



Article An Asymmetric Intramolecular Rauhut-Currier Reaction Initiated by Chiral Selenolate-BINOL Complexes

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Abstract: This work reports the new method of Rauhut-Currier reaction (RC) with the use of lithium selenolates, which provided up to 80% yield in a non-asymmetric IRC reaction. Therefore, our paper involves the search for an efficient chiral additive in the asymmetric version. The influence of various reaction parameters, such as solvent, additives, temperature, and time, was examined. The results for the non-asymmetric version were significantly higher with the presence of water, but surprisingly different observations were obtained in the asymmetric version. Here, the chiral scandium complex with tertiary amine played an important role. The reaction carried out in the presence of chiral complexes gave the expected product with up to 60% yield and up to 70% *ee*.

Keywords: Rauhut-Currier reaction; lithium selenolates; intramolecular cyclization; asymmetric synthesis



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1. Introduction

The Rauhut-Currier (RC) reaction [1], also known as the vinylogous Morita–Baylis– Hillman reaction, is one of the methods of C-C bond formation, which involves the dimerization of electron-deficient alkenes in the presence of a nucleophilic catalyst. Initially, tertiary phosphines were used in intermolecular variants [2]. Over the decades, several catalysts were used for this reaction, including phosphines [3–6], tertiary amines [7], organocatalysts [8,9], and NHC catalysts [10]. Recently, we have observed an increase in interest in the of chalcogen in the Rauhut-Currier reaction [11–13]. On the basis of our experience in the seleno-Michael/aldol reaction, we turned our attention to the intramolecular RC reaction, which can be described as the tandem Michael–Michael reaction [14,15]. We expect that lithium selenolate can be an efficient initiator of the IRC reaction.

2. Results and Discussion

We began our investigation of intramolecular Rauhut-Currier (IRC) reactions from typical reactions based on those described in the literature. The most common substrate used for the intramolecular Rauhut-Currier reaction is α , β -unsaturated bisenone **3**, which after the RC cyclization reaction gives product **4** (Scheme 1). The synthesis of **3** was carried out using the classic Wittig reaction between ylide **1** and glutaraldehyde (**2**).



Scheme 1. Schematic synthesis of the IRC product (4).

Using tributylphosphine, we obtained a yield of less than 30% of the desired product 4, (Table 1, entry 1). The application of the cysteine derivative (AcOMeCys) introduced by Miller resulted in a yield of 33% and 73% *ee* (Table 1, entry 3). The reaction results presented in the literature show a 41% yield with *ee* equal to 91% [16–18]. The repeated reaction from entry 4 with additional *n*-BuSeLi gave a racemic mixture with a 38% yield (entry 5).

Table 1. Literature reaction screening.

Entry	Additives [1 Equiv]	Solvent	T [°C]	Time [h]	Yield [%]	Ref.
1. ^a	PBu ₃	Acetone	RT	24	29	[4]
2.	PBu ₃	t-BuOH	RT	72	-	[4]
3. ^{b,c}	AcOMeCys	Acetonitrile	-40	5	33	[19]
4.	AcOMeCys	Acetonitrile	-40	24	30	[19]
5. ^d	AcOMeCys n-BuSeLi	Acetonitrile	-40	24	38	

^a Reagents and conditions: **3** (1 equiv), PBu₃ (1 equiv), acetone (2 mL), RT, 24 h; ^b Reagents and conditions: **3** (1 equiv), H₂O (20 equiv), AcOMeCys (1 equiv), t-BuOK (6 equiv), ACN (2 mL), -40 °C, 24 h; ^c *ee* = 73%, measured by chiral HPLC; ^d enantiomeric excess = 0%, measured by chiral HPLC.

2.2. Investigations of the Reaction with n-BuSeLi

On the basis of our experience, we decided to use lithium *n*-butylselenolate as a nucleophile in the IRC reaction. In this reaction, we are able to observe an intermediate 5 that was then oxidized and eliminated with H_2O_2 and pyridine, as shown in Scheme 2. Product 5 was observed on the MS spectrum. Unfortunately, we were not able to isolate this compound in a pure form. Compound 5 contains three new stereogenic centers, highly complicating NMR analysis.



