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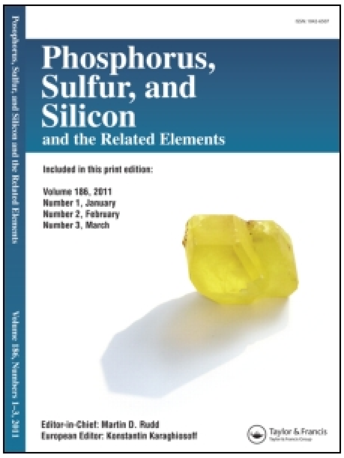

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Studies on the Silylation Reaction of α,β-Epoxy Esters Synthesized by Darzen's Condensation Reaction

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STUDIES ON THE SILYLATION REACTION OF α,β-EPOXY ESTERS SYNTHESIZED BY DARZEN'S CONDENSATION REACTION

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(Received May 6, 2003; accepted June 10, 2003)

Me_3SiCl/Mg in HMPA was used for silylation of α,β-epoxy esters resulting in the corresponding β-silylated esters in a one pot reaction with reasonable yields.

Keywords: Epoxidations; epoxides; esters; ring opening; silicon

RESULTS AND DISCUSSION

Since Si—C bond forming reactions are the key for organosilicon chemistry and silicon industry, the search for a new Si—C bond forming reaction is an important task.[1,2] Si—C bond forming reactions such as the direct synthesis,[3] hydrosilylation,[4] and general organometallic reactions,[5] are important methods for the preparation of various organosilicon compounds. Another established Si—C bond forming reaction is the direct silylation of activated alkenes with trimethylsilylchloride (TMSCl) in the presence of Mg and hexamethylphosphorictriamide (HMPA) as solvent.[6–8] This reaction generally proceeds in good yields, and the reaction conditions require stoichiometric amounts of alkene and TMSCl. Furthermore, this reaction cannot be applied to unactivated alkenes and all attempts to utilize TMSCl as silylating agent have been unsuccessful.[9] Our research has focused on the developments of new synthetic methods and reactions of organosilicon

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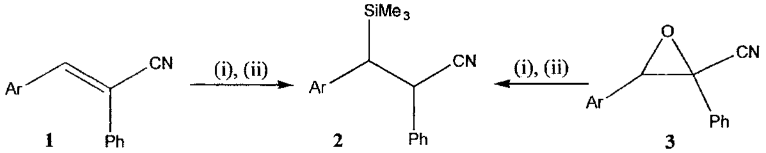
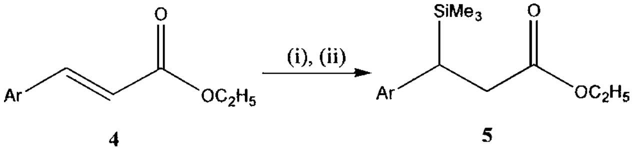
compounds. We are particularly interested in the modified direct synthesis of organosilicon compounds via silylation reactions.

In the previous work, Bolourtchian and coworkers reported that, β-silylated nitriles **2** can be produced by the silylation of α,β-unsaturated nitriles **1** and cyanoepoxides **3** (Scheme 1).[10,11] We also reported that silylation of α,β-unsaturated esters could lead to the related β-silyl esters (Scheme 2).[13]



Reagents: (i) Me_3SiCl, Mg, HMPA (ii) H_3O^+

SCHEME 1

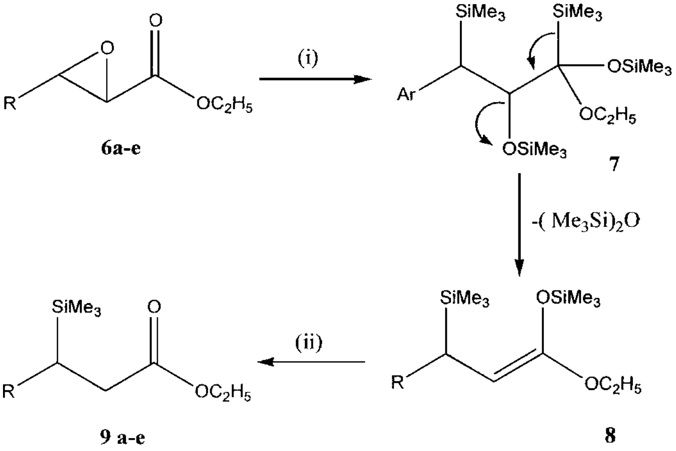


Reagents: (i) Me_3SiCl, Mg, HMPA (ii) H_3O^+

SCHEME 2

In continuation of our interest for the synthesis of organosilicon compounds and mechanistic studies of silylation reactions, herein we extend our methodology to the silylation of α,β-epoxy esters for production of the corresponding β-silylated esters. The reaction of Me_3SiCl/Mg with α,β-epoxy esters in the presence of HMPA as solvent gave the related β-silylesters (Table I). Ring cleavage at the β-position of the epoxy esrer **6**, followed by the addition of TMS groups, leads to **7** that is a tetrasilylated compound, which is the results of the addition of two TMS groups to the epoxide ring and two TMS groups to the carbonyl function. After elimination of $(Me_3Si)_2O$, silylated enoxysilane **8** is obtained. Hydrolysis of **8** in acidic conditions gives β-silylated ester **9** (Scheme 3).

