

Domino Michael–seleno Pummerer type reaction (additive seleno Pummerer reaction)

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Domino Michael–seleno Pummerer type reaction (additive seleno Pummerer type rearrangement) has been realised by the reaction of 1,3-dicarbonyl compounds with vinyl selenoxides in the presence of amine and chlorosilane.

Pummerer rearrangement of sulfoxide is a versatile reaction which transfers the oxidation state of sulfoxide onto a carbon at the α -position through acylation of sulfoxide to give α -acyloxysulfide.¹ The synthetic utility of α -acyloxysulfide has been exemplified by the formation of aldehydes by hydrolysis² or vinyl sulfide by elimination of carboxylic acid.³ Intermediary thionium ions have also been utilised as initiators for cationic cyclisation⁴ or asymmetric induction.⁵ In addition, various additive Pummerer reactions involving domino Michael–Pummerer type reactions⁶ have also been reported as useful synthetic transformations. However, in spite of the abundance of sulfoxide Pummerer reactions, the reaction of selenoxide has not been common because facile elimination of the selenenic acid residue from selenoxide occurs soon after oxidation of selenide even at low temperature. Thus, limited and specific examples have been reported so far,^{7,8} in which there were no β -hydrogens to the selenoxide in most cases.⁸ To the best of our knowledge, there is only one example of additive seleno Pummerer reaction, which involves the reaction of vinyl selenoxide with ketene via a 3,3-sigmatropic rearrangement of oxy-selenonium enolate.⁹

We herein show our first observation of a domino Michael–seleno Pummerer type reaction (additive seleno Pummerer type rearrangement) by the reaction of 1,3-dicarbonyl compounds with vinyl selenoxides in the presence of amine and chlorosilane in the course of our investigation on reactivity of vinyl selenoxide as a partner for domino Michael–Michael-substitution reaction (bicycloannulation).¹⁰

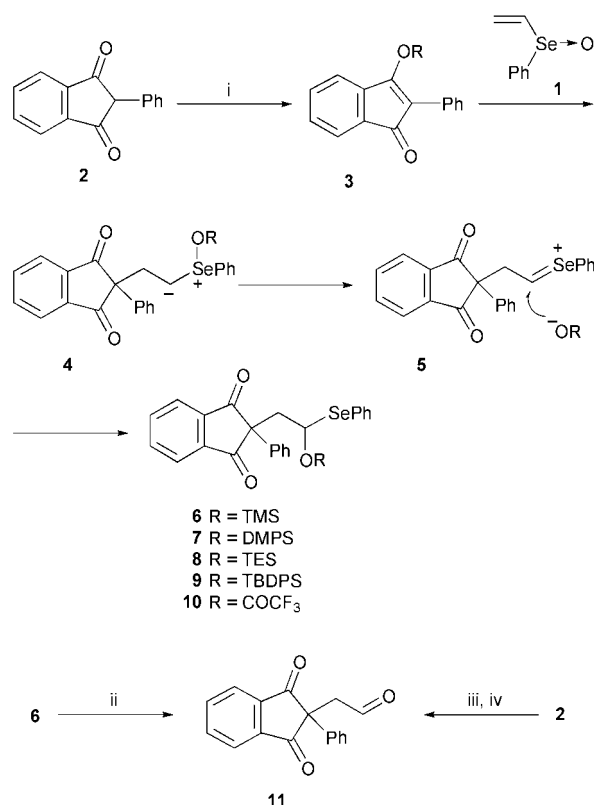
As a representative example, reaction of 2-phenylindane-1,3-dione **2** with phenyl vinyl selenoxide **1**¹¹ in the presence of hexamethyldisilazane [(TMS)₂NH] and chlorotrimethylsilane (TMSCl) in dichloromethane provided trimethylsilyloxyselenide **6** in 52% yield. Some results are shown in Table 1 and Scheme 1.

