found in the products enters *via* a side reaction not involved in the isomerization. These results do not exclude the possibility that the isomerization takes place by repeated use of a very small number of Bronsted sites, but an upper limit is defined for the number of these, *i.e.*, not more than several per cent of n_g. By generous estimate, this amounts to $n_a = 0.01$ mmole ($n_g = 0.37$ mmole) or $1 \times 10^{12}/\text{cm.}^2$, a value much lower than current estimates of Bronsted[2] or Lewis[3] acidity. Taking $1.5 \times 10^{14}/\text{cm.}^2$ as the surface concentration of OD groups,[4] the total available deuterium was 1.1 mmole. The cumulative deuterium removed from the catalyst was 0.06 mmole while 0.54 mmole of olefin was produced.

In these experiments, a portion of the first slug (and smaller amounts of succeeding ones) was retained on the catalyst and lost from the mass balance. This was particularly noticeable in experiments where larger amounts of catalyst and smaller slug size were employed, here, nearly all of the first slug and large portions of the second were so consumed. In all cases, however, about the same amount of hydrocarbon disappeared from 5 slugs, *viz.*, $\sim 10^{13}/\text{cm.}^2$. In order to test for the possible interaction of such residues, propylene-d_6 was circulated over a deuterated catalyst at 155° for 20 min. During this treatment, the gas phase was monitored by a mass spectrometer and C_5 and C_6 species were observed; it was estimated that $8 \times 10^{12}/\text{cm.}^2$ propylene molecules had been irreversibly adsorbed. Slugs of cyclopropane were then passed using helium carrying gas. The results obtained did not differ substantially from those shown in Fig. 1. Similarly, when the conversion level was raised to over 90% by increasing the temperature from 148 to 160°, the extent of deuteration was not greatly different; in fact, the cyclopropane-d_1 fraction from this experiment exceeded that of propylene-d_1. These observations strengthen the view that isomerization and hydrogen exchange do not involve a common mechanism, although they may involve a common intermediate.

Some further insight into the processes taking place was gained from an experiment in which slugs of an equimolar mixture of cyclopropane and cyclopropane-d_6 were passed over the same catalyst at the same temperature. Extensive mixing occurred and multiply deuterated products were formed. The distribution of these did not appear to change with slug number. The mole percentages of the possible cyclopropane products from the third slug were: $d_0, d_1-d_6 = 31, 14, 7, 3, 7, 14$, and 24. The corresponding values for the propylenes were: 13, 18, 11, 10, 15, 20, and 13. These results are consistent with the recent finding of Larson and Hall[5] that a bimolecular complex is operative in the exchange of isobutane hydrogen with deuterated cracking catalysts.

The distribution of products is not the equilibrium distribution; it is inverted and suggests that the exchange process is stepwise. No large isotope effects were found. The ratio of reacting cyclopropane-d_6 to cyclopropane was about 1.05. This would seem to rule out any concerted mechanism or any step involving the transfer of hydrogen as rate determining.

This work is continuing and is being extended to studies of the double bond isomerization of butene-1 and the dealkylation of cumene. A full report of this work will be made at a later date.

(2) A. E. Hirschler, Preprints, Petroleum Division, 114th Meeting, American Chemical Society, General Papers, Vol. 8, 1963, p. 87.

(3) H. P. Leftin and W. K. Hall, *Actes Congr. Intern. Catalyse, 2e, Paris, 1960,* **1,** 1353 (1961).

(4) W. K. Hall, H. P. Leftin, F. J. Cheselske, and D. E. O'Reilly, *J. Catalysis,* in press.

(5) J. G. Larson and W. K. Hall, *J. Am. Chem. Soc.,* **85,** 3570 (1963).

