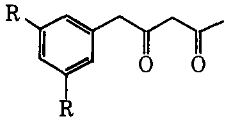
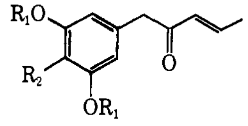
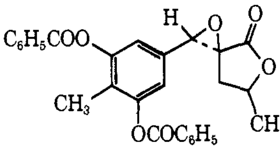
reduced with lithium aluminum hydride in ether and the resulting crude triol **17** was treated with lead tetraacetate in moist acetic acid to give **18** (45% based on **16**). Oxidation of **18** (Jones' reagent) provided diketone **19**, identified as the copper(II) chelate.[13]



7, R = OCH_3
19, R = H



8, $R_1 = CH_3$; R_2 = H
10, R_1 = H; $R_2 = CH_3$



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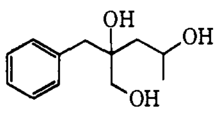

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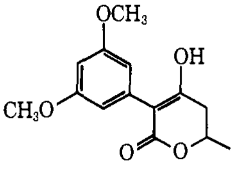
Functionality present within the system represented by **2** and **3** suggested the possibility of its rearrangement to a 5,6-dihydro-α-pyrone, an array found in a variety of acetogenins.[14] In fact, passage of boron trifluoride through a solution of **2** and **3** in benzene–dichloromethane (6:1) at 0° for 20 min initiated smooth conversion to dihydropyrone **20** (69%) (mp 150.5–153°; ν_{max} 3400, 2670, and 1700 cm^{-1}; nmr δ 1.42 (3 H, d, J = 6.5 Hz), 2.57 (2 H, d, J = 7.5 Hz), 3.74 (6 H, s), 4.58 (1 H, m), 5.8–6.5 (4 H, m, 1 H exchanged with D_2O)). Preferred migration of the carbonyl group to the benzylic cation is in accord with the recently noted rearrangement of glycidic esters to β-keto esters.[15] Treatment of **3** in dimethyl sulfoxide with 20% sulfuric acid at 80° for 3 hr, on the other hand, resulted in clean rearrangement to hydroxy acid **21** (33%; mp 131.5–132.5°; ν_{max} 3450, 1750, and 1600 cm^{-1}; nmr δ 1.30 (3 H, d, J = 6 Hz), 1.9 (2 H, m), 3.73 (6 H, s), 4.6 (1 H, m), 4.75 (1 H, s), 5.8 (1 H, broad, exchanged with D_2O), 5.98 (1 H, broad s, exchanged with D_2O), 6.38 (1 H, t, J = 2 Hz), 6.60 (2 H, d, J = 2 Hz)). Further applications of the foregoing and related transformations to synthesis of polyketide systems will be reported subsequently.



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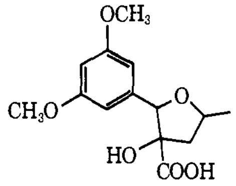

21

[13] K. G. Hampton, T. M. Harris, and C. R. Hauser, *J. Org. Chem.*, **29**, 3512 (1964).

[14] F. M. Dean, "Naturally Occurring Oxygen Ring Compounds," Butterworths, London, 1963, p 82.

[15] S. P. Singh and J. Kagan, *J. Amer. Chem. Soc.*, **91**, 6198 (1969).

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New Anionic Rearrangements. XII. 1,2-Anionic Rearrangement of Alkoxysilanes[1-3]

Sir:

Many organic ethers may be converted to isomeric alcohols in the presence of excess organolithium reagent by the classical Wittig rearrangement.[4,5] However, no analogous rearrangement has been described for alkoxysilanes. Instead, the reverse rearrangement in which a silylcarbinol rearranges to an alkoxysilane is a well-known reaction in organosilicon chemistry, due to studies by Brook and his students.[6] This "anti-Wittig" rearrangement takes place by an intramolecular anionic mechanism, *catalyzed* by a small amount of base.

$$R_3SiCR'_2OH \xrightarrow{\text{base}} HCR'_2OSiR_3$$

We now report the first example of a Wittig-type[7] rearrangement of an alkoxysilane to give the isomeric α-silylcarbinol. The rearrangement is expected to be quite general provided, as in the Wittig rearrangement, a proton on the carbon attached to oxygen in the alkoxysilane can be selectively metalated by an alkyllithium reagent.[8] Evidence indicates the silyl-Wittig and Brook rearrangements involve equilibration between deprotonated and neutral pairs of isomers, respectively.