The yield was improved when a solution of the indanedione **2**, (TMS)₂NH and TMSCl in dichloromethane was stirred for 2 h prior to addition of the vinyl selenoxide **1** (Table 1, entry 2). The reaction also proceeded without TMSCl albeit in lower yield (Table 1, entry 5). Without amine, the starting indanedione **2** was recovered completely. (TMS)₂NH gave the best result among other amines tested (diethylamine, triethylamine, diethylaminotrimethylsilane, DBU or dicyclohexylamine). TMSCl was the best among other chlorosilanes due to higher reactivity and diminished steric bulkiness towards *O*-silylation as well as nucleophilic attack on the selenonium ion (Scheme 1). Actually, in Table 1, entry 3 or 4, the TMS group of (TMS)₂NH was introduced selectively even in the presence of chloro(*tert*-butyl)dimethylsilane (TBDMSCl) or chlorodimethylphenylsilane (DMPSCl) while in entry 6 in the absence of (TMS)₂NH bulkier DMPS group was introduced. These observations indicate that the yields of the products do not depend on the

Table 1 Domino Michael–seleno Pummerer reaction

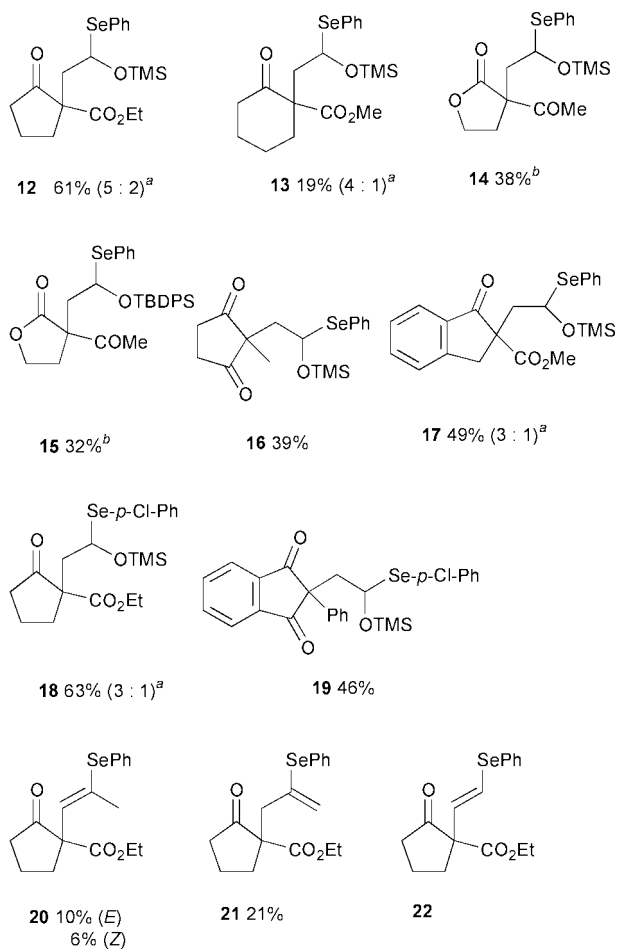
Entry	Reagents ^a	Product	Yield (%)
1	(TMS) ₂ NH–TMSCl	6	52
2 ^b	(TMS) ₂ NH–TMSCl	6	70
3	(TMS) ₂ NH–TBDMSCl	6	38
4	(TMS) ₂ NH–DMPSCl	6	39
5	(TMS) ₂ NH	6	25
6	(C ₆ H ₁₁) ₂ NH–DMPSCl	7	27
7	(C ₆ H ₁₁) ₂ NH–TESCl ^c	8	36
8	(C ₆ H ₁₁) ₂ NH–TBDPSCI ^c	9	43
9	(C ₆ H ₁₁) ₂ NH–(CF ₃ CO) ₂ O	10	18

^a Reaction was carried out at ice bath temperature for 2–3 h. ^b Vinyl selenoxide **1** was added 2 h after stirring indanedione **2**, (TMS)₂NH and TMSCl. ^c TESCl = chlorotriethylsilane; TBDPSCI = chloro(*tert*-butyl)-diphenylsilane.



