

A novel role of zeolite NaY in the thermal reaction of alkyl aryl selenoxides in its supercages

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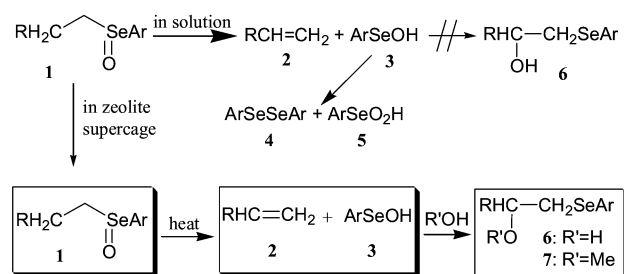
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Thermal reaction of alkyl aryl selenoxides in the presence of water or methanol in the supercage of zeolite NaY gave β -hydroxy- or β -methoxyalkyl aryl selenides, respectively, and NaY played a novel role to stabilize reactive ArSeOH and to separate an anion of ^-OH from a carbonium ion which was simultaneously present with the ^-OH in a supercage.

Organoselenium compounds have been intensively studied and their reactions have been employed as useful tools in organic synthesis. One of their significant reactions is the fragmentation of an alkyl aryl selenoxide **1** in solution into an alkene **2** and an arylselenenic acid **3**. The latter acid readily undergoes a disproportionation reaction to give a diaryl diselenide **4** and an arylselenenic acid **5**, as illustrated in Scheme 1. In this case, the theoretically expected addition reaction of **3** with **2** to a β -hydroxyalkyl aryl selenide **6** hardly occurs.¹ We discovered, however, that in supercages of zeolite NaY, the disproportionation reaction between two molecules of **3** leading to **4** and **5** was inhibited, and that **2** and **3** in the presence of water or methanol NaY gave β -hydroxyalkyl aryl selenide **6** or β -methoxyalkyl aryl selenide



Scheme 1 The thermal reaction of alkyl aryl selenoxides **1** in solution and in the supercage of zeolite NaY.

7, respectively.[†] Zeolite supercages have been widely used as microreactors in organic synthesis, for example as catalysts, hosts of photoreactions and stabilizers of radical cations.^{2,3} In our case the zeolite NaY was used to stabilize reactive intermediate **3**, providing a new route to the synthesis of β -hydroxy- and β -methoxyalkyl aryl selenides.⁴

Results of the reaction of alkyl aryl selenoxides (**1a–1g**) adsorbed on zeolite NaY are summarized in Table 1. In a typical run, a solution of *n*-octyl phenyl selenoxide **1c** (51 mg, 0.179 mmol) dissolved in 150 ml of petroleum ether (b.p. 30–60 °C) at 0–5 °C was mixed with NaY (3.5 g, 17.5 mmol supercage⁵) which was preheated to dry at 500 °C for 6 h and the mixture was stirred below 10 °C for 10 h. The NaY was collected by filtration, washed with petroleum ether and dried by continuous degassing (<8 Pa) for 2.5 h. Following this, the selenoxide loaded NaY was stood in the open air for 12 h, heated at 70–75 °C for 8 h, then extracted with diethyl ether. The ethereal solution was evaporated and the residue (41 mg, mass balance: 81%) was purified by preparative TLC (silica gel, eluent, 4:1(V/V) petroleum ether and diethyl ether) to afford 31 mg (60%) of β -hydroxyoctyl phenyl selenide **6c**.

In the above experiment, the ratio of the starting selenoxides **1** to zeolite NaY, which may stabilize ArSeOH **3** in the supercages, was selected by the following consideration. According to a Poisson distribution, as long as the loading level is less than a 5% probability of finding two guest molecules in one supercage.⁵ Namely, if the loading level is at or less than 50 μmol of selenoxides per gram of dry NaY, the contacts between two molecules of ArSeOH **3** formed by the fragmentation of selenoxide in the supercages should be inhibited and the disproportionation of **3** is avoided. Then it is possible for the stabilized **3** to react with the alkene *in situ* to afford β -hydroxyalkyl selenide (Scheme 1).

