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OLEFINS FROM VINYLSILANES WITH STRICT RETENTION OF CONFIGURATION

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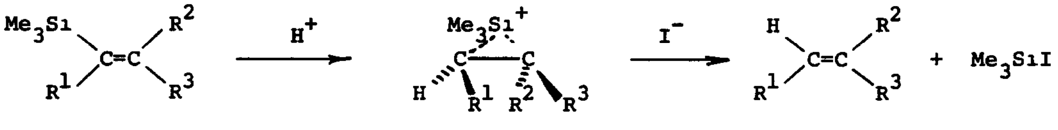
We wish to report the stereospecific exchange of Me_3Si for H proceeding on the olefinic carbon by the action of hydrogen iodide. This unprecedented reaction[1] appears of potential synthetic value in view of the availability of vinylsilanes.[2]

A benzene[3] solution of (E)-1-trimethylsilyl-1-octene[4] was treated with 0.5 equiv. of hydriodic acid[6] at room temperature. Glc analyses indicated that the vinylsilane was consumed within 4 h and that the sole product was 1-octene (yield 92%). (Z)-1-Trimethylsilyl-1-octene[7] gave that same product (yield 97%) and remarkably (E)-7-trimethylsilyl-7-tetradecene[8] afforded (Z)-7-tetradecene[9] (yield 91%; glc of which indicated the contamination of about 6% of (E)-isomer).[10, 11, 12]

Instead of hydriodic acid a small amount of iodine and water or deuterium oxide were also effective for the reaction, as this was anticipated from the recorded iodination of vinylsilanes.[2h] This modification opens a novel route for stereospecific deuteration of olefinic carbon.

To a benzene solution of (E)-1-trimethylsilyl-1-octene, 0.1 equiv. of iodine and excess deuterium oxide were added and the mixture was heated at reflux for 3 h. (E)-1-Deuterio-1-octene was obtained in 97% yield (d_1 90%). Analogously, (Z)-1-trimethylsilyl-1-octene gave (Z)-deuterio-1-octene (yield 100%, d_1 92%)[13] and finally (E)-7-trimethylsilyl-7-tetradecene afforded (Z)-7-deuterio-7-tetradecene (yield 90%, d_1 89%).[14]

The above described highly stereospecific reaction can be explained as follows. In accord with the Koenig-Weber postulation,[1a] protonation gives rise to carbocation stabilized and fixed by β-trimethylsilyl group. The iodide ion attacks the silicon atom to produce the olefin with retention of configuration. Regeneration of hydrogen iodide is suggested by the detection of hexamethyldisiloxane from the reaction mixture.



$$2\ \mathrm{Me_3SiI} + \mathrm{H_2O} \longrightarrow \mathrm{Me_3SiOSiMe_3} + 2\ \mathrm{HI}$$

A trisubstituted vinylsilane has raised a problem. When 3-ethyl-4-trimethylsilyl-3-nonene[15] was treated with catalytic amount of hydriodic acid or 0.1 equiv. of iodine in benzene,[3] 3-ethyl-3-nonene was obtained in about 90% yield. Treatment of this silane with 0.5 equiv. of hydriodic acid afforded, however, a mixture of 3-ethyl-3-nonene and 3-ethyl-2-nonene. Iodine (0.1 equiv.) and excess deuterium oxide provided a mixture of multideuterated olefins.[16] With this exception in mind, the sequence is shown to be applicable to a wide variety of vinylsilanes to give the corresponding olefins.

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REFERENCES AND NOTES

1. Preparation of olefins from vinylsilanes has been reported on some special cases; (a) Styrylsilane: K. E. Koenig and W. P. Weber, J. Amer. Chem. Soc., **95**, 3416 (1973); (b) With anchimeric assistance of hydroxy group: T. H. Chan and W. Mychajlowskij, Tetrahedron Letters, 3479 (1974).

2. Synthetic application of alkenylsilanes: (a) G. Stork and E. Colvin, J. Amer. Chem. Soc., **93**, 2080 (1971); (b) G. Stork and B. Ganem, ibid., **95**, 6152 (1973); (c) G. Stork and M. E. Jung, ibid., **96**, 3682 (1974); (d) G. Stork, M. E. Jung, E. Colvin and Y. Noel, ibid., **96**, 3684 (1974); (e) R. K. Boeckman, Jr., ibid., **96**, 6179 (1974); (f) G. Stork and J. Singh, ibid., **96**, 6181 (1974), (g) T. H. Chan, M. P. Li, W. Michajlowskij and D. N. Harpp, Tetrahedron Letters, 3511 (1974); (h) R. B. Miller and T. Reichenbach, ibid., 543 (1974).
3. Commercially available material was used without any purification.
4. Chloroplatinic acid-catalyzed reaction of trichlorosilane and 1-octyne and the following treatment with methylmagnesium iodide gave (E)-1-trimethylsilyl-1-octene in 80% yield.[5]
5. Regio- and stereoselectivity of the hydrosilylation: R. A. Benkeser, M. L. Nelson and J. V. Swisher, J. Amer. Chem. Soc., **83**, 4385 (1961).
6. Commercially available constant boiling hydriodic acid was used.
7. Obtained from 1-trimethylsilyl-1-octyne by hydroboration and successive treatment with acetic acid. Analogous vinylsilane preparation was reported.[2h]
8. Prepared from 7-tetradecyne by hydrosilylation, cf. note 4.
9. Structure of the olefin could be determined by comparison of the corresponding epoxide with the authentic sample.
10. Typical reaction procedure: To a benzene (1 ml) solution of (E)-7-trimethylsilyl-7-tetradecene (134 mg, 0.5 mmol), 0.04 ml of hydriodic acid was added. The mixture was stirred at room temperature for 15 min and alkali treatment and chromatography of the reaction mixture gave (Z)-tetradecene (89.5 mg).
11. Hexamethyldisiloxane was detected from the reaction mixture by glc and ms.
12. When 0.1 equiv. of hydriodic acid was treated with the above described silanes, the corresponding olefins were obtained after prolonged reaction time.
13. Nmr spectra of (E)- and (Z)-isomers indicated that both isomers were formed stereoselectively.

14. Representative reaction conditions: The mixture of (E)-7-trimethylsilyl-7-tetradecene (268 mg, 1 mmol), 2 ml of benzene, 0.1 ml of D_2O (purity 99%) and iodine (25.4 mg, 0.1 mmol) was heated at reflux for 2 h. Chromatographic separation of the reaction mixture gave (Z)-7-deuterio-7-tetradecene.
15. Preparation from trimethylsilylacetylene by successive treatment with butyllithium, triethylborane, aqueous alkali and iodine. Detailed description of this type of reaction will be published; K. Utimoto, M. Kitai, M. Naruse and H. Nozaki, in preparation.
16. A mixture of 3-ethyl-3-nonene, (Z)- and (E)-3-ethyl-2-nonene, roughly equimolar each, was obtained. These olefins contained deuterium in allylic positions in addition to the olefinic one (d_4 19%, d_3 38%, d_2 29% d_1 11%).