This article was downloaded by: [University of California Santa Cruz] On: 09 October 2014, At: 12:34 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/gpss20

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

Mohammed Bolourtchian^a, Manouchehr Mamaghani^b & Abed Badrian^b

^a Chemistry and Chemical Engineering Research Center of Iran, Tehran, Iran

^b Guilan University, Rasht, Iran

Published online: 18 Jun 2010.

To cite this article: Mohammed Bolourtchian, Manouchehr Mamaghani & Abed Badrian (2003) Studies on the Silylation Reaction of α , β -Epoxy Esters Synthesized by Darzen's Condensation Reaction, Phosphorus, Sulfur, and Silicon and the Related Elements, 178:12, 2545-2550, DOI: <u>10.1080/714040968</u>

To link to this article: <u>http://dx.doi.org/10.1080/714040968</u>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions



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

Mohammed Bolourtchian,^a Manouchehr Mamaghani,^b and Abed Badrian^b Chemistry and Chemical Engineering Research Center of Iran, Tehran, Iran^a and Guilan University, Rasht, Iran^b

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

 Me_3SiCl/Mg in HMPA was used for silulation of α,β -epoxy esters resulting in the corresponding β -silulated 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

We are grateful to the Iranian National Research Council for financial support of our research program.

Address correspondence to Manouchehr Mamaghani, Department of Chemistry, Faculty of Sciences, Guilan University, P.O. Box 41335-1914, Rasht, Iran. E-mail: m-chem41@ guilan.ac.ir

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



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 Me₃SiCl/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 esters **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 (Me₃Si)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) Me₃SiCl, Mg, HMPA (ii) H₃O⁺

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

Entry	Epoxy ester 6	Products 9	Yields ^a (%)
a	OC ₂ H ₅	SiMe ₃ O OC ₂ H ₅	60
b	MeO O OC2H5	SiMe ₃ OC ₂ H ₅	65
С		Me OC ₂ H ₅	58
d	OC ₂ H ₅	SiMe ₃ O OC ₂ H ₅	70
e		SiMe ₃ O OC ₂ H ₅	53

TABLE I Silulation of α, β -Epoxy Esters

^aIsolated 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 ¹HNMR 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 silulation of α,β -epoxy esters to give β -silulated 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 carbonsilicon bond formation.

EXPERIMENTAL

General

Chemicals were purchased from Merck and Fluka. IR spectra were determined on a Shimadzo IR-470 spectrometer. ¹H NMR spectra were recorded on a Brucker AC, FT-NMR (80 MHZ) in deuteriochloroform (CDCl₃) 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 NaHCO₃ solution. The aqueous layer was extracted three times with diethylether. The ethereal layer was dried over Na₂SO₄ 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, ¹H 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. C₁₄H₂₂O₂Si requires C, 64.28; H, 8.57; O, 17.1; Si, 10.00%); IR (liquid film); 3030, 1755, 1254, 845 cm⁻¹; ¹H NMR (CDCl₃); 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; ¹H NMR (CDCl₃); 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 (CDCl₃); 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 (CDCl₃); 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 (CDCl₃); 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.

REFERENCES

- [1] E. W. Colvin, Silicon Reagents in Organic Synthesis (Academic Press, London, 1988).
- [2] W. Weber, Silicon Reagents for Synthesis (Springer-Verlag, Berlin, 1983).
- [3] K. M. Lewis and D. G. Rethwisch, *Catalyzed Direct Reactions of Silicon* (Elsevier, Amsterdam, 1993).
- [4] B. Marciniec, Comprehensive Handbook on Hydrosilylation (Pergamon Press, Oxford, 1992).
- [5] W. Noll, Chemistry and Technology of Silicones (Academic Press, New York, 1968).
- [6] a) M. Bolourtchian, P. Borgeois, J. Dunogues, N. Duffaut, and R. Calas, J. Organometal. Chem., 43, 139 (1972); b) J. Dunogues, M. Bolourtchian, R. Calas, N. Duffaut, and J. P. Picard, J. Organometal. Chem., 34, 157 (1972).
- [7] R. Calas, M. Bolourtchian, J. Dunogues, and N. Duffaut, J. Organometal. Chem., 34, 269 (1972).
- [8] J. Dunogues, R. Calas, M. Bolourtchian, C. Biran, and N. Duffaut, J. Organometal. Chem., 57, 55 (1973).
- [9] M. Bolourtchian, R. Calas, J. Dunogues, and N. Duffaut, J. Organometal. Chem., 33, 303 (1971).
- [10] M. Bolourtchian, A. Saednya, and R. Nouri, J. Sci. I. R. Iran, 3, 177 (1990).
- [11] M. Bolourtchian and A. Saednya, J. Sci. I. R. Iran, 4, 57 (1990).
- [12] R. Calas, J. Dunogues, and M. Bolourtchian, J. Organometal. Chem., 26, 195 (1971).
- [13] M. Bolourtchian and A. Badrian, Phosphorus, Sulfur and Silicon, 152, 129 (1999).