hence of arylphosphonous acids, of potentially as wide versatility as the Doak–Freedman phosphonic acid synthesis. Work is continuing to define the scope of the synthesis and establish optimum reaction conditions.

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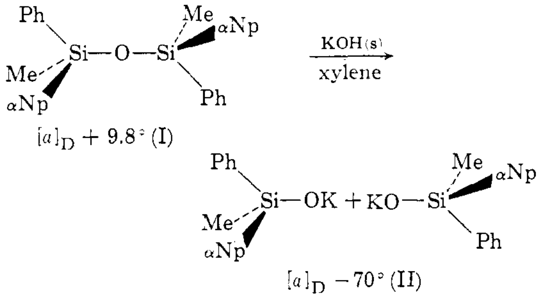
STEREOCHEMISTRY OF SUBSTITUTION AT SILICON. REACTIONS OF THE SILICON-OXYGEN BOND WITH INVERSION AND RETENTION OF CONFIGURATION

Sir:

For the first stereochemical studies of the silicon–oxygen bond we have used the optically active compounds R_3Si^*—O—, all of which contain the α-naphthylphenylmethylsilyl group (α-NpPhMeSi-). Reaction (1) below is an unusual case in stereochemistry. Formation of optically pure potassium silanolate (II) rigorously proves *retention* of configuration as the stereochemical path.



[α]D + 9.8° (I)

[α]D −70° (II)

(1)

The *optically active disiloxane* (I) was synthesized from II and (+)R_3Si^*Cl, and II was obtained from reaction of (+)R_3Si^*OH with either potassium hydroxide or potassium.

$$R_3Si^*\text{—}OCH_3 \xrightarrow[\text{xylene}]{\text{KOH (s)}} R_3Si^*\text{—}OK \qquad (2)$$

[α]D −16° (III) [α]D +68° (IV)

Retention of configuration in (2) is rigorously demonstrated by formation of III from IV and dimethyl sulfate, a reaction which does not involve the asymmetric center.

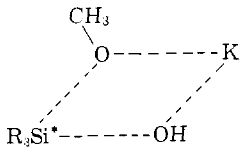
$$R_3Si^*\text{—}O\text{—}COCH_3 \xrightarrow[\text{xylene}]{\text{KOH (s)}} R_3Si^*\text{—}OK \qquad (3)$$

[α]D +18° (V) [α]D +60° (VI)

$$R_3Si^*\text{—}O\text{—}COCH_3 \xrightarrow[\text{pentane; amine}]{CH_3OH} R_3Si^*\text{—}OCH_3 \qquad (4)$$

[α]D +16° (V) [α]D −12° (VII)

Predominant *inversion* in reactions (3) and (4) is demonstrated rigorously by formation of (−) R_3Si^*—$OCOCH_3$ from VI and acetyl chloride, a reaction which does not involve the asymmetric center. Sensitivity of stereochemistry to variations in leaving group and solvent is apparent. For more basic leaving groups (methoxy and siloxy relative to acetoxy) poor ionizing solvents favor retention probably by favoring SNi reaction of relatively undissociated complexes.



SNi retention in xylene

The change to a good ionizing solvent results in inversion reactions even for the methoxysilane (III). Thus, III is rapidly racemized in methanol solvents by small concentrations of methoxide ion. Furthermore, III is hydrolyzed by base in aqueous acetone to (+)R_3Si^*OH, [α]D +2°, with predominant inversion in a reaction competitive with silanol racemization.

For the less basic leaving groups, inversion seems to be favored in both types of solvents for the α-naphthylphenylmethylsilyl compounds.

R_3Si^*OH,[1] [α]D +26°, in xylene, shaken with powdered potassium hydroxide (KOH, 85%; H_2O, 13–14%) gave II. (Hydrolysis of II under controlled conditions yields the original silanol.) Reaction II with (+)R_3Si^*Cl[2] gave I (m.p. 88–89°; found: Si, 11.1; characteristic Si-O-Si infrared maximum at 9.55 microns). Reactants were heated (steam-bath) for one hour in reactions (1) and (2). Reaction of IV with dimethyl sulfate gave rapid formation of III,[1] [α]D −16°, m.p. 64°. Reaction of II with excess acetyl chloride gave V (found: Si, 9.2; sapn. equiv., 306). Reaction (3) is rapid at 25° and gave VI in a reaction at least 85% stereospecific. Reaction (4) gave VII in 27% yield in a reaction at least 90% stereospecific.

We thank Dow Corning Corporation for generous support.

[1] L. H. Sommer and C. L. Frye, THIS JOURNAL, in press.

[2] L. H. Sommer and C. L. Frye, *ibid.*, **81**, 1013 (1959).

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THE MECHANISM OF THE VON RICHTER REACTION

Sir:

The transformation of aromatic nitro compounds to carboxylic acids through the agency of alcoholic potassium cyanide was first described in 1871 by von Richter.[1] Since the reaction was invariably attended by loss of the nitro function, von Richter initially assumed that cyanide ion, from which the carboxyl group derived, displaced the nitro group directly from its position on the aromatic nucleus.

The concurrent structural investigations of Meyer, Wurster, Solkowsky and especially of Griess and Korner[2] ultimately compelled von Richter to revise the structures assigned to his acidic products and, in 1875, in the last of his papers on the subject, he concluded that the carboxyl function must take up a position on the aromatic ring *ortho* to that vacated by the nitro group. This formulation of the reaction has since been amply

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[1] V. von Richter, *Ber.*, **4**, 21 (1871), and succeeding papers, *ibid.*, **4**, 459, 553 (1871); **7**, 1145 (1874); **8**, 1418 (1875).

[2] P. Griess, *ibid.*, **5**, 192 (1872); W. Korner, *Gazz. Chim. Ital.*, 306 (1874).