Table 1 The yields of **6** and **7** in the thermal reaction of alkyl aryl selenoxides **1** in the presence of water or methanol in the supercage of NaY

Entry	Selenoxide ^a	R	Ar	R'	Mass balance (%) ^b	Product (yield,%) ^c	Identification of products ^d
1	1a	CH ₃ (CH ₂) ₉	Ph	H	86	6a , 69	Ref. 10
2	1b	CH ₃ (CH ₂) ₉	<i>p</i> -MePh	H	87	6b , 72	†
3	1c	CH ₃ (CH ₂) ₅	Ph	H	81	6c , 60	Ref. 11
4	1d	Ph	Ph	H	86	6d , 57	Ref. 4
5	1e	CH ₃ (CH ₂) ₅	<i>p</i> -MePh	H	84	6e , 56	†
6	1f	(CH ₃) ₂	Ph	H	71	6f , 46	Ref. 4
7	1g	CH ₃	Ph	H	68	6g , 37	Ref. 12
8	1a	CH ₃ (CH ₂) ₉	Ph	Me	79	7a , 27	†
9	1b	CH ₃ (CH ₂) ₉	<i>p</i> -MePh	Me	81	7b , 30	†
10	1c	CH ₃ (CH ₂) ₅	Ph	Me	75	7c , 21	Ref. 13
11	1d	Ph	Ph	Me	78	7d , 19	Ref. 13

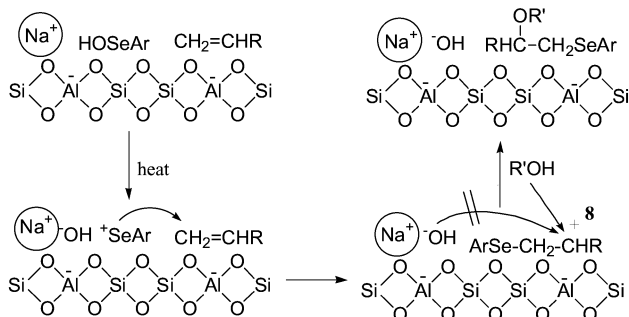
^a Selenoxides were prepared, ⁸ and **1a** and **1b** were recrystallized, but purification of the others before use was not attempted because they were unstable.

^b Mass balance is the ratio of recovered mass from washing zeolite to that of starting material. ^c The impurities of crude products were corresponding selenides, alkenes and ArSeSeAr. ^d The products were identified by comparison with the authentic sample or spectral and elemental analyses.

For the interpretation of these results, we considered the following mechanism for the present reaction. Theoretically β -hydroxyalkyl aryl selenides, **6** but these acids **3** are thermally unstable and readily undergo disproportionation into **4** and **5**. This disproportionation appears to suffer much inhibition in the supercage of zeolite NaY. Thus **2** and **3** recombine to **6** or **7** with the participation of R'OH (H₂O or MeOH, respectively). Control experiments for the formation of **6a** were carried out. (The petroleum ether used in control experiments was pre-dried over 4A zeolite.) (i) Dried NaY loaded with **1a** was heated at 70~75 °C for 8 h under N₂ (99.999%) and gave no **6a**; 1-dodecene and diphenyl diselenide were obtained as main products. (ii) Heating dried NaY loaded with **1a** at 70~75 °C under dried air also afforded no **6a**. The main products were the same as for (i) and the color of the powder NaY turned to slightly pink from white. (iii) Heating dried NaY loaded with **1a** at 70~75 °C under wet N₂ afforded **6a**. (iv) Grinding dried NaY, loaded with one of selenoxides **1a–1d**, with several drops of dry methanol, followed by standing overnight under N₂ and then heating at 70~75 °C under N₂ afforded **7a–7d**, respectively (Table 1). These experiments support that **6a** was not formed by the direct addition of ArSeOH **3** to the alkene **2**, but by the participation of water.

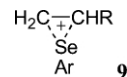
Since the supercages are highly polar and possess strong electric fields,⁷ the above interpretation can be understood by a mechanism involving carbonium ion **8** (Scheme 2).⁹ In the supercage of NaY, selenoxides undergo fragmentation into alkenes and ArSeOH. Arylselenenic acids (ArSeOH **3**) are stable because sterically they cannot contact each other in the supercages. The stabilized ArSeOH ionises into ArSe⁺ and -OH when it is heated. It is conceivable that the hydroxide anions move to relatively positive electric field and the ArSe⁺ move to relatively negative field. This results in separation between the hydroxide anions and the ArSe⁺. On the other hand, hydroxide anions may coordinate with Na⁺ into NaOH (or ion pair) because Na⁺ is a hard acid and -OH is a hard base, whereas the ArSe⁺ tends to coordinate with oxygen atoms of the zeolite framework because ArSe⁺ is a relatively soft cation. The coordination immobilizes -OH because the sodium cations are located on relatively fixed sites in the supercage of NaY, and almost immovable when water is absent.² Thus -OH is obstructed from attacking the carbonium ion **8** produced by the attack of ArSe⁺ to an alkene upon heating. Namely, only neutral nucleophilic reagents such as water and methanol could move relatively freely in supercages under those conditions, so β -hydroxyselenides could not be obtained in the absence of water. In fact, to the best of our knowledge, organic reactions between anions and cations in the supercages of zeolites are seldom found in literature. This fact may be another support to the proposed mechanism.