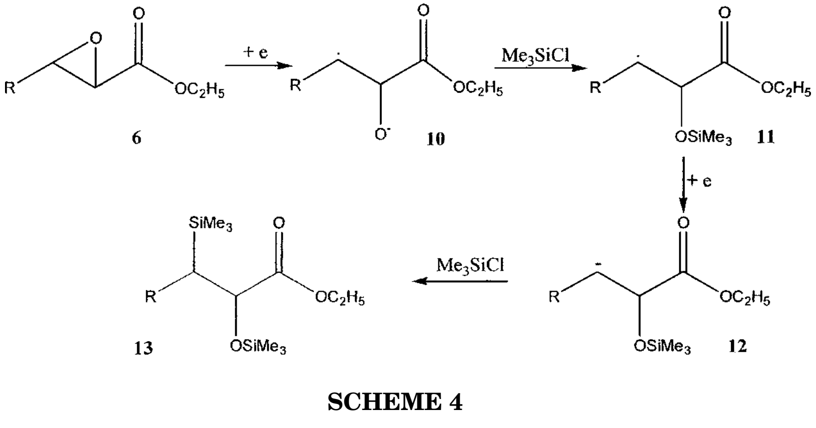
The mechanism of the reaction is depicted in Scheme 4. 2 The reaction is initiated by one electron transfer from Mg metal to the epoxy ester **6** to give the corresponding radical anion **10**. The radical anion **10** is subjected to the electrophilic attack by TMSCl, generating the



Reagents: (i) Me_3SiCl, Mg, HMPA (ii) H_3O^+

SCHEME 3

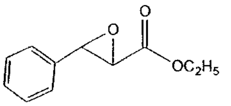
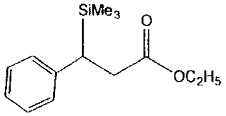
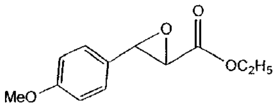
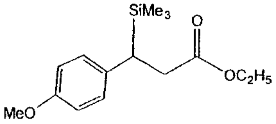
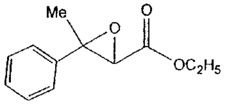
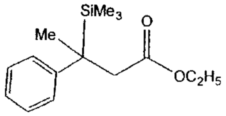
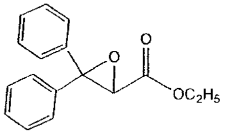
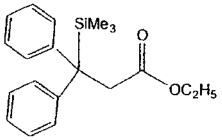
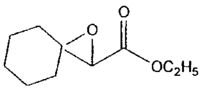
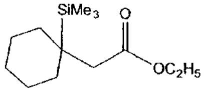
radical species **11**, followed by the fast second electron transfer. Subsequently, the anionic intermediate **12** reacts with another TMSCl to produce O-trimethylsilyl β-silylated ester **13** (Scheme 4) which is subjected to further silylation reaction at the carbonyl group to produce the tetrasilylated product (**7**).



SCHEME 4

In this reactions, three roles for TMSCl may be postulated: activation of the epoxide ring as electrophiles by coordination to the oxygen atom of the epoxide, stabilization of the anion intermediates, and activation of Mg metal. The prepared α,β-epoxy esters and β-silylated esters are summarized in Table I. The reactions also were examined in different

TABLE I Silylation of α,β-Epoxy Esters

Entry	Epoxy ester **6**	Products **9**	Yields[a] (%)
a			60
b			65
c			58
d			70
e			53

[a] Isolated yields.

solvent media by using DMF which resulted in radical coupling and reduced the yields of silylated products.

In the research undertaken epoxy esters **6a–c**, which were prepared by Darzen's methodology, were produced as a mixture of *cis/trans* isomers (**6a**: 43/57; **6b**: 32/68; **6c**: 39/61). In a silylation reaction on isomeric mixture of **6c**, examination of the isolated disilylated intermediate (**13**) by ^{1}HNMR showed that the *cis* isomer reacts much faster than the *trans* isomer, leaving appreciable amount of *trans* isomer unreacted.

Therefore the epoxy ester isomers (**6a–c**) were separated by an enzymatic method using Pig's liver esterase (PLE) as a catalyst in phosphate buffer (0.1M, pH = 8) at room temperature. The enzyme hydrolyzed the *trans*-isomer leaving the *cis*-isomer intact. The silylation reaction was conducted on the *cis* isomer. In this respect, the research is underway.

In conclusion a practical and convenient protocol has been developed for the silylation of α,β-epoxy esters to give β-silylated esters. This reaction appears to be general for activated alkenes and epoxide systems. It can be applied to the synthesis of multiple-point pharmacophores of bioorganosilicon compounds and also of carbon-silicon bond formation.