Benzyloxytriethylsilane (**1**), bp 162° (20 Torr), n^{24}D 1.4867 [lit.[10] bp 262.6° (760 Torr), n^{20}D 1.4852], was prepared by condensation of benzyl alcohol and triethylchlorosilane in the presence of excess pyridine. The product was shown to be pure by gas chromatography, and the nmr spectrum confirmed structure **1**. When **1** was treated with a slight excess of *tert*-butyllithium in pentane at room temperature, and the mixture was subsequently neutralized with aqueous acid, the rearranged compound **2** was produced in high yield.

In a typical experiment, 26.8 mmol of *tert*-butyllithium was added to 5.0 g (22.4 mmol) of **1** in 50 ml of dry pentane at room temperature. A deep yellow-brown color, yellow in dilute solution, developed over the next 48 hr without any suspended solids appearing.

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[1] Previous paper in this series: R. West and H. F. Stewart, *J. Amer. Chem. Soc.*, **92**, 853 (1970).

[2] For a review of silyl anionic rearrangements see R. West, *Pure Appl. Chem.*, **19**, 291 (1969).

[3] Research sponsored by Air Force Office of Scientific Research (SRC)-O.A.R., USAF, Grant No. AF-AFOSR 69-1772 and 70-1904.

[4] G. Wittig and L. Löhmann, *Justus Liebigs Ann. Chem.*, 550, 260 (1942).

[5] D. L. Dalrymple, T. L. Kruger, and W. N. White in "The Chemistry of the Ether Linkage," S. Patai, Ed., Interscience, New York, N. Y., 1967, p 617.

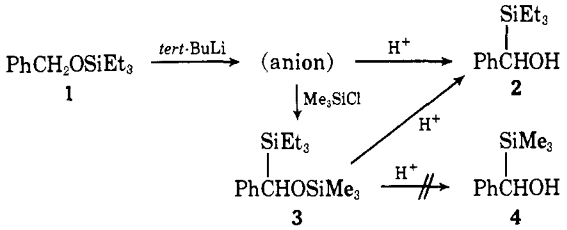
[6] A. G. Brook, *J. Amer. Chem. Soc.*, **80**, 1886 (1958); **81**, 981 (1959); A. G. Brook and B. Iachia, *ibid.*, **83**, 827 (1961); A. G. Brook, *Pure Appl. Chem.*, **13**, 215 (1966).

[7] The alkoxysilane → α-silylcarbinol rearrangement is formally analogous to the Wittig rearrangement, but whether or not it should be considered a true Wittig rearrangement is a matter of definition. The alkoxysilane rearrangement probably proceeds by an intramolecular mechanism involving a pentacoordinate silicon intermediate, whereas many Wittig rearrangements apparently proceed by cleavage–recombination reactions. See H. Schäfer, U. Schollköpf, and D. Walter, *Tetrahedron Lett.*, 2809 (1968); P. T. Lansbury, V. A. Pattison, J. D. Sidler, and J. B. Bieber, *J. Amer. Chem. Soc.*, **88**, 78 (1966).

[8] The reaction may however be limited by competing metalation at methyl groups attached to silicon. Thus benzyloxytrimethylsilane cannot be used as a substrate because metalation of the silylmethyl protons occurs.[9]

[9] H. F. Stewart, Ph.D. Thesis, University of Wisconsin, 1969, and G. A. Gornowicz and R. West, *J. Amer. Chem. Soc.*, **90**, 4478 (1968).

[10] B. N. Dolgov, N. P. Kharitonov, and M. G. Voronkov, *Zh. Obshch. Khim.*, **24**, 1178 (1954); *Chem. Abstr.*, **49**, 12275 (1955).



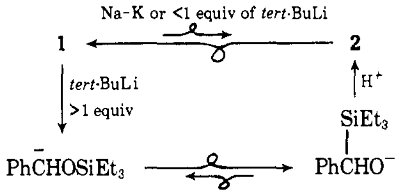
Excess *tert*-butyllithium remained after this time, as shown by a positive Gilman color test I. The solution was neutralized with dilute HCl, becoming pale yellow. The organic layer was immediately separated from the aqueous layer and the solvent evaporated. Vacuum distillation yielded 4.0 g of a clear oil which contained 75% rearranged isomer **2**, 18% **1**, and 7% benzyl alcohol and hexaethyldisiloxane, hydrolysis products of **1**. Repeating the experiment with a fivefold excess of *tert*-butyllithium, 96% **2**, 0.8% **1**, and 3% hydrolysis products were obtained after 144-hr reaction time, showing that not more than 0.8% **1** remained protonated in *tert*-butyllithium–pentane solution. Unlike the Wittig rearrangement there are no significant competing reactions apart from hydrolysis of starting material.

