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

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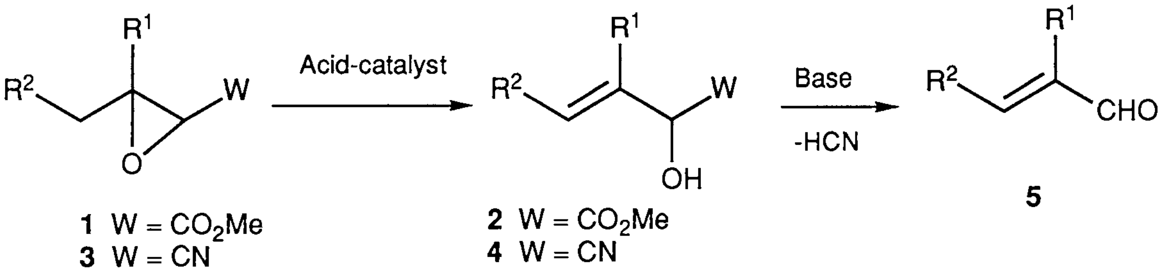
Isomerization of glycidic esters and nitriles to the corresponding 2-hydroxy-3-alkenoates and their nitrile derivatives occurred on treatment with triphenylsilyl perchlorate or electrogenerated acid (EG acid). The cyanohydrin moiety of the nitriles **4** was transformed to a formyl group, giving the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

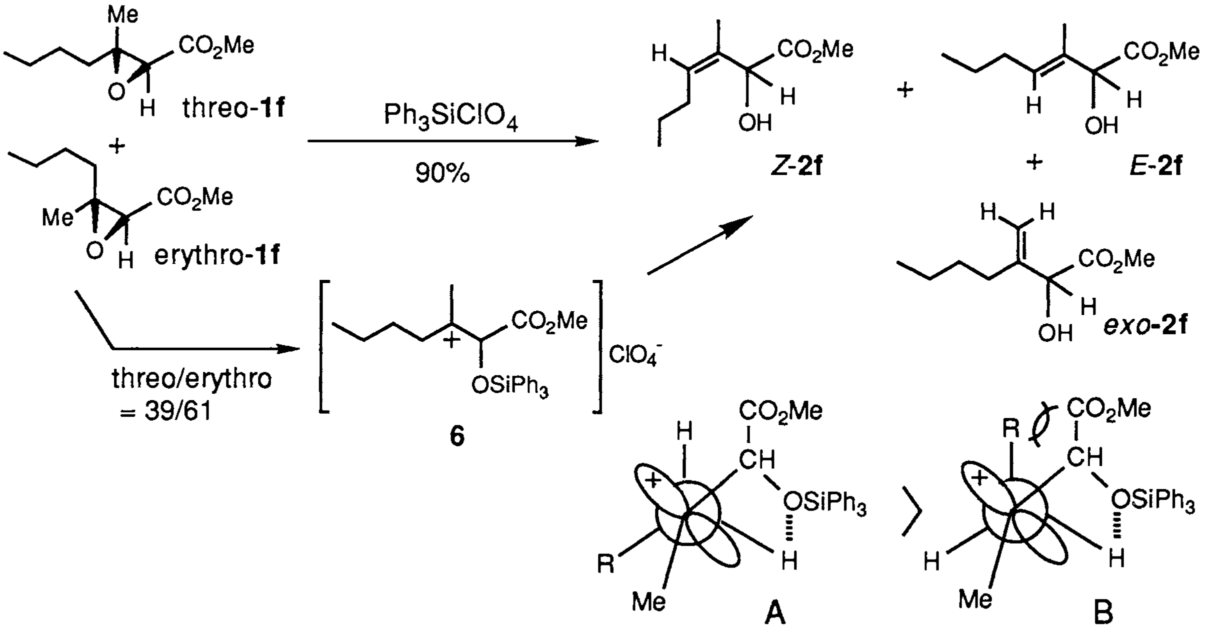
Acid-catalyzed isomerization of glycidic esters is useful in obtaining 2-hydroxy-3-alkenoates, versatile building blocks for the synthesis of bioactive compounds[1) and liquid crystals.[2) A variety of conventional Brønsted acids,[3) Lewis acids (stoichiometric use),[4) and transition metal (Pd, Rh)-olefin complexes[5) are proposed for this purpose. However, some of them require the operation at high temperature[5) 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 (Ph_3SiClO_4), prepared from chlorotriphenylsilane (Ph_3SiCl) and silver perchlorate,[6) or electrogenerated acid (EG acid) as an acid catalyst.[7)



1 W = CO_2Me
3 W = CN
2 W = CO_2Me
4 W = CN
5

Treatment of **1a** with 0.1 equivalent of Ph_3SiClO_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 CH_2Cl_2-$LiClO_4$-Bu_4NClO_4-(Pt) system[7) 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 perchlorate[8) (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 Ph_3SiClO_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 Ph_3SiClO_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)siloxylated methyl group.[11]



Scheme 1.