MELLON INSTITUTE   W. KEITH HALL
PITTSBURGH, PENNSYLVANIA   JOHN G. LARSON
                                    H. R. GERBERICH
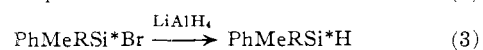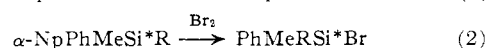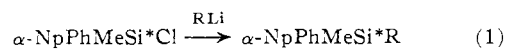   RECEIVED SEPTEMBER 18, 1963

Stereochemistry of Asymmetric Silicon: Synthesis, Stereochemistry, and Absolute Configurations of New Optically Active Organosilicon Systems

Sir:

Studies of optically active triorganomonofunctional silicon systems have previously been limited to compounds containing the α-naphthylphenylmethylsilyl group, α-NpPhMeSi-. The finding of many stereospecific reactions of compounds containing this group and elucidation of their stereochemistry[1-4] have made it important to determine whether parallel behavior would obtain for other optically active organosilicon systems.

We wish to report: (a) a synthetic route (which is widely applicable) for conversion of compounds containing the α-NpPhMeSi- group to optically active compounds containing the groups PhMeRSi- in which R is neopentyl, benzhydryl, or ethyl, (b) a high degree of stereospecificity for reactions of the new systems which thus far parallel those of the original system, (c) assignment of absolute configuration to compounds containing the new systems.

The synthetic route to new systems uses optically active α-NpPhMeSi*Cl and an organolithium compound, RLi, for conversion to α-NpPhMeSi*R,[5] and cleavage of the α-naphthyl group with bromine, as α-bromonaphthalene to give PhMeRSi*Br,[6] which is then converted to PhMeRSi*H by lithium aluminum hydride reduction. Purification of the new system, removal of α-bromonaphthalene and small amounts of other organic products, is best accomplished after reduction.

$$\alpha\text{-NpPhMeSi*Cl} \xrightarrow{\text{RLi}} \alpha\text{-NpPhMeSi*R} \qquad (1)$$

$$\alpha\text{-NpPhMeSi*R} \xrightarrow{\text{Br}_2} \text{PhMeRSi*Br} \qquad (2)$$

$$\text{PhMeRSi*Br} \xrightarrow{\text{LiAlH}_4} \text{PhMeRSi*H} \qquad (3)$$

The first Walden cycle for silicon[7] involved conversion of α-NpPhMeSi*H to its enantiomer *via* chlorination followed by lithium aluminum hydride reduction. For the new systems similar Walden cycles were found. For the new system in which R = neopentyl, $\equiv$Si*H ($[\alpha]_D +2.5°$) gives $\equiv$Si*Cl ($[\alpha]_D +5.9°$), which upon reduction furnishes $\equiv$Si*H ($[\alpha]_D -2.5°$). For the new system in which R = benzhydryl, $\equiv$Si*H($[\alpha]_D$

(1) L. H. Sommer, C. L. Frye, M. C. Musolf, G. A. Parker, P. G. Rodewald, K. W. Michael, Y. Okaya, and R. Pepinsky, *J. Am. Chem. Soc.,* **83,** 2210 (1961).

(2) L. H. Sommer, *Angew. Chem. Intern. Ed. Engl.,* **1,** 143 (1962).

(3) A. G. Brook and C. M. Warner, *Tetrahedron Letters,* **18,** 815 (1962).

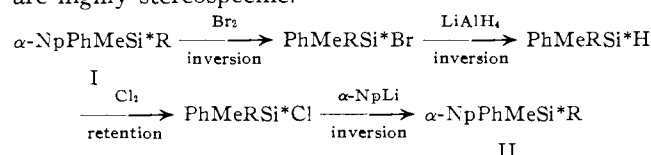(4) L. H. Sommer, P. G. Rodewald, and G. A. Parker, *ibid.,* **18,** 821 (1962).

(5) Coupling of α-NpPhMeSi*Cl with RLi has been found to proceed with inversion of configuration (see ref. 3 and 4) in accord with the principle of inversion of configuration for good leaving groups on Si in their reactions with strong nucleophiles, see ref. 1 and 2.

(6) The bromine cleavage of α-NpPhMeSi*-C$_6$H$_4$-p-OMe proceeds with inversion of configuration: C. Eaborn and O. W. Steward, *Proc. Chem. Soc.,* 59 (1963).

(7) L. H. Sommer and C. L. Frye, *J. Am. Chem. Soc.,* **81,** 1013