Scheme 2. IRC reaction with *n*-BuseLi.

Based on the reaction conditions published by Miller [17], we have made further attempts to optimize the reaction, in the presence of water and potassium *tert*-butoxide as additives. According to the literature, the best result was obtained in the presence of ACN at -40 °C with 10 equiv of H₂O and 6 equiv of *t*-BuOK. Lithium selenolate was generated in dry THF, and we decided to use the THF:ACN mixture. Our first attempt focused on the impact of *n*-BuSeLi amount at different temperatures. The reaction was carried out by adding *n*-BuLi to selenium suspended in a dry THF to generate *n*-BuSeLi at 0 °C. Then, the colorless mixture was cooled to the set temperature, and the substrate and additives (20 equiv of water and 6 equiv of *tert*-BuOK) were added under Argon atmosphere.

It should be noted that the generation of the selenolate in situ minimizes the contact with unpleasant odors. The results are shown in Table 2.

Entry	<i>n-</i> BuSeLi [Equiv]	Solvent [1:6]	Τ _t [° C]	T ₂ [°C]	Yield of 4 [%]
1.	1	THF:ACN	0	RT	15
2.	1	THF:ACN	0	RT	18
3. ^a	1	THF:ACN	-40	RT	52
4. ^b	1	THF:ACN	-40	RT	82
5. ^c	1	THF:ACN	-40	RT	35
6.	1	THF:ACN	-78	RT	18
7.	0.2	THF:ACN	-78	RT	-
8.	0.2	THF:ACN	-40	RT	15
9.	0.2	THF:ACN	0	RT	-
10.	1	THF:ACN	-40	RT	-
11.	1	THF:DMF	0	RT	15
12.	1	THF:DMF	-40	RT	24
13.	1	THF:DCM	-40	RT	75

Reagents and conditions: **3** (1 equiv), H₂O (20 equiv), *t*-BuOK (6 equiv), for 24 h (10 h in T₁; 14 h in T₂), quenched by 5 equiv of H₂O₂ and 5 equiv of pyridine, C = 0.04 M; ^a reaction stopped after 2 h at -40 °C; ^b for the reaction was the use of freshly dried THF; ^c reaction without the use of 20 equiv of water and 6 equiv of *t*-BuOK.

The quenching of the reaction after 2 h caused a lower yield (**entry 3**) in contrast to the quenching reaction after 24 h (entry 4). Reaction conditions described in Table 2, entry 4, provide the cleanest product with the highest yield up to 82% in the THF: ACN mixture. Replacing ACN with DCM gave major product in a yield of 75%. The reduced amount of *n*-BuSeLi to 0.2 equiv gave a lower yield (entry 8). As mentioned above, we expect that the reaction is going through the cyclic product (**5**).

Based on previous results, we focused on the influence of oxidants in the last step of the reaction (Table 3).

Entry	Oxidant	T ₁ [° C]	T ₂ [°C]	Yield of 4 [%]
1.	Х	-78	RT	11
2.	Х	-40	RT	13
3.	H_2O_2	-40	RT	84
4. ^a	O ₂	-40	RT	27
5. ^b	O ₂	-40	RT	30
6. ^c	Oxone®	-40	RT	-
7.	NaIO ₄	-40	RT	58
8. ^d	mCPBA	-40	RT	_

Table 3. Screening of oxidative agents.

Standard reaction conditions—1 equiv *n*-BuSeLi, 1 equiv **3**, 20 equiv H₂O, 6 equiv *t*-BuOK, THF: ACN 1:6, 24 h (10 h in T₁; 14 h in T₂), water added after the substrate. The reaction was quenched by adding 5 equiv of oxidative agent and 5 equiv of pyridine, C = 0.08 M. ^a an oxygen purge since the substrate has been added, ^b reaction time was extended to 72 h in RT, ^{c,d} after adding the oxidizing agent the reaction was heated for 3 h at 65 °C.