Furthermore, isomerization of the glycidic nitrile **3a** was achieved on treatment with the EG acid or Ph_3SiClO_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.

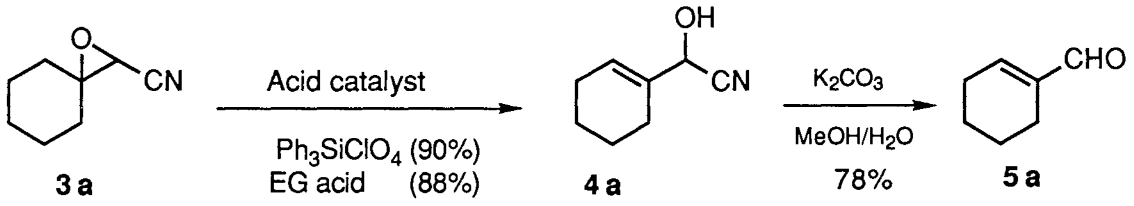
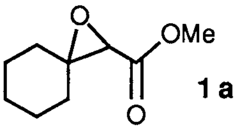
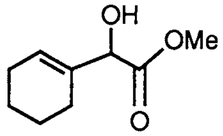
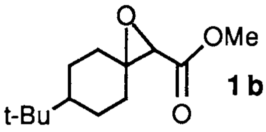
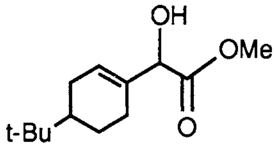
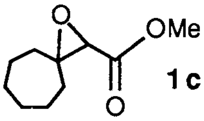
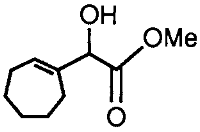
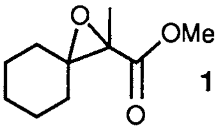
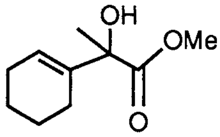
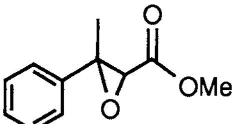
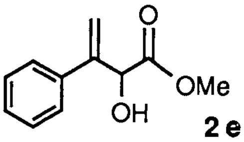


Table 1. Isomerization of Glycidic Esters **1** with Ph_3SiClO_4 or EG acid[a)]

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

a) Unless otherwise noted, the substrate (1 mmol) was treated with a solution of Ph_3SiClO_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 (Ph_3SiClO_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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References

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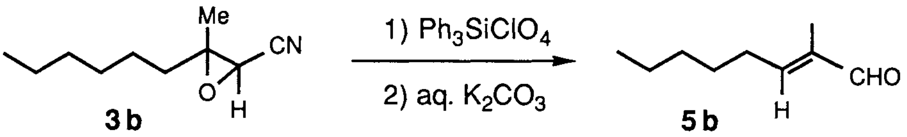
8) T. Inokuchi, Y. Kurokawa, M. Kusumoto, S. Tanigawa, S. Takagishi, and S. Torii, *Bull. Chem. Soc. Jpn.*, **62**, 3739 (1989).

9) 2-Hydroxy-3-phenyl-3-butenoate (**2e**) derived from the glycidic ester **1e** is useful as a precursor of bioactive β-methylenephenylalanine$^{12)}$ 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 μm 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 $\mathrm{CH_2Cl_2}$ (3 ml) was added a 0.2M $\mathrm{Ph_3SiClO_4}$ in $\mathrm{CH_2Cl_2}$ (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 $\mathrm{Et_3N}$ (3 drops). Evaporation of the volatiles and purification of the residue by column chromatography ($\mathrm{SiO_2}$, hexane-AcOEt = 5:1) gave 163 mg (95%) of **2a**: IR (neat) 3440 (OH), 1740 (C=O) cm^{-1}; ^{1}H NMR (500 MHz) δ 1.50-1.68 (m, 4H, $\mathrm{CH_2}$), 1.72-1.79 (m, 1H, $\mathrm{CH_2}$), 3.06 (brs, 1H, OH), 3.77 (s, 3H, $\mathrm{OCH_3}$), 5.80 (m, 1H, HC=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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