

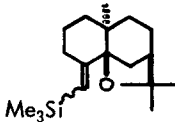
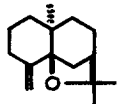
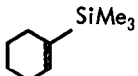

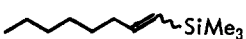

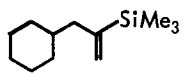

OLEFINS FROM VINYLSILANES BY HYDROLYSIS
IN THE PRESENCE OF p-TOLUENESULFINIC ACIDGeorge Büchi and Hans Wüest
Department of Chemistry,
Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139, USA

(Received in USA 11 July 1977; received in UK for publication 14 October 1977)

Vinylsilanes have become important intermediates and many synthetic schemes call for their conversion to olefins.¹ Traditionally this has been accomplished by hydrolysis in the presence of strong acids, such as hydrochloric,^{2, 3} hydrobromic² or trifluoromethane sulfonic acid.² In the presence of hydriodic acid the hydrolysis is sufficiently rapid that vinylsilane isomerization does not compete with cleavage and the transformation thus proceeds with retention of configuration at the carbon-silicon bond.⁴ We have utilized this last mentioned method for the hydrolysis of silane 1⁸ and obtained the olefin in 77% yield. This product was dark colored and contained minor amounts of by-products, which proved to be difficult to remove.

We have found that vinylsilanes can be converted to olefins in wet refluxing acetonitrile in the presence of catalytic amounts of p-toluenesulfonic acid. The results are summarized in the Table. Entries

Table Hydrolysis of Vinylsilanes in Refluxing Wet Acetonitrile Containing p-Toluenesulfonic Acid.

| | Vinylsilane | Conditions | Product | Yield % |
|---|---|--|--|------------------|
| 1 |  | 0.2 eq TsH, 1.5 h (or 1 eq TsH, 10 h/20°) |  | 92 |
| 2 |  | 0.2 eq TsH, 3h |  | 81 |
| 3 |  | 0.2 eq TsH, 3h |  | 85 |
| 4 |  | 1 eq TsH, 18h |  | < 5 ⁹ |

1 - 3 demonstrate the utility of the method. Vinylsilane 4 is exceptionally unreactive. It was resistant to treatment with p-toluenesulfonic acid and exposure to hydriodic acid in benzene⁴ for 24 hours at 20° produced only 10% olefin. The p-toluenesulfonic acid promoted cleavage of vinylsilanes lacks stereo-specificity. Both E- and Z-isomers of vinylsilane 3 gave the same mixture of deuterated olefins when cleaved with deuterio-p-toluenesulfonic acid. A comparison of our method with that using hydriodic acid⁴

revealed the latter to be a much faster reaction and the new method will probably only be superior when acid sensitive groups are present in a compound (e.g., silane 1).

The course of the reaction can be rationalized as follows: Protonation of the vinylsilane to give a bridged cation² followed by attack of sulfinate on silicon to produce the olefin and trimethyl-p-tolyl-sulfinate. The latter then combines with water yielding hexamethyldisiloxane and regenerating the catalyst.

General Procedure. The vinylsilane (10 mmol) and p-toluenesulfonic acid⁵ (2 mmol) in moist acetonitrile⁶ (10 - 30 ml) was heated at reflux for 1.5 - 3 h. The solvent was evaporated, and the residue filtered in hexane through alumina. Low boiling olefins were separated by pouring the reaction mixture into aqueous 5% Na₂CO₃ and separating the oily layer.⁷

Example. Silane 1⁸ (1.46 g; 5 mmol) and p-toluenesulfonic acid (0.16 g; 1 mmol) in 15 ml of moist acetonitrile⁶ was heated at reflux for 1.5 h. Evaporation, followed by filtration in hexane through 20 g of aluminum oxide, gave 1.01 g (92%) of β-agarofuran, bp 55⁰ (0.1 mm).

Acknowledgment. We are indebted to Firmenich SA Geneva for generous financial support.

REFERENCES AND NOTES

1. General references: C. Eaborn, "Organosilicon Compounds", Academic Press, New York, N.Y., 1960. S. S. Washburne, *J. Organometal. Chem.*, **123**, 1 (1976). I. Fleming, *Chem. Ind.*, 449 (1975). P. F. Hudrlík in "New Applications of Organometallic Reagents in Synthesis", D. Seyferth Ed., Elsevier Scientific Publishing Comp., Amsterdam, 1976, p. 127.
2. K. E. Koenig, W. P. Weber, *J. Am. Chem. Soc.*, **95**, 3416 (1973).
3. T. H. Chan, W. Mychajlowskij, B. S. Ong and D. N. Harpp, *J. Organometal. Chem.*, **107**, C₁ (1976).
4. K. Utimoto, M. Kitai and H. Nozaki, *Tetrahedron Letters*, 2825 (1975).
5. Prepared as follows: Commercial p-toluenesulfonic acid sodium salt was dissolved in water and acidified with dilute sulfuric acid. The sulfonic acid was collected by filtration and dried at 20⁰/0.1 mm. It was stable for at least 2 weeks when stored at room temperature.
6. Water (2%) was added to reagent grade acetonitrile. Although only partially soluble at 20⁰, the silanes dissolved at reflux temperature. The reaction can also be carried out in glyme or ethanol, however, longer reaction times are required.
7. The oily layer consisted of the olefin and hexamethyldisiloxane. Separation was achieved by fractional distillation or preparative glc.
8. The preparation of all vinylsilanes will be described in a paper by G. Büchi and H. Wüest, submitted to *J. Am. Chem. Soc.*
9. The balance consisted of starting material; the ammonium salt of p-toluenesulfonic acid, mp 340⁰ (dec.), had precipitated.