In the presence of oxidative agents, we observed the best reaction efficiency for H_2O_2 . As shown in Table 3, reactions without any oxidant agent result in very low yields, which indicated partial spontaneous elimination at room temperature (entries 1 and 2). The reaction purged with O_2 resulted in a 30% yield, even with the extension of the reaction time to 72 h (entry 4 and 5). We obtained a good result for sodium periodate (58%), but still lower than that for the hydrogen peroxide and pyridine mixture. The use of pyridine contributed to accelerating the elimination of selenoxide formed after oxidation. In these optimized conditions, we decided to check the influence of the solvents (Table 4). We decided also to reduce the volume and increase the concentration to 0.08 M using a solvent mixture in a ratio 1:3 instead of 1:6. We did not observe any difference in results.

Entry	Solvent	T _t [°C]	T ₂ [°C]	Yield [%]
1.	THF	-40	RT	62
2.	THF:DMF	-40	RT	35
3.	THF:DCM	-40	RT	68
4.	THF:ACN	-78	RT	57
5.	THF:ACN	-40	RT	76
6. ^a	THF:ACN	-40	RT	84
7.	THF:ACN	0	RT	-
8.	THF:EtOH	-40	RT	-
9.	THF:Hx	-40	RT	-
10.	THF:CHCl ₃	-40	RT	-

Table 4. Screening of solvents.

Standard reaction conditions—1 equiv *n*-BuSeLi, 1 equiv **3**, 20 equiv H_2O , 6 equiv *t*-BuOK, THF: other solvent 1:3, for 24 h (10 h at T_1 ; 14 h at T_2). The reaction was quenched with 5 equiv of H_2O_2 and 5 equiv of pyridine. C = 0.08 M; ^a water added to selenolate.

As presented in Table 4, entry 6, the direct addition of water to the generated in situ selenolate at 0 °C improved the reaction efficiency from 76% to 84%. In entries 1–5 and 7–10, we added water after adding the substrate. These results are related to the stabilization of selenolates by water [19,20]. The use of other solvents (chloroform, ethanol, hexane) in a 3:1 mixture with THF did not result in the expected cyclic product **4**.

2.3. Searching of a Chiral Additive in Asymmetric Version

With promising results obtained under achiral conditions, we decided to move to the asymmetric version of the IRC reaction. In search of chiral additives, we first analyze the role of chiral amines: (1R,2R)-1,2-diphenylethane-1,2-diamine (6) [21], L-proline (7) [22], (*R*)-2-(diphenylhydroxymethyl)pyrrolidine (8), (*R*)-BINAM (9) and other compounds including (*S*)-*t*-BuBOX (10), (*R*)-PhBOX (11), (*R*)-BnBOX (12), (*S*,*S*)-Trost catalyst (13) and (*S*)-BINOL (Scheme 3). The main reaction conditions assume the addition of water to a selenolate generated in situ, followed by equimolar amount of substrate, and *t*-BuOK. We tested the addition of chiral additive in three different variants: after the addition of water, after the addition of the substrate, and finally after the addition of the base. Unfortunately, each reaction led to a racemic mixture. After unsuccessful attempts, we decided to use complexes of Lewis acids, such as scandium(III), ytterbium(III), and europium(II) triflate and chiral ligands presented in Scheme 3. Triflate complexes were prepared a priori by reaction and after 30 min of pre-mixing, added directly to the selenolate generated in situ on the order of selenolate, complex, substrate, and water. What is interesting here is that only the (*S*)-BINOL (14) and the scandium triflate(III) complex gave a promising result [23].

