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Enantioselective Darzens reaction using organoselenide–lithium hydroxide complexes

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ABSTRACT

Asymmetric Darzens reaction catalyzed by chiral selenides is described. A novel Lewis acid/Brønsted base catalyst formed by C_2 symmetric chiral selenide-bearing isoborneol skeletons, which were readily prepared from (1*S*)-10-camphorsulfonic acid, and LiOH promoted the reaction of phenacyl bromide with aldehydes to afford the desired *trans* oxiranes with up to 62% ee.

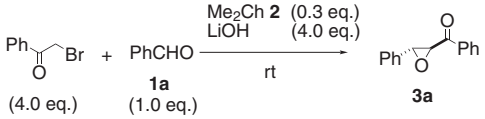
The Darzens reaction is considered to be one of the most common and powerful tool for the synthesis of oxiranes bearing electron-withdrawing groups.[1] Enantiomerically enriched oxirane derivatives have been particularly demonstrated as useful chiral intermediates in organic synthesis.[2] The vigorously investigated methods to approach catalytic asymmetric synthesis of oxiranes are represented by ylide-mediated epoxidation in the category of direct oxirane formation with carbonyl-containing compounds.[2e] Despite this developing research, relatively few procedures using chiral phase-transfer agents are available for the enantioselective catalytic Darzens reaction.[3] More recently, an asymmetric Darzens reaction with a chiral Lewis acid giving moderate to high enantioselectivity has been reported.[4]

In the course of our investigations into the reactivities of selenonium salts, we disclosed the reactivities of selenonium ylides, which were formed by the reactions of selenonium salts bearing unsaturated carbon–carbon bond groups with nucleophiles.[5] Due to the interesting features of these compounds, we focused on the catalytic formation of chiral β-ketoselenonium ylides, which were generated by the treatment of α-halocarbonyl compounds with optically pure selenides, and applications reacted to the asymmetric epoxidation, because selenium ylides react easily with aldehydes to give oxiranes.[5i,6] Interestingly, the reaction of phenacyl bromide with aldehydes was found to be promoted by a selenide catalyst under basic conditions to give oxiranes. We report herein a novel type of oxirane formation catalyzed by selenides and the development of an asymmetric version of the reaction with a novel chiral Lewis acid/Brønsted base catalyst derived from the optically active selenide and lithium hydroxide.

In order to verify the efficacy of a chalcogenide as catalyst, the oxirane formation reaction was undertaken with phenacyl bromide and benzaldehyde under basic conditions using lithium hydroxide (Table 1). The reaction in CH_2Cl_2 without a chalcogenide proceeded hardly at all within 12 h (entries 1 and 2). In the case of using 0.3 equiv of dimethyl selenide **2a**, a 10% yield of **3a** was detected after 5 h. However, a prolonged reaction time up to 12 h gave the *trans* oxirane **3a** in 45% yield with a small amount of *trans*-1,2,3-tribenzoylcyclopropane[7] (entries 3 and 4). Surprisingly, dimethyl sulfide also catalyzed the reaction to afford the epoxide in 50% yield with trans selectivity after 12 h (entries 5 and 6). In general, sulfur ylides bearing an anion-stabilizing group are too stable to react with an aldehyde.[8] The results indicate that chalcogenides promoted the reaction and that the oxirane formation proceeds not via chalcogen-ylides but via a Darzens reaction.

To develop enantioselective oxirane synthesis using a chalcogenide, we designed new chiral C_2 symmetric chalcogenides with a bornane structure because there are many examples for the ylide-mediated epoxidation using bornane derivatives as a chiral source.[9] In addition, high enantioselectivities have been reported

Table 1
Reactions of $PhC(O)CH_2Br$ and PhCHO with LiOH in the presence of a chalcogenide



Entry	Chalcogenide **2**	Time (H)	Yield of **3a** (%)
1	—	5	Trace
2	—	12	Trace
3	**2a** (Ch=Se)	5	10
4	**2a** (Ch=Se)	12	45
5	**2b** (Ch=S)	5	Trace
6	**2b** (Ch=S)	12	50

