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Reaction of selenofenchone with propiolic acid: first instance of Wagner–Meerwein rearrangement in selone

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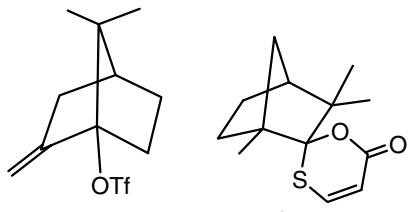
Abstract—The reaction of selenofenchone (**3a**) with propiolic acid in refluxing chloroform produced selenodioxenone (**4**) along with rearranged product (**5b**), while **5b** was obtained in almost quantitative yield under solvent-free conditions. In the presence of Lewis acid, selenofenchone **3a** reacted with methyl propiolate to afford corresponding rearranged adduct (**7**).

The Wagner–Meerwein rearrangement is a popular acid-catalyzed reaction. Alkenes possessing the norbornane-type skeleton are useful starting materials or intermediates for chiral auxiliaries and natural products.[1] Martinez et al. reported that the reaction of fenchone with trifluoromethanesulfonic anhydride produced Wagner–Meerwein rearranged product (**1**).[2] Previously, we reported that the reaction of thiofenchone with propiolic acid gave corresponding thiodioxenone (**2**) exclusively (Chart 1).[3] These results prompted us to investigate the possibility of the formation of a Wagner–Meerwein rearranged product in the reaction of selenofenchone (**3a**) with propiolic acid. Herein, we communicate the first isolation of Wagner–Meerwein rearranged product in the reaction of **3a** with propiolic acid.



1 **2**

Chart 1.

Selenofenchone **3a** was synthesized by reacting fenchone hydrazone with diselenium dibromide, using the method reported by Guziec and Moustakis.[4] Treatment of **3a** with propiolic acid (2 equiv) in refluxing chloroform for 16 h resulted in the formation of selenodioxenone (**4a**) (48%) along with side product (**5**). The spectroscopic nature of **4a** was similar to that of *exo*-thiodioxenone **2**.[3] Regarding the structure of **5**, ^{1}H NMR spectrum showed two each of methyl signals (0.93 and 1.12 ppm), *exo*-methylene signals (4.94 and 5.03 ppm), and alkene signals (6.35 and 7.82 ppm), along with norbornane's proton signals. The coupling constant between these vinylic protons (10 Hz) suggested that this product has *Z*-configuration. Its ^{13}C NMR spectrum showed methyl signals at 20.16 and 20.97 ppm and an *exo*-methylene signal at 107.33 ppm, indicating that one of three methyl substituents was converted into an *exo*-methylene group. We initially thought that the reaction proceeded through carbocation intermediate (**6**), the methyl migration of which led to **5a** (Scheme 1). The structure of **4a** was finally confirmed by X-ray crystallographic analysis. ORTEP drawing of **4a** is shown in Figure 1.

If this reaction mechanism is correct, other selenoketones will also afford methyl-migrated products. However, the reaction of tetramethylindan-2-selone (**3b**) with propiolic acid afforded not the rearranged product but selenodioxenone (**4b**) in 76% yield (Scheme 2). Additionally, this mechanism cannot explain the exclusive formation of *Z*-**5a**.

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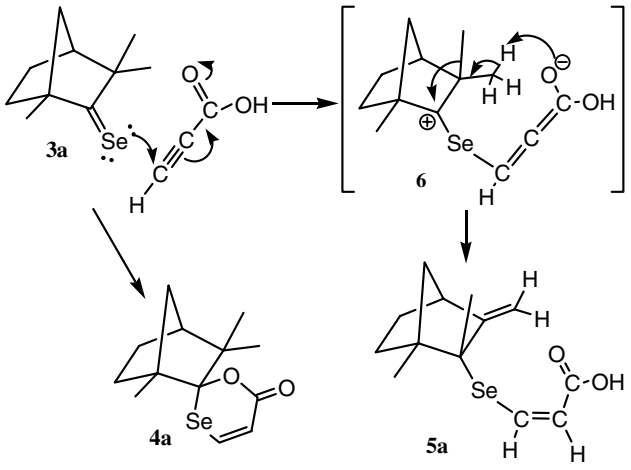


Scheme 1.