Elemental analysis and mass spectroscopy showed that **2** was isomeric with **1**. Structure **2** was assigned from the proton nmr which showed the characteristic triethylsilyl multiplet between τ 8.9 and 9.8, a broadened singlet at 8.2 (OH), a singlet at 5.45 (CH), and a singlet at 2.84 (C_6H_5), with relative intensities 15.8:1.0:0.92:4.9. The ir spectrum (neat) shows a broad (OH) stretch between 3200 and 3650 cm^{-1}; $n^{22}{}_{\mathrm{D}}$ 1.5164.

When the rearrangement was repeated with the anionic species being trapped with trimethylchlorosilane, hydrolysis of the product **3** produced **2** in 67% yield but none of **4**, showing that **3** had the structure PhCH($SiEt_3$)$OSiMe_3$. Therefore derivatization both with water and $(CH_3)_3SiCl$ suggests that the anion is in the form of **2** at the instant of reaction with the derivatizing agent.

"Anti-Wittig" rearrangement of the usual type studied by Brook also takes place for **2**. Treatment of **2** in anhydrous diethyl ether with sodium–potassium alloy gave 100% **1** after 2-min contact, without observable evolution of hydrogen or attack on the alkali metal. The reaction, repeated in pentane, required 40 min for 99.5% completion. Since this is still much faster than the silyl-Wittig rearrangement it was of interest to add sodium–potassium alloy to the completely deprotonated product of the silyl-Wittig rearrangement, known to give only **2** upon neutralization, to see if **1** would still form. No **1** was observed after 24-hr treatment of the anion solution with sodium–potassium alloy. Thus, with sodium–potassium alloy, **2** is the preferred product when anions are equilibrated, and **1** the preferred product when neutral species are equilibrated. Catalytic quantities of *tert*-butyllithium also cause rearrangement of **2** to **1**. When 1 mmol of **2**, neat, was treated with 0.50 mmol of 1.25 *M* *tert*-butyllithium in pentane, 0.53 mmol of **1** was formed at equilibrium after 24 hr.

These rearrangements can be summarized in the following cyclic reaction scheme.[11]



Rearrangements of silylcarbinols and related compounds to alkoxysilanes have been explained as proceeding in the observed direction because of the stability of the Si–O bond in the product. This explanation may be valid when neutral species are equilibrated, as with sodium–potassium alloy. In our example the anions are equilibrated and the rearrangement proceeds in the opposite direction. We believe this is because the greater stability of the oxyanion *vs.* the carbanion outweighs the energy difference between the Si–O and C–O bonds. Further experiments should establish whether this is true for silylcarbinolate anions generally.[12]

[11] However, it is also possible that the anion of **2** has a unique bridged structure, rather than being a simple alkoxide ion as drawn.

[12] Examples of probable 1,3 and 1,4 anionic rearrangements of silyl groups from O to C have also been found. See ref 9.

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On the Stereochemical Aspects of the Photochemistry of Mixed-Ligand Chromium(III) Complex Ions

Sir:

Some discussion is being generated[1,2] about the stereochemical implications of Adamson's empirical rules[3–6] governing the photolysis of nonoctahedral chromium(III) complexes. Some of our recent results have an important bearing on this subject.

The question is the extent to which the rules as stated by Adamson in a series of papers on Cr(III) photolysis[3–6] imply stereochemical consequences with regard to the course of photoreaction and the final configuration of the products. If one reads this series of papers carefully one is left with the definite impression that the author does expect such stereochemical consequences[5,6] despite his occasional denials that they are required by the rules.[5,6] The recent paper by Balzani[2] draws attention to this apparent inconsistency and to the question of whether the rules can be considered empirical should they not imply stereochemical consequences. It seems that the stereochemical question has not, however, been clearly separated into its components.

Fundamentally there are two points at issue, both meaningful and susceptible to experimental proof, at least in principle. They are as follows.

[1] V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, London, 1970, p 101.

[2] M. F. Manfrin, L. Moggi, and V. Balzani, *Inorg. Chem.*, **10**, 207 (1971).

[3] A. W. Adamson, *J. Phys. Chem.*, 71, 798 (1967).

[4] A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, and R. D. Lindholm, *Chem. Rev.*, **68**, 541 (1968).

[5] A. W. Adamson, *Coord. Chem. Rev.*, **3**, 169 (1968).

[6] E. Zinato, R. D. Lindholm, and A. W. Adamson, *J. Amer. Chem. Soc.*, **91**, 1076 (1969).