with the reported data.⁷

As shown in Table 1, when the ratio of MoCl₅ to styrene oxide increased to 2, the yield of 8-membered ring product decreased. But when the ratio decreased to 0.5, the yield of the 8-membered ring product did not increase. The similar yield was achieved (34% yield). It indicates that the yield of 1 was not remarkably dependent on the amount of MoCl₅ under the conditions we used here. In this ratio, it is noteworthy that 1,2dichloro-1-phenylethane **2** was formed in 11% yield (Table 1, Entry 3) but no formation of halohydrins was observed. This is quite different from the case of the usual Lewis acid such as AlCl₃.^{8a} TiCl₄,^{8b} FeCl₃,^{8c} and SnCl₂.^{8d} TaCl₅, WCl₆, and NbCl₅ also showed results similar to MoCl₅ (Table 1, Entries 4–6). Other cyclic ethers such as THF, THP, and oxepane could be selectively converted into dihaloalkane or dihaloalkyl ethers by the reaction with group 5 and 6 metal halide.^{3b}

 Table 1. Reactions of styrene oxide with group 5 and 6 metal chlorides

$ \begin{array}{c} & & \\ & & $					
X eq				1	2
Entry	MCI	V eq	Time /h	Yield ^a , GC(iso.)% ^b	
Liitti y	IVICI _n	лц	Time/II	1	2
1	MoCl ₅	1	3	41(36)	0
2	MoCl ₅	2	1	30(17)	0
3	MoCl ₅	0.5	24	34(30)	11(9)
4	WCl ₆	1	3	15	27
5	NbCl ₅	1	24	34	0
6	TaCl ₅	1	3	15	0

^aAll the yields were based on styrene oxide. Temperature; r.t. ^bIsolated yields were in the parentheses.

A reaction of the racemic 2-phenylpropylene oxide with MoCl₅ afforded a mixture of two diastereoisomers as shown in Eq 3. Symmetric isomer 3^9 and unsymmetrical isomer 4^{10} were obtained in 23 and 14% yields, respectively. They were characterized by NMR.



As for the solvent, 1,2-dichloroethane was the best so far. Hexane was also good but the reaction was slower (r.t., 48 h, G.C. yield was 40%) than the case of 1,2-dichloroethane.

The first example of the preparation of 1, which was called

Kagan's ether, was reported by Kagan and co-workers by the reaction of phenylacetaldehyde with fluorosulfonic acid in carbon tetrachloride at 0 °C.⁴ Some improved methods have been developed for the transformation of phenylacetaldehyde to Kagan's ether or its derivatives.¹¹ For example, treatment of phenylacetaldehyde with Me₃SiI quantitatively afforded **1**. On the other hand, **1** has been prepared from 1-carbomethoxy-2-indanone by 5 steps. However, there is no report for the formation of Kagan's ether from styrene oxide.

In order to understand our reaction mechanism, we carried out the reaction of phenylacetaldehyde with $MoCl_5$ under the conditions we used here. In fact, compound 1 was obtained in a comparable yield (30%). This shows that styrene oxide was converted into phenylacetaldehyde or its related compound which, in turn, dimerized to compound 1 through Kagan's mechanism.^{11b}

Interestingly, when benzene was used as a solvent, 1,1,2-triphenylethane **5** and a new 8-membered ring product, tribenzobicyclo[3.3.2]decatriene **6**, were obtained as shown in Eq 4. During the reaction, the formation of **1** was not detected. Two phenyl groups of **5** might come from the benzene. The structure of the new 8-membered ring compound **6** was also determined by Xray analysis. One phenylene ring also might come from the solvent benzene.



In this case, the formation of halohydrins was not detected. When WCl₆, NbCl₅, and TaCl₅ were employed as the reagent, the similar results were also observed.

Compound **6** has been prepared from 9,10-triptycenedicarbonyl chloride as the starting compound via amination, reduction, chlorination, rearrangement, and dechlorination.⁵ But there is no report for the formation of **6** from styrene oxide. It is interesting to note that Firouzabadi and co-worker reported that the reaction of styrene oxide with WCl₆ at reflux in CH₂Cl₂ or a mixed solvent CH₂Cl₂/CH₃CN (2/1) gave a chlorination deoxygenation product, 1,2-dichloro-1-phenylethane in high yield. This is in sharp contrast to our results reported here. The formation of an 8-membered ring product was not reported in the reaction with WCl₆ in CH₂Cl₂.¹²

In this paper we described the novel type of 8-membered ring formation. The reaction mechanisms for the formation of 1 and 6 are not clear yet. But in both cases, we believe that coordination of oxygen of styrene oxide to $MoCl_5$ is the first step. Friedel–Crafts reaction between two molecules of styrene oxide on $MoCl_5$ gives Kagan's ether. On the other hand, Friedel–Crafts reaction of styrene oxide on $MoCl_5$ with benzene affords **5** and **6**.

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- 9 NMR data for **3**. ¹H NMR (CDCl₃, Me₄Si) δ 1.54 (d, J = 6.90 Hz, 6H), 2.86 (q, J = 7.10 Hz, 2H), 4.91 (s, 2H), 6.97–7.00 (m, 2H), 7.04–7.12 (m, 6H). ¹³C NMR (CDCl₃, Me₄Si) δ 23.18, 40.17, 75.41, 125.03, 125.91, 126.94, 129.09, 137.20, 137.22.
- 10 NMR data for 4. ¹H NMR (CDCl₃, Me₄Si) δ 1.35 (d, J = 7.50 Hz, 3H), 1.51 (d, J = 6.90 Hz, 3H), 2.89 (q, J = 7.00 Hz, 1H), 3.60 (dq, J = 6.60, 7.10 Hz, 1H), 4.96 (s, 1H), 5.00 (d, J = 5.40 Hz, 1H), 7.01–7.18 (m, 8H). ¹³C NMR (CDCl₃, Me₄Si) δ 15.35, 23.71, 36.75, 41.41, 74.08, 76.29, 124.80, 124.83, 125.63, 125.79, 126.84, 127.02, 127.17, 129.32, 133.07, 136.70, 137.36, 144.45.
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