EXPERIMENTAL

General

Chemicals were purchased from Merck and Fluka. IR spectra were determined on a Shimadzo IR-470 spectrometer. ^{1}H NMR spectra were recorded on a Brucker AC, FT-NMR (80 MHZ) in deuteriochloroform ($CDCl_3$) with tetramethylsilane (TMS). Preparative thin layer chromatography was prepared from Merck Kieselgel 60 H, F_{254}, Art No 7730. GC was carried out using Buck Scientific 910 (capillary column, MXT-5, 15 m). All solvents used were dried and distilled according to standard procedures.

General Procedure for Silylation of Epoxy Esters

To a three-necked flask Mg powder (2.5 equiv) and TMS-Cl (5 equiv) in HMPA (20-mL mmol^{-1}) was added. The flask was heated and the temperature of the solution was kept at 60°C. Then the epoxy ester **6** (1 equiv) was added dropwise during 60 min under Argon. The resulting solution was stirred for an additional 48 h at the same temperature. The mixture was poured into 20 mL of cold water. Hydrolysis of the compounds was carried out with saturated $NaHCO_3$ solution. The aqueous layer was extracted three times with diethylether. The ethereal layer was dried over Na_2SO_4 and the solvent was evaporated. The crude product was distillated under reduced pressure (10 mmHg) to give β-silylated ester **9** as an oil. The isolated yield for each product is given in parentheses and the IR, ^{1}H NMR data for the compounds **11a–e** are given below.

6a: Colorless oil (60%, 140°C/10 mmHg); (Found: C, 64.15; H, 8.61; O, 16.91; Si, 10.1. $C_{14}H_{22}O_2Si$ requires C, 64.28; H, 8.57; O, 17.1; Si, 10.00%); IR (liquid film); 3030, 1755, 1254, 845 cm^{-1}; ^{1}H NMR ($CDCl_3$); δ, 0.0 (s, 9H), 0.2 (t, J 6.3 Hz, 3H), 1.0–1.18 (t, J 6.1 Hz, 3H), 2.74 (d, J 6.1 Hz, 2H), 3.84–4.2 (q, J 7.1 Hz, 2H), 7.1–7.2 (m, 5H) ppm.

6b: Colorless oil (65%, 146°C/10 mmHg); (Found: C, 64.20; H, 8.50; O, 17.21; Si, 10.19. $C_{15}H_{24}O_3Si$ requires C, 64.28; H, 8.57; O, 17.1; Si, 10.00%); IR (liquid film); 3029, 1753, 1256, 847 cm^{-1}; ^{1}H NMR ($CDCl_3$); δ, 0.0 (s, 9H), 0.15 (t, J 6.3 Hz, 1H), 1.0–1.2 (t, J 6.1 Hz, 3H), 2.74 (d, J 6.2 Hz, 2H), 3.5 (s, 3H), 3.8–4.18 (q, J 7.1 Hz, 2H), 6.5–7.2 (m, 5H) ppm.

6c: Colorless oil (58%, 130°C/10 mmHg); (Found: C, 68.10; H, 9.05; O, 12.21; Si, 10.71. $C_{15}H_{24}O_2Si$ requires C, 68.18; H, 9.09; O, 12.12; Si, 10.60%); IR (liquid film); 3032, 2972, 1760, 1253, 847 cm^{-1}; ^1H NMR ($CDCl_3$); δ, −0.9 (s, 9H), 0.7 (s, 3H), 1.1–1.21 (t, J 6.1 Hz, 3H), 2.69 (s, 2H), 3.9–4.2 (q, J 7.1 Hz, 2H), 7.2 (m, 5H) ppm.

6d: Colorless oil (70%, 155°C/10 mmHg); (Found: C, 73.68; H, 8.05; O, 9.78; Si, 8.59. $C_{20}H_{26}O_2Si$ requires C, 73.61; H, 8.09; O, 9.82; Si, 8.62%); IR (liquid film); 3030, 2952, 1762, 1253, 844 cm^{-1}; ^1H NMR ($CDCl_3$); δ, −0.1 (s, 9H), 1.0–1.2 (t, J 6.1, 3H), 2.70 (s, 2H), 3.8–4.2 (q, J 7.1, 2H), 7.1–7.4 (m, 10H) ppm.

6e: Colorless oil (53%, 130°C/10 mmHg); (Found: C, 64.50; H, 10.71; O, 13.41; Si, 11.38. $C_{13}H_{26}O_2Si$ requires C, 64.46; H, 10.74; O, 13.22; Si, 11.57%); IR (liquid film); 3050, 2962, 1750, 1252, 845 cm^{-1}; ^1H NMR ($CDCl_3$); δ, 0.0 (s, 9H), 0.9–1.1 (t, J 6.1. Hz, 3H), 1.2–1.5 (m, 10H), 2.71 (s, 2H), 3.82–4.2 (q, J 7.1 Hz, 2H)., 2H), 3.8–4.2 (q, J 7.1 Hz, 2H). 7.1–7.4 (m, 10H) ppm.

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