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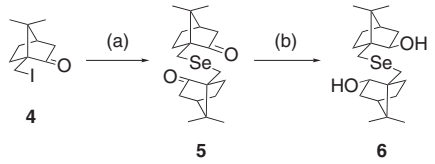
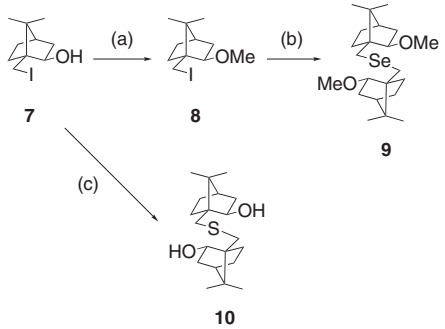
from the reaction with C_2 symmetric sulfide and selenide catalysts.[10] Novel C_2 symmetric selenides can be easily prepared from (1*S*)-10-iodocamphor **4**.[11] Thus (1*S*)-10-iodocamphor **4** was treated with lithium selenide, which was prepared from elemental selenium and lithium triethylborohydride,[12] to afford di-10-camphoryl selenide **5** in 87% yield. Fortunately, the reduction of ketone groups with $LiAlH_4$ gave highly symmetrical di-*exo*-2-hydroxy-10-bornyl selenide **6** bearing isoborneol skeletons as a single diastereomer in good yield (Scheme 1).[13] The stereochemistry of the hydroxy groups was determined to be an *exo*-configuration by comparison of the NMR chemical shift of the hydroxymethine proton with those of analogs of **6**.[14] Hydroxymethine protons of 10-chalcogenomethyl-substituted borneol and isoborneol were observed at δ 4.46–4.53 and δ 3.86–3.94, respectively. The 10-methylselenomethylisoborneol showed a methine signal at δ 3.86, which is very close to that at δ 3.85 of **6**.

Di-*exo*-2-methoxy-10-bornyl selenide **9** was synthesized in 51% yield by the reaction of *exo*-2-methoxy-10-bornyl iodide **8**, which was derived by methylation from *exo*-2-hydoxy-10-bornyl iodide **7**[11] using methyl triflate, with lithium selenide at 80 °C. The compound **7** reacted with lithium sulfide in DMF at room temperature to give di-*exo*-2-hydroxy-10-bornyl sulfide **10** (31%). However, the reaction with lithium selenide yielded a complex mixture, and compound **6** was not obtained (Scheme 2).

We first investigated the asymmetric Darzens reaction with chiral chalcogenide catalysts (Table 2). The reaction was carried out with a variety of catalysts bearing bornane structures for 5 h under the same conditions as shown in Table 1. The selenide catalysts **5** and **9** behaved similarly to dimethyl selenide to give the oxirane **3a** in low yields without enantioselectivity (entries 1 and 3). However, the reaction was dramatically promoted by using selenide **6**, and the yield of **3a** was improved to 66% with 48% ee (entry 2). On the other hand, when sulfide **10**, the sulfur analog of **6**, was employed, the outcome was unsuccessful (entry 4). The best result for **3a** was obtained with $CHCl_3$ up to a 71% yield and 62% ee, although the use of CCl_4, which is one of the chlorinated solvents, gave no enantioselectivity (entries 5 and 6). In the cases of other solvents, the reactions gave good chemical yields with very low enantiomeric excess (entries 7–10). To broaden the scope, we carried out the asymmetric Darzens reaction with a variety of

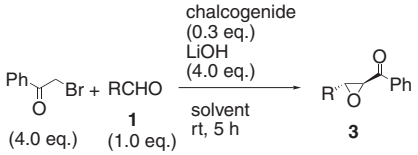


Scheme 1. Reagents and conditions: (a) Se, $LiEt_3BH$, DMF, 80 °C (87%); (b) $LiAlH_4$, THF, 0 °C–rt (88%).



Scheme 2. Reagents and conditions: (a) TfOMe, proton sponge, DCM, reflux (70%); (b) Se, $LiEt_3BH$, DMF, 80 °C (51%); (c) Li_2S, DMF, 80 °C (31%).