Scheme 1 Reagents: i, Chlorosilane or (CF₃CO)₂O; ii, MCPBA–CH₂Cl₂ or PTSA–H₂O–THF; iii, allyl bromide–NaH–THF; iv, O₃–CH₂Cl₂–Me₂S.

stability of products **6–10**. More reactive silylating reagent such as trimethylsilyl iodide or trimethylsilyl trifluoromethanesulfonate provided complex mixtures.



^aA mixture of diastereomers was obtained.

^bSingle diastereomer was obtained.

Fig. 1

The structure of the selenide **6** was determined by spectroscopic and synthetic means. *m*-Chloroperbenzoic acid oxidation or acid catalyzed hydrolysis of **6** provided aldehyde **11** which was identical with authentic **11** independently prepared by allylation of the indanedione **2** followed by ozonolysis (Scheme 1).

Based on the results cited above, generality of the present reaction was further investigated and some representative examples are compiled in Fig. 1. Not only phenyl vinyl selenoxide **1** but also *p*-chlorophenyl vinyl selenoxide or isopropenyl phenyl selenoxide provided domino products **18–21**, though elimination of trimethylsilanol occurred in the reaction of isopropenyl phenyl selenoxide to afford vinyl selenides **20** and **21**. Under prolonged reaction time, the latter reaction led to the formation of **22** or the aldehyde **11**. Some of the diastereomeric mixtures were separable by medium pressure liquid chromatography. These diastereomers were stable enough to recover intact after reflux in dichloromethane.

Reaction of trimethylsilylenol ether **3** (R = TMS) of the indanedione **2** with the vinyl selenoxide **1** provided the selenide **6** in 67% yield. This result along with the results in Table 1, Entries 1–4 supports the theory that the present reaction

proceeds *via* domino silyl transfer (Mukaiyama) type Michael addition followed by seleno Pummerer type reaction as shown in Scheme 1.

In summary, among many possible combinations of domino process,¹² the present reaction offers the first example of domino Michael–seleno Pummerer type reaction (additive Pummerer reaction) and a new alternative procedure to introduce a formylmethyl unit to 1,3-dicarbonyl compounds.

Experimental

Phenyl vinyl selenoxide **1** was prepared according to the known procedure.¹¹

To a stirred solution of 2-phenylindane-1,3-dione **2** (221 mg, 0.99 mmol) in dichloromethane (2 ml) was added (TMS)₂NH (254 μ l, 1.2 mmol) at 0 °C under a nitrogen atmosphere. After being stirred for 10 min, TMSCl (152 μ l, 1.2 mmol) was added and the solution was stirred for a further 2 h at 0 °C. A solution of phenyl vinyl selenoxide (245 mg, 1.23 mmol) in dichloromethane (2 ml) was added and stirring was continued at room temperature for 30 min. Evaporation of the solvent *in vacuo* followed by medium pressure liquid chromatography (eluent: ethyl acetate–*n*-hexane = 1 : 3) provided the domino product **6** (343 mg, 70%); needles, mp 96–98 °C; IR (CCl₄) ν_{\max} /cm⁻¹ 3061, 2957, 1747, 1712, 1601, 1479, 1253, 1111; ¹H-NMR (200 MHz, CDCl₃) δ (ppm) –0.30 (s, 9H), 2.77 (dd, 1H, *J* 14.3, 3.61 Hz), 3.34 (dd, 1H, *J* 14.3, 10.8 Hz), 5.49 (dd, 1H, *J* 10.8, 3.61 Hz), and 7.18–8.01 (m, 14H Ph); ¹³C-NMR (125 MHz, CDCl₃) δ (ppm) –0.7 (q) \times 3, 46.6 (t), 61.6 (s), 75.0 (d), 123.2 (d), 124.0 (d), 126.7 (d) \times 2, 127.4 (d), 127.6 (d), 128.8 (d) \times 2, 129.1 (d) \times 2, 129.1 (s), 134.0 (d) \times 2, 135.2 (d), 135.6 (d), 137.0 (s), 141.7 (s), 142.0 (s), 198.9 (s), and 200.7 (s).

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