Scandium triflate is stable in water and, therefore, does not decompose under aqueous conditions, unlike other Lewis acids. The reaction involved the equimolar addition of water and the BINOL-triflate complex to the selenolate generated under standard conditions (dry THF, 0 °C). Then, the reaction mixture was cooled to the set temperature and the substrate was added. First, we started our optimization from the screening of equivalents of water. We decided to remove the *tert*-BuOK. Our investigation of the asymmetric reaction focused on the determination of the enantiomeric excess of the product. We used a preparative TLC method for product purification. Reactions with significant *ee* were repeated and purified by column chromatography. The results are presented in Table 5.

The highest *ee* was observed with the use of 10 equiv of water. Surprisingly, we obtained a racemic mixture under both anhydrous and, for the reaction, with 100 equiv of water. We decide to retest the influence of the solvent mixture (Table 6). The reaction performed with (*R*)-BINOL-scandium triflate (III) complex gave the opposite enantiomer of product 4 with 60% yield (Table 6, entry 9). Detailed HPLC data please find in Supplementary Information.



Scheme 3. Chiral additives used in IRC.

Table 5. Screening of equivalents of water for (S)-BINOL-scandium triflate(III) complex.

Entry	Water [Equiv]	ee [%]
1.	0	rac
2.	1	rac
3.	5	10
4. ^a	10	32
5.	15	22
6.	20	11
7.	100	rac

All reactions were carried out in mixture 1:3 THF (to generate selenolate): ACN (for solving a complex and substrate) at -40 °C for 24 h. The reaction was stopped with 5 equiv of H₂O₂ and 5 equiv of pyridine, C = 0.08 M ^a yield = 54%.

Table 6. Screening of solvents for the (S)-BINOL-scandium triflate(III) complex.

Entry	Solvent (1:3)	ee [%]
1.	THF	10
2.	THF:Hx	rac
3.	THF:Tol	rac
4.	THF:EtOH	18
5.	THF:CHCl ₃	30
6.	THF:DMF	rac
7.	THF:DCM	28
8. ^a	THF:ACN	32
9. ^b	THF:ACN	-29

Standard reaction conditions—1 equiv *n*-BuSeLi, 10 equiv H₂O, 1 equiv **3**, 1 equiv **14**, -40 °C. Reaction was stopped by 5 equiv of H₂O₂ and 5 equiv of pyridine; ^a yield = 58%, ^b reaction with (*R*)-BINOL, yield = 60%.

As presented in Table 6, the highest result we obtained was only 32% ee with a yield of 58%. On examination of the influence of various reaction parameters, we decided to expand the complex with tertiary amines (DABCO, DBU, Et₃N, NMM), which are shown in Table 7.

Entry	H ₂ O [Equiv]	Amine	Solvent	T [°C]	ee [%]
1.	10	DABCO	DCM	-40	rac
2.	10	DBU	DCM	-40	rac
3.	10	Et ₃ N	DCM	-40	rac
4.	10	NMM	DCM	-40	rac
5.	10	NMM	DCM	-20	rac
6.	10	NMM	DCM	0	rac
7.	10	NMM	DCM	RT	rac
8.	10	NMM	ACN	-40	rac
9.	10	NMM	ACN	-20	rac
10.	10	NMM	ACN	0	rac
11.	1	NMM	DCM	-40	rac
12.	1	NMM	ACN	-40	rac
13. ^a	0	NMM	DCM	-40	62

Table 7. Screening of complexes with tertiary amines.

Standard reaction conditions—1 equiv n-BuSeLi, 10 equiv H₂O, 1 equiv **3**, 1.2 equiv amine, 1 equiv **14**. The reaction was stopped by 5 equiv of H₂O₂ and 5 equiv of pyridine, C = 0.08 M; ^a reaction with 39% yield.

What is interesting here is that the addition of *N*-methylmorpholine to the complex gave the best results in the presence of DCM. We believe that this is related to better solubility in DCM of this type of compound. In this chiral catalyst, the axial chirality of (*S*)-BINOL is transferred through the hydrogen bonds to the amine. Encouraged by these results, we started further research with complex **15** (Scheme 4) in the absence of water and using DCM as a cosolvent.



Scheme 4. Chiral (S)-BINOL-Scandium triflate (III) complex.

