

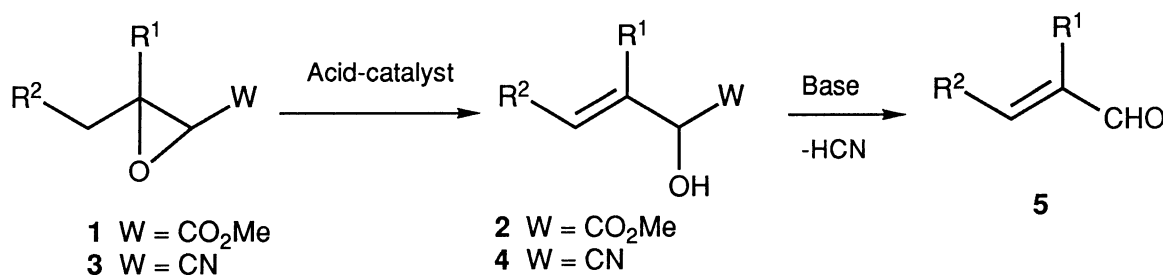
Selective Isomerization of Glycidates and Their Analogues
with Triphenylsilyl Perchlorate or Electrogenerated Acid

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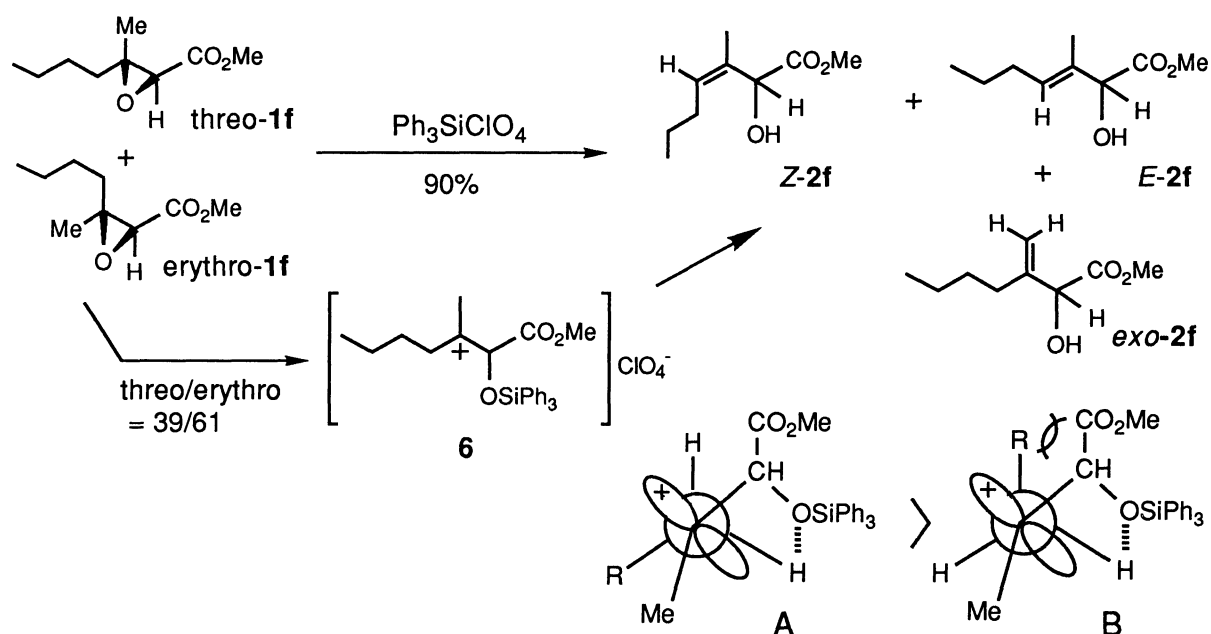
Isomerization of glycidic esters and nitriles to the corresponding 2-hydroxy-3-alkenoates and their nitrile derivatives occurred on treatment with triphenylsilyl perchlorate or electrogenerated acid (EG acid). The cyanohydrin moiety of the nitriles **4** was transformed to a formyl group, giving the corresponding enals on treatment with weak base.