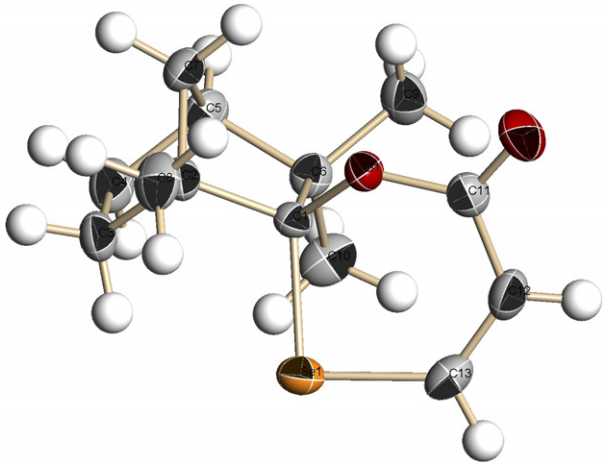
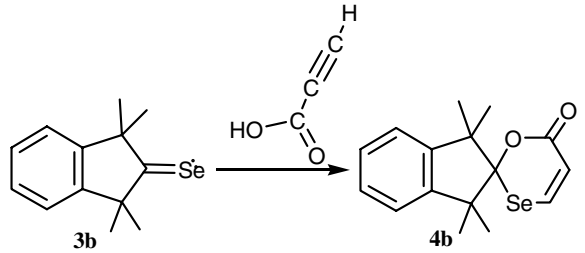


Figure 1. ORTEP drawing of selenodioxenone **4a**. Selected bond lengths: Se(1)–C(13) 1.870(2) Å, Se(1)–C(1) 1.980(2) Å, C(1)–O(1) 1.450 Å, O(1)–C(11) 1.350 Å, C(11)–O(2) 1.199 Å, C(12)–C(13) 1.317(4) Å. Selected bond angles: C(13)–Se(1)–C(1) 93.44(10)°, O(1)–C(1)–Se(1) 108.43(13)°, C(11)–O(1)–C(1) 124.52(18)°, O(1)–C(11)–C(12) 119.4(2)°, C(11)–C(12)–C(13), 124.7(2)°, C(12)–C(13)–Se(1) 124.1(2)°.

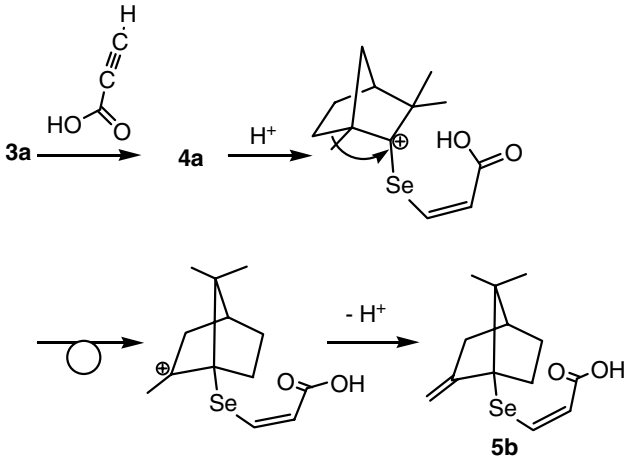


Scheme 2.

Thus, another reaction mechanism is required to explain the reaction. Recently, Mloston and co-workers reported the reaction of thiocamphor or thiofenchone with α-chloroalkane sulfenyl chloride, producing Wagner–Meerwein rearranged products.[5] After carefully checking the ^{1}H NMR spectrum of **5**, we have found a small coupling between *exo*-methylene signals and norbornane methylene signals. Thus, we concluded that the product was Wagner–Meerwein rearranged product (**5b**). The fact that only the *Z*-isomer was formed clearly shows that initially formed selenodioxenone (**4a**) further reacted with propiolic acid to afford a cation intermediate, and this intermediate rearranged to give **5b** (Scheme 3). When the reaction of **3a** with propiolic acid (3 equiv) was carried out under solvent-free conditions, only the rearranged product **5b** was obtained in 97% yield. The results are shown in Table 1.

To confirm this reaction mechanism, the reaction of selenodioxenone **4a** with propiolic acid was carried out. When propiolic acid was used as a solvent at rt, the rearranged product **5b** was obtained in almost quantitative yield. The reaction of **4a** with acetic acid in chloroform also gave rearranged product **5b**.

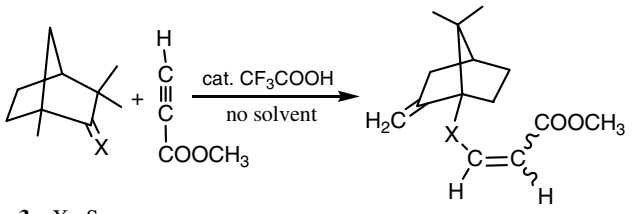
Since the Wagner–Meerwein rearrangement might proceed through this reaction, we attempted to react **3a** with methyl propiolate in the presence of cat. $AlCl_3$. As shown in Scheme 4, corresponding rearranged product (**7**) (a mixture of *E*- and *Z*-isomers) was obtained in 65% yield. Similarly, thiofenchone (**8**) reacted with methyl propiolate in the presence of $AlCl_3$ to afford the rearranged product (**9**) (a mixture of *E*- and *Z*-isomers) in 75% yield. The present results are quite different from the results obtained in the reaction of selones with benzyne, which gave methyl-migrated products along with [2+2] cycloadducts.[6]



Scheme 3.