On the basis of the above observations, we screened the temperature influence of the reaction (Table 8). Short reaction temperature optimization shows that this process is very sensitive to the different temperatures. Low temperatures cause a significant drop in yield and selectivity (Entry 1 and 2). The use of a syringe pump to add the substrate does not significantly change the results (Entry 5). The reaction performed in the ice bath temperature gave a complex mixture of side products (Entry 7).

Entry	Tt [°C]	T ₂ [°C]	ee [%]
1.	-78 (6 h)	-15 (18 h)	10
2.	-50 (6 h)	-15 (18 h)	55
3.	-40 (6 h)	-15 (18 h)	72
4. ^a	-40 (6 h)	-15 (66 h)	70
5. ^b	-30 (6 h)	-15 (18 h)	78
6.	-30 (6 h)	-	82
7.	0 (6 h)	-15 (18 h)	-

Table 8. Screening of temperature for complex 15.

Standard reaction conditions—1 equiv n-BuSeLi, 1 equiv 3, 1 equiv 15, THF:DCM 1:3. The reaction was quenched by 5 equiv of H_2O_2 and 5 equiv of pyridine, C = 0.08 M; ^a yield = 42%; ^b substrate in RT was added by syringe pump flow 0.01 mL/s yield = 39%.

3. Conclusions

In this paper, we develop a new method for the intramolecular Rauhut-Currier reaction with the use of lithium selenolates. Under achiral conditions, we were able to obtain a cyclic product with a yield of more than 80%. In the presence of chiral catalysts, we observed that the (*S*)-BINOL-scandium triflate(III)-NMM complex leads to satisfactory results up to 80% *ee* with moderate yield (up to 40%). The reaction exclusively provided cyclic product under mild reaction conditions. The presented methodology shows some interesting advantages in comparison to the classic Rauhut-Currier reaction catalyzed by phosphines or amines. Extensive studies of the mechanism and catalytic cycle are performed.

4. Experimental

4.1. General

All chemicals were purchased from Sigma-Aldrich, Apollo Scientific, and commercial suppliers. All solvents were dried prior to use. The progress of the reactions was monitored by TLC using Merck 60 F254 plates. The products were purified by column chromatography using silica gel 60 (240–400 mesh). All reactions were performed under argon. The ¹H and ¹³C NMR spectroscopic data were recorded with a Bruker Advance 300 instrument in CDCl₃. Chemical shifts were reported in parts per million (ppm) relative to TMS as internal standards. The coupling constants (J) are described as a s (singlet), d (doublet), t (triplet), dd (doublet of doublet), ddd (doublet of doublet of doublets), q (quartet), and m (multiplet). HPLC analysis was performed on Knauer systems using CHIRALCEL OD-H or CHIRALPACK AD-H chiral columns with UV detection and propan-2-ol/hexane as eluent. The reaction carried out at temperatures below 0 °C was cooled in SP Scientific refrigerant.

4.2. General Procedure for Ylide Preparation

To a stirred solution of halide (0.1 mol) in toluene (200 mL) was added PPh₃ stoichiometrically, and the mixture was stirred for 48 h at room temperature. After a time, the resulting mixture was transferred to the funnel and washed with toluene (100 mL), hexane (100 mL), and diethyl ether (2 × 100 mL). The residue was dissolved in water, and finally a few drops of phenolphthalein were added. All constituents were titrated with 2 M NaOH until the mixture was colored. A precipitate formed in the flask was washed with water (2 × 200 mL), filtrated, and dried under vacuum.

4.3. General Procedure for Synthesis of 1,9-Diphenylone-2,7-diene-1,9-dione (1)

To a stirred solution of 2.5 equiv of ylide in ethanol (10 mL/g of ylide) at room temperature, 1 equiv of glutaric aldehyde was added and the reaction was allowed to stir overnight. Then, water was added (50 mL/g of ylide), and the mixture was extracted with diethyl ether (3×200 mL). The resulting suspension was derived from triphenylphosphine oxide. The residue was washed with a mixture of diethyl ether and hexane (7:3) and filtered through celite. The filtrate was concentrated and washed several times with the same

hexane:ether mixture until no precipitate appeared. After reconcentration, the obtained product was purified by column chromatography (hexane: ethyl acetate 9:1).