Table 2
Asymmetric Darzens reaction with aldehydes using chiral chalcogenides



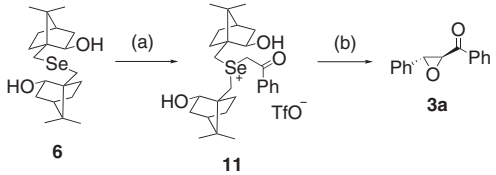
Entry	R	Solvent	Chalcogenide	Yield of **3** (%)	Ee[a] (%)
1	Ph	CH_2Cl_2	**5**	**3a** (14)	1 (2*S*,3*R*)
2	Ph	CH_2Cl_2	**6**	**3a** (66)	48 (2*S*,3*R*)
3	Ph	CH_2Cl_2	**9**	**3a** (3)	0
4	Ph	CH_2Cl_2	**10**	**3a** (8)	5 (2*S*,3*R*)
5	Ph	$CHCl_3$	**6**	**3a** (71)	62 (2*S*,3*R*)
6	Ph	CCl_4	**6**	**3a** (42)	0
7[b]	Ph	THF	**6**	**3a** (89)	1 (2*S*,3*R*)
8	Ph	Et_2O	**6**	**3a** (74)	4 (2*S*,3*R*)
9[b]	Ph	MeCN	**6**	**3a** (85)	2 (2*S*,3*R*)
10	Ph	MeCN	—	**3a** (40)	—
11[c]	Ph	Toluene	**6**	**3a** (61)	2 (2*S*,3*R*)
12	4-$NO_2C_6H_4$	$CHCl_3$	**6**	**3b** (86)	46 (2*S*,3*R*)
13	4-ClC_6H_4	$CHCl_3$	**6**	**3c** (95)	48 (2*S*,3*R*)
14	4-BrC_6H_4	$CHCl_3$	**6**	**3d** (65)	56 (2*S*,3*R*)
15	4-MeC_6H_4	$CHCl_3$	**6**	**3e** (28)	45 (2*S*,3*R*)
16	Et	$CHCl_3$	**6**	**3f** (49)	4 (2*S*,3*R*)
17[b]	$Ph(CH_2)_2$	$CHCl_3$	**6**	**3g** (20)	7 (2*R*,3*S*)

[a] Determined by HPLC with CHIRALCEL OD and CHIRALPAK IB.
[b] Reaction time is 3 h.
[c] Reaction time is 12 h.

aldehydes in $CHCl_3$. The reaction with aromatic aldehydes gave **3b**, **3c**, and **3d** in good yields except for **3e** with moderate enantioselectivities (entries 12–15). The *cis* isomers of **3** were not obtained in these reactions. Meanwhile, the reaction with aliphatic aldehydes produced complicated mixtures, and the *trans* epoxides **3f** and **3g** were isolated with lower enantiomeric excesses (entries 16 and 17). These reactions proceeded under heterogeneous conditions. The absolute configurations of the major enantiomers of **3** were determined to be (2*S*,3*R*) (**3g** is (2*R*,3*S*)) by comparison of the optical rotation and HPLC data with the reported ones.[3j,15]

To determine the mechanism for the formation of oxiranes through the ylide pathway or the Darzens reaction, we prepared the selenonium salt **11** corresponding to the intermediate for the ylide formation pathway and carried out its reaction with benzaldehyde. The synthesis of selenonium triflate **11** was achieved by the reaction of selenide **6** and phenacyl bromide with silver triflate in 85% yield. Next, the reaction of **11** with benzaldehyde using 4 equiv of LiOH toward the selenonium salt hardly proceeded and gave low enantioselectivity (Scheme 3). The findings suggest that the Darzens reaction is more feasible for oxirane formation using the selenide catalyst than the ylide pathway.