Table 1. Reaction of selenofenchone **3a** with propiolic acid

Propiolic acid (equiv)	Conditions			Products	Yields (%)
	Solvent	Time	Temperature	**4a**	**5b**
2	$CHCl_3$	16	Reflux	48	13
2	CH_2Cl_2	18	Reflux	46	12
2	None	12	60	0	97
3	None	48	rt	0	97
2	None	72	rt	0	97



3a: X= Se
8: X= S

7: X=Se (*E*:*Z* = 2:3)
9: X=S (*E*:*Z* = 10:7)

Scheme 4.

In summary, we have synthesized Wagner–Meerwein rearranged products by reacting selenofenchone with propiolic acid derivatives. Previously, many workers reported the enantioselective reduction, substitution, epoxidation, and protonation by using camphor derived hydroxyl sulfides or hydroxyl selenides.[7] The present reaction provides a new access to another type of chiral auxiliary bycyclic sulfides or selenides.

Reaction of selenofenchone **3a** *with propiolic acid*: To a solution of **3a** (2 mmol) in chloroform was added propiolic acid (4 mmol). After refluxing for 16 h, the reaction mixture was evaporated to afford a pale yellow oil, which was chromatographed over silica gel by elution with hexane and dichloromethane–ethyl acetate (3:1) to afford selenodioxenone **4a** (0.96 mmol) and rearranged product **5b** (0.26 mmol). Compound **4a**: yellow plates: mp 134.5–135.8 °C; ^{1}H NMR ($CDCl_3$) $\delta = 1.22$ (s, 6H, 2 Me), 1.29 (s, Me), 1.20–1.66 (m, 5H, CH_2), 1.77 (br, 1H, CH), 2.20 (br d, $J = 11$ Hz, CHH), 6.32 (d, $J = 10$ Hz, =CH), 7.82 (d, $J = 10$ Hz, =CH). ^{13}C NMR ($CDCl_3$) $\delta = 19.00$ (Me), 25.27 (CH_2), 28.45 (Me), 29.69 (Me), 32.04 (CH_2), 40.32 (CH_2), 51.79 (q-C), 55.76 (q-C), 106.46 (q-C), 118.20 (=CH), 140.20 (=C), 164.12 (C=O). IR: $\nu_{C=O} = 1687$ cm^{-1}. Anal. Calcd for $C_{13}H_{18}O_2Se$: C; 54.74; H, 6.36. Found: C, 54.53; H, 6.28. X-ray crystallographic data for **4a**:[8] crystal data for $C_{13}H_{18}O_2Se$ crystallized from dichloromethane–hexane. Mo Kα radiation. $M = 285.23$, $a = 6.4640(4)$ Å, $b = 13.5900(8)$ Å, $c = 14.1050(8)$ Å, $V = 1239.06(13)$ Å^3, $T = 243$ K, orthorhombic, space group = $P2_12_12_1$, $Z = 4$, 2953 independent reflections, $R = 0.0239$, $wR = 0.0531$.

Compound **5b**: yellow plates: mp 156–158 °C; ^{1}H NMR ($CDCl_3$) $\delta = 0.93$ (s, 3H, Me), 1.12 (s, 3H, Me), 1.35–1.39 (m, 1H, CHH), 1.70–1.75 (m, 1H, C*H*H), 1.85–1.97 (m, 2H, CH and C*H*H), 2.00–2.12 (m, 2H, C*H*H), 2.56 (br d, 1H, $J = 16$ Hz, C*H*H), 4.94 (dd, 1H, $J = 1$ and 2 Hz, =CH_2), 5.03 (dd, 1H, $J = 1$ and 2 Hz, =CH_2), 6.35 (d, 1H, $J = 10$ Hz, =CH_2) 7.82 (d, 1H, $J = 10$ Hz, =CH). ^{13}C NMR ($CDCl_3$) $\delta = 20.16$ (Me), 20.97 (Me), 28.62 (CH_2), 35.51 (CH_2), 37.36 (CH_2), 43.79 (CH), 50.70 (q-C), 63.08 (q-C, $J_{Se-C} = 43$ Hz), 107.33 (=CH_2), 116.11 (=CH), 149.84 (=CH, $J_{Se-C} = 80$ Hz), 154.08 (=C), 172.49 (C=O). Anal. Calcd for $C_{13}H_{18}O_2Se$: C; 54.74; H, 6.36. Found: C, 55.04; H, 6.41.

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