¹H NMR (300 MHz, CDCl₃) δ 7.95–7.92 (m, 4H), 7.55 (tt, J = 6.4, 1.4 Hz, 2H), 7.48–7.45 (m, 4H), 7.06 (ddd, J = 15.4, 8.5, 5.0 Hz, 2H), 6.91 (dt, J = 15.4, 1.2 Hz, 2H), 2.38 (t, J = 7.4 Hz, 4H), 1.82–1.73 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 191.2, 149.1, 138.5, 133.3, 129.2, 129.1, 127.1, 32.8, 27.3.

4.4. General Procedure for the Non-Asymmetric IRC Reaction

Dry THF (1 mL) was injected into the flask containing selenium (0.013 g, 0.165 mmol, 1 equiv) under argon. The suspension was cooled to 0 °C. Then, n-BuLi (0.08 mL, 0.165 mmol, 1 equiv 1.6 M solution in hexane) was added. After dissolved selenium, a solution of **3** (0.05 g, 0.165 mmol, 1 equiv) in THF (3 mL) was added in the next step, followed by 20 equiv water and 6 equiv t- BuOK. The reaction was stopped with 5 equiv of H_2O_2 and 5 equiv of pyridine. Then, ethyl acetate (10 mL) was added and the resulting solution was extracted with two portions of H_2O (5 mL). The organic phase was dried over magnesium sulfate and concentrated under reduced pressure to give a crude product **4**. This compound was purified by column chromatography (hexane:ethyl acetate 9:1).

¹H NMR (300 MHz, CDCl₃) δ 8.11–8.06 (m, 2H), 7.69–7.67 (m, 2H), 7.52–7.43 (m, 6H), 6.63 (td, J = 4.0, 1.1 Hz, 1H), 3.52–3.48 (m, 1H), 3.42 (dd, J = 14.8, 3.2 Hz, 1H), 2.81 (ddd, J = 13.6, 9.2, 4.5 Hz, 1H), 2.38–2.23 (m, 2H), 1.74–1.71 (m, 4H).

¹³C NMR (75 MHz, CDCl₃) δ 200.6, 198.4, 145.9, 142.2, 139.4, 137.4, 133.6, 132.2, 129.9, 129.2, 129.1, 128.8, 43.1, 31.0, 27.1, 26.8, 18.7.

4.5. General Procedure for an Asymmetric IRC Reaction

Dry THF (1 mL) was injected into the flask containing selenium (1 equiv) under the argon. The suspension was cooled to 0 °C. Then, n-BuLi (1 equiv 1.6 M solution in hexane) was added. After dissolved selenium, a solution of (*S*)-BINOL (1.2 equiv), Sc(OTf)₃ (1 equiv) and N-methylmorpholine (2.4 equiv) in 0.5 mL of DCM was added. The resulting mixture was then cooled to -30 °C and stirred for 15 min. Then, 1,9-diphenylo-2,7-diene-1,9-dione (1 equiv) in DCM (3 mL) was added in the next step. The mixture obtained was quenched by adding H₂O₂ (5 equiv) and pyridine (5 equiv) and concentrated under reduced pressure to give a crude product. This compound was purified by column chromatography (hexane: ethyl acetate 9:1).

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/appliedchem2020004/s1.

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Conflicts of Interest: The authors declare no conflict of interest.

Abbereviations

IRC	intramolecular Rauhut-Currier
mCPBA	meta-chloroperoxybenzoic acid
DABCO	1,4-diazabicyclo [2.2.2]octane
DBU	1,8-diazabicyclo(5.4. 0)undec-7-ene
Hx	Hexane
AcOMeCys	methyl ester of acetylcysteine
Oxone	potassium peroxomonosulfate

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