We believe that carbonium ion **8** instead of seleniranium **9** suggested by J. Remion¹⁰ was involved in the final step because the reactions gave only one of the two possible regioisomers exclusively. Similar high regioselectivity was also observed in the presence of MgSO₄.⁶ The priority of **8** over **9** may result



Scheme 2 A possible mechanism of the formation of **6** and **7** from **2** and **3** by the participation of R'OH in the supercage of NaY.

from the lack of space in the supercage for formation of the more bulky **9**, the steric hindrance of substituent R, the role of NaY in stabilizing charges and the absence of solvent.



The methanol participating reactions (Entries 8–11 in Table 1) had low yields because the molecule size of methanol is larger than that of water and methanol has more difficulties in going into the supercages. Further investigation indicated that ethanol and *n*-butanol could participate in the thermal reactions of **1a** within NaY and gave considerably decreasing yields (9% and a trace respectively) of corresponding β -alkoxyselenides with the increase of the size of the alkanols. However 2-propanol could not be adsorbed into the supercages of the NaY to form β -2-propoxyselenide. All these results revealed that the valid diameter of entrance considerably diminished after the adsorption of **1a** to NaY.

In conclusion, in addition to the establishment of a new procedure for preparing β -hydroxyselenides **6** and β -methoxyselenides **7** from alkyl aryl selenoxides **1** by utilizing zeolite NaY as a microreactor, the possible generalities, that zeolite NaY is able to stabilise reactive intermediates and to separate the small inorganic anions from organic cations in organic reactions in the supercages, were disclosed.

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Notes and references

† The structures of four new compounds are determined by the spectra and element analytical data. **6b**: white plates, Mp.28–29 °C IR(KBr): 3377 cm⁻¹ (OH). ¹H NMR (200 MHz, CDCl₃): δ 7.41 (d, 2H, ³J = 7.9 Hz), 7.06 (d, 2H, ³J = 7.9 Hz), 3.60 (m, 1H), 3.05 (q, 1H, ²J_{AB} = 13.1 Hz, ³J_{AC} = 4.3), 2.85 (q, 1H, ²J_{AB} = 13.1 Hz, ³J_{BC} = 8.7 Hz), 2.41 (s, 1H), 2.30 (s, 3H), 1.50–1.10 (m, 18H), 0.86 (t, 3H, ³J = 6.4 Hz). Anal. Calcd. for C₁₉H₃₂OSe (355): C, 64.22; H, 9.01. Found: C, 64.13; H, 9.00. **6c**: yellow oil. IR(KBr): 3420 cm⁻¹ (OH). ¹H NMR (200 MHz, CDCl₃): δ 7.40 (d, 2H, ³J = 7.9 Hz), 7.05 (d, 2H, ³J = 7.9 Hz), 3.60 (m, 1H), 3.18 ~ 2.73 (m, 2H), 2.30 (s, 3H), 1.51 ~ 1.18 (m, 10H), 0.87 (t, 3H, ³J = 6.8 Hz). Anal. Calcd. for C₁₅H₂₄OSe (299): C, 60.20; H, 8.03. Found: C, 60.24; H, 8.07%. **7a**: yellow oil. ¹H NMR (200 MHz, CDCl₃): δ 7.50 ~ 7.21 (m, 5H), 3.57 ~ 3.44 (m, 1H), 3.31 (s, 3H), 3.15 ~ 2.85 (m, 2H), 1.65 ~ 1.13 (m, 18H), 0.86 (t, 3H, ³J = 6.8 Hz). Anal. Calcd. for C₁₉H₃₂OSe (355): C, 64.23; H, 9.01. Found: C, 64.17; H, 9.06%. **7b**: yellow oil. 7.41 (d, 2H, ³J = 7.9 Hz), 7.05 (d, 2H), 3.40 ~ 3.53 (m, 1H), 3.13 ~ 2.87 (m, 2H), 2.30 (s, 3H), 1.65 ~ 1.13 (m, 18H), 0.86 (t, 3H, ³J = 6.8 Hz). Anal. Calcd. for C₂₀H₃₄OSe (365): C, 65.04; H, 9.21. Found: C, 65.02; H, 9.18%.

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