1,2-Anionic Rearrangement of Organosilylhydroxylamines[1,2]

Sir:

The 1,2-anionic rearrangement of hydrazines, in which organosilyl and aryl groups move from one nitrogen atom to another, was discovered in 1964[3] and has been described in a recent series of papers.[4] We now report the first 1,2-anionic rearrangement of a group from oxygen to nitrogen.

Pure N,O-bis(trimethylsilyl)hydroxylamine (**1**),[5] bp 65° (50 Torr), $n^{20}D$ 1.4120, was prepared by the reaction of excess hexamethyldisilazane with dry hydroxylamine in tetrahydrofuran (THF) at room temperature. That the product from this reaction has structure **1** is indicated by its nmr spectrum, which shows two sharp nmr peaks in the trimethylsilyl region at τ 9.85 and 9.92 and a broad resonance in the N–H region at τ 5.43, with relative intensity 9:9:1, respectively.

When **1** is converted to its lithium salt and added to a solution of methyl iodide in THF–pentane at room temperature, the rearranged anion of **1** is trapped as its methyl derivative **2** in high yield.

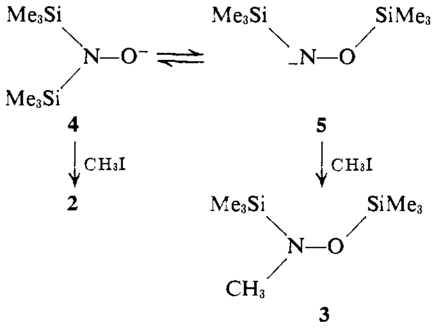
$$\underset{\mathbf{1}}{\mathrm{Me_3SiNHOSiMe_3}} \xrightarrow[\text{2. MeI}]{\text{1. } t\text{-BuLi}} \underset{\mathbf{2}}{\mathrm{(Me_3Si)_2NOMe}}$$

In a typical experiment, 4.05 g (22.9 mmol) of pure N,O-bis(trimethylsilyl)hydroxylamine was dissolved in 23 ml of pentane. To this was added at room temperature an equivalent amount of *t*-butyllithium dissolved in pentane, producing a white suspension and heat sufficient to reflux the pentane. The mixture was allowed to stir at room temperature for 24 hr to ensure complete reaction. The slurry was then added to a solution of 6.8 g (48 mmol) of methyl iodide in a mixture of 15 ml of pentane and 10 ml of THF and allowed to stir at room temperature for an additional 20 hr. Lithium iodide was separated from this reaction mixture by filtration under nitrogen. The clear filtrate was distilled to remove solvents and the residue afforded only one product, N,N-bis(trimethylsilyl)-O-methylhydroxylamine (**2**). Pure samples of **2** were obtained by preparative gas chromatography.

The nmr spectrum of **2** shows a single peak in the trimethylsilyl region, τ 9.90, and a single resonance at τ 6.57 assigned to the O-methyl protons, with relative areas 6.1:1, respectively, compared to the calculated ratio of 6:1. Unambiguous proof of the structure of **2** was obtained by synthesis of the compound by an independent route. The infrared and nmr spectra of the compound obtained from the reaction of hexamethyldisilazane with O-methylhydroxylamine hydrochloride are superimposable with those of **2**.

If the white suspension obtained from the reaction of **1** with *t*-butyllithium is derivatized immediately with methyl iodide, a mixture is obtained consisting of about 95% **2** with 5% of the unrearranged isomer, N,O-bis(trimethylsilyl)-N-methylhydroxylamine (**3**). Compound **3** shows two trimethylsilyl resonances in the nmr at τ 9.92 and 9.98, and an N-methyl resonance at τ 7.31, in the expected intensity ratio. The structure of **3** was further established by independent synthesis from N-methylhydroxylamine hydrochloride and hexamethyldisilazane.

The above results indicate that rearrangement of the anion of **1** is rapid under the conditions employed. However, when the white suspension of lithiated **1**, prepared at room temperature and stirred 24 hr, was slowly added to a methyl iodide–THF–pentane solution kept at −78°, *an approximately 1:1 mixture of* **2** *and* **3** *was obtained.* This finding suggests that the rearranged O anion **4** is in equilibrium with the unrearranged anion **5**, and that this equilibrium shifts toward **5** at lower temperatures.



The experiments described above provide conclusive evidence for a third kind of heteroatomic 1,2-anionic rearrangement, to be added to the known Wittig (O → C) and Stevens (N → C) rearrangements. The absence of mono- or trisilylated hydroxylamine derivatives in the products suggests that the rearrangement is intramolecular, like the hydrazine rearrangements described earlier.[4] Studies of the mechanism of the transformation are in progress.

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[1] Paper IX in the series, New Anionic Rearrangements. Previous paper in this series: R. West, M. Ishikawa, and S. Murai, *J. Amer. Chem. Soc.*, **90**, 727 (1968).

[2] This work was supported by the Air Force Office of Scientific Research (SRC), Office of Aerospace Research, U. S. Air Force, Grant No. AF-AFOSR 1061-66.

[3] R. E. Bailey and R. West, *J. Amer. Chem. Soc.*, **86**, 5369 (1964).

[4] R. West, H. F. Stewart, and G. R. Husk, *ibid.*, **89**, 5050 (1967); R. West, *Pure Appl. Chem.*, in press; and references given in these publications.

[5] The compounds reported in this communication all gave satisfactory analyses for C, H, Si, and N. Syntheses of **1**, **2**, and **3** have recently been described: U. Wannagat and O. Smrekar, *Monatsh. Chem.*, **100**, 750 (1963); O. Smrekar and U. Wannagat, *ibid.*, **100**, 760 (1969).

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Secondary Isotope Effects as Photochemical Mechanistic Criteria. Photosensitized *cis–trans* Olefin Isomerization Not Involving the Olefin Triplet State

Sir:

Simple olefins interact photochemically with carbonyl compounds possessing n–π^* lowest triplets to give both *cis–trans* isomerization and oxetane formation.[1] Until recently, it was thought that electronic energy transfer from the carbonyl triplet to give the olefin triplet (reactions 2–4) was the mechanism of isomerization.[2,3]

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[1] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965.

[2] D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968).

[3] D. R. Arnold, R. L. Hinman, and A. Glick, *Tetrahedron Letters*, 1425 (1964).