Acid-catalyzed isomerization of glycidic esters is useful in obtaining 2-hydroxy-3-alkenoates, versatile building blocks for the synthesis of bioactive compounds¹⁾ and liquid crystals.²⁾ A variety of conventional Brønsted acids,³⁾ Lewis acids (stoichiometric use),⁴⁾ and transition metal (Pd, Rh)-olefin complexes⁵⁾ are proposed for this purpose. However, some of them require the operation at high temperature⁵⁾ which limits feasibility in their applications and induces side-reactions such as dehydration and formation of 2-oxoalkanoates. We describe an improved procedure by using triphenylsilyl perchlorate ($\text{Ph}_3\text{SiClO}_4$), prepared from chlorotriphenylsilane (Ph_3SiCl) and silver perchlorate,⁶⁾ or electrogenerated acid (EG acid) as an acid catalyst.⁷⁾



Treatment of **1a** with 0.1 equivalent of $\text{Ph}_3\text{SiClO}_4$ at -78 to -30 °C in dichloromethane produced the corresponding 2-hydroxy-3-alkenoate **2a** in 95% yield (Table 1, entry 1). The electrolysis of **1a** in a $\text{CH}_2\text{Cl}_2\text{-LiClO}_4\text{-Bu}_4\text{NClO}_4\text{-(Pt)}$ system⁷⁾ at -78 to -30 °C for 0.1 F/mol of electricity afforded the same hydroxy ester **2a** in 90% yield (entry 2). Furthermore, the electrogenerated trityl perchlorate⁸⁾ (Ph_3CClO_4) from phenylthiotriphenylmethane was found to be effective for this isomerization, giving **2a** in 92% yield. In all cases, the formation of the corresponding 2-oxoalkanoate was not observed.

As shown in Table 1, 2-hydroxy-3-alkenoates **2** are prepared from good to excellent yields by isomerization of the glycidic esters **1**.⁹⁾ Of interest to note is that the treatment of a 39:61 threo/erythro mixture of **1f** with $\text{Ph}_3\text{SiClO}_4$ gave the corresponding *E*-isomer of 2-hydroxy-3-alkenoate (*E*-**2f**), predominantly. The ratio of *E*-**2f**, *Z*-**2f**, and *exo*-**2f** was determined to be 94:4:2 by GC analyses.¹⁰⁾ We assume that this isomerization proceeds through a cationic intermediate **6** which may be stabilized by participation of perchlorate ion. The elimination of $\text{Ph}_3\text{SiClO}_4$ and deprotonation from **6** would lead exclusively to one of the olefinic alcohols *E*-**2f**, *Z*-**2f**, and *exo*-**2f**. As shown in Scheme 1, the high *E*-selectivity can be ascribed to a transition state A, a favorable one over B because of the gauche interaction between R and the (triphenyl)siloxyated methyl group.¹¹⁾



Scheme 1.

Furthermore, isomerization of the glycidic nitrile **3a** was achieved on treatment with the EG acid or $\text{Ph}_3\text{SiClO}_4$ to the corresponding cyanohydrin **4a**, smoothly. The cyanohydrin **4a** was converted to the α,β -unsaturated aldehyde **5a** on treatment with aqueous potassium carbonate in methanol at 5–10 °C. Since the epoxy nitriles are easily available from the corresponding ketones, an acid-catalyzed isomerization and base-catalyzed decyanation sequence would provide a facile route to useful α,β -enals.

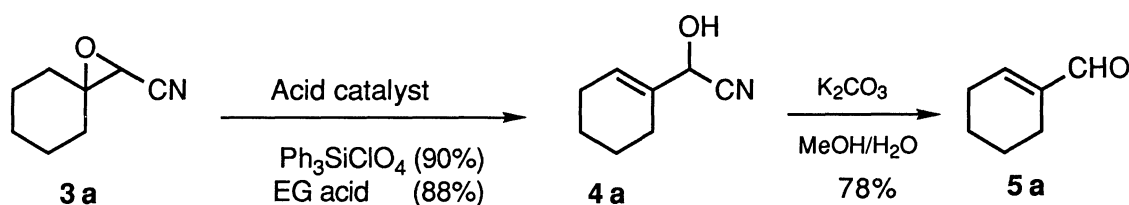
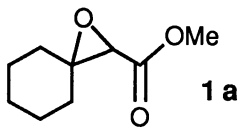
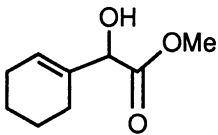
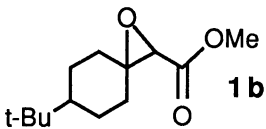
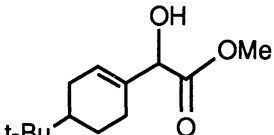
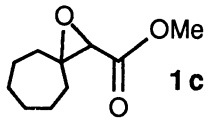
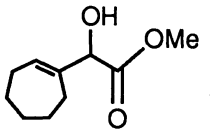
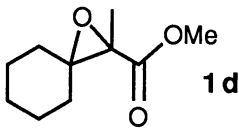
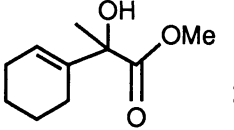
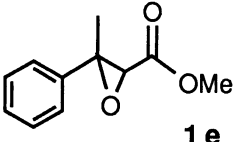
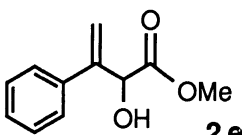