Only a modest accelerative effect of a chalcogenide on oxirane formation would be caused by the Lewis acid–Lewis base interaction between the lithium cation and the chalcogen atom as solvation. The use of solvents having a higher coordinating ability for lithium cations increased the yields of oxiranes (entry 10 in Table



Scheme 3. Reagents and conditions: (a) $PhC(O)CH_2Br$, AgTfO, acetone, rt (85%); (b) PhCHO, LiOH, CH_2Cl_2, rt, 3 h (5%, 8% ee) or 24 h (8%, 0% ee).

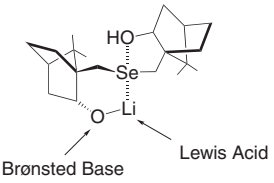


Figure 1. Formation of the complex between selenide **6** and LiOH.

2). The lower solubility of lithium hydroxide for CH_2Cl_2 was improved by the addition of chalcogenides as a Lewis base, which can interact with lithium cations. On the other hand, the yields and enantioselectivities are greatly enhanced by using bis hydroxy selenide **6**, which would form the chair conformation with the lithium cation, selenium atom, and oxygen atom after the deprotonation from one of the hydroxy groups. In addition, the weak interaction between selenium atoms and lithium cations makes the selenium atom electron-deficient, and the oxygen atom in another hydroxy group would then interact with the electron-poor selenium atom to construct a selenurane-type intermediate[14c] possesses both a Lewis acid part and a Brønsted base part (Fig. 1). The difference in the reactions using **6** and **10** is attributed to easy formation of selenuranes compared to that of sulfuranes. Unfortunately, the observation of the interaction between Se and Li by NMR was unsuccessful.

In conclusion, we found that a catalytic amount of chalcogenides accelerated the oxirane preparation reaction of phenacyl bromide and an aldehyde with lithium hydroxide. In particular, the complexation of di-*exo*-2-hydroxy-10-bornyl selenide **6** with lithium hydroxide formed a novel Lewis acid/Brønsted base catalyst to give good yield and moderate stereoselectivities through the Darzens reaction pathway. The mechanism for the enantioselectivity in the reaction is currently under investigation.

Acknowledgment

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13. *(1R,1′R,2R,2′R,4R,4′R)-1,1′-(Selenobis(methylene)bis(7,7-dimethylbicyclo[2.2.1]-heptan-2-ol)* (**6**): To a mixture of lithium aluminum hydride (209 mg, 5.51 mmol) in 6 mL of dry THF a solution of di-10-camphoryl selenide (**5**) (1.50 g, 3.93 mmol) in 39 mL of dry THF was added at 0 °C under Ar in small portions. The mixture was stirred at room temperature overnight. The excess of hydride was cautiously quenched with water and finally with 15% sodium hydroxide. The resulting mixture was filtered through a Celite pad and washed thoroughly with ethyl acetate, and the filtrate was washed with brine. The ethyl acetate extracts were dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (benzene/diethyl ether = 10:1) to afford 1.33 g (88%) of **6** as a white solid: mp 212–224 °C; ^{1}H NMR (400 MHz) ($CDCl_3$) δ: 0.85 (6H, s, $2CH_3$), 1.01–1.08 (2H, m, 2CH), 1.06 (6H, s, $2CH_3$), 1.16–1.22 (2H, m, 2CH of CH_2), 1.53 (2H, td, J = 12.1, 4.2, 2CH of CH_2), 1.67–1.82 (8H, m, $2CH_2$), 2.64 (2H, d, J = 10.5, 2CH of CH_2), 2.86 (2H, d, J = 10.5, 2CH of CH_2), 3.85 (2H, dd, J = 7.9, 3.5, 2CH); ^{13}C NMR (100 MHz) δ: 19.9 (q), 20.6 (q), 25.6 (t), 27.1 (t), 31.9 (t), 39.3 (t), 45.3 (d), 47.8 (s), 52.7 (s), 77.6 (d); MS (EI) m/z (rel int. %) 386 (M^+, 5%), 135 (100); HRMS calcd for $C_{20}H_{34}O_2Se$: 386.1724. Found: 386.1727; $[\alpha]_D^{21} = -66.7$ (c 1.0 in CH_2Cl_2).
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