Table 1. Isomerization of Glycidic Esters **1** with $\text{Ph}_3\text{SiClO}_4$ or EG acid^{a)}

Entry	Substrate	Method	Time/h ^{b)}	Product	Yield/% ^{c)}
1	 1 a	A	1.5	 2 a	95
2	1 a	B	1.5	2 a	90
5	 1 b	A	2	 2 b	95
6	1 b	B	2	2 b	90
7	 1 c	A	2	 2 c	95
8	1 c	B	2	2 c	94
9	 1 d	A	2	 2 d	96
10	1 d	B	2	2 d	95
11	 1 e	A	4	 2 e	78

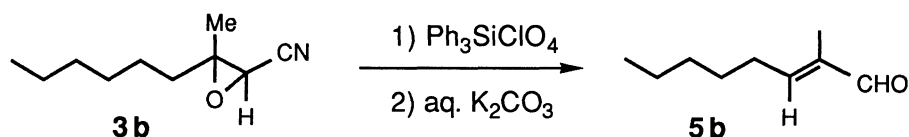
a) Unless otherwise noted, the substrate (1 mmol) was treated with a solution of $\text{Ph}_3\text{SiClO}_4$ (0.5 M) in CH_2Cl_2 (3 ml) at -78 to -30 °C (Method A). b) Method B: Electrolysis in a CH_2Cl_2 - LiClO_4 - Bu_4NClO_4 -(Pt) system. c) Based on isolated products.

In this study, triphenylsilyl perchlorate ($\text{Ph}_3\text{SiClO}_4$) dissolved in CH_2Cl_2 and stored in cool is shown to be an alternative to the EG acid as well as trityl perchlorate generated in electrolysis media.⁸⁾

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- 9) 2-Hydroxy-3-phenyl-3-butenate (**2e**) derived from the glycidic ester **1e** is useful as a precursor of bioactive β -methylenephénylalanine¹²⁾ and phenylpyruvic ester.⁵⁾
- 10) The trimethylsilyl ethers from a mixture of *E*-**2f**, *Z*-**2f**, and *exo*-**2f** were analyzed on a "Quadrex" Bond-Fused Silica capillary column (Methyl Silicone 20M: 0.25 μ m film thickness, 25 m x 0.25 mm I.D.) by a Yanaco G6800. Programmed from 100 °C to 270 °C with gradient at the rate of 10 °C/min after 10 min period at the starting.¹³⁾ Retention times (min) of *E*-**2f**, *Z*-**2f**, and *exo*-**2f**: 15.4, 14.7, and 14.9 min.
- 11) Similarly, *E*-selectivity was observed in the rearrangement of unsymmetrical glycidic nitrile **3b**. Purity of the corresponding α,β -enal **5b** (retention time, 15.4 min) was determined as 94% by GC analysis.



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- 13) All reactions were carried out under an argon atmosphere and a typical procedure is as follows: To a solution of **1a** (172 mg, 1 mmol) in CH_2Cl_2 (3 ml) was added a 0.2M $\text{Ph}_3\text{SiClO}_4$ in CH_2Cl_2 (0.5 ml) at -78 °C. The mixture was stirred for 1.5 h at -78—30 °C for 1.5 h and quenched with Et_3N (3 drops). Evaporation of the volatiles and purification of the residue by column chromatography (SiO_2 , hexane-AcOEt = 5:1) gave 163 mg (95%) of **2a**: IR (neat) 3440 (OH), 1740 ($\text{C}=\text{O}$) cm^{-1} ; ^1H NMR (500 MHz) δ 1.50-1.68 (m, 4H, CH_2), 1.72-1.79 (m, 1H, CH_2), 3.06 (brs, 1H, OH), 3.77 (s, 3H, OCH_3), 5.80 (m, 1H, $\text{HC}=\text{C}$); ^{13}C NMR (126 MHz) δ 22.0, 22.2, 23.6, 25.0, 52.7, 75.3, 127.5, 134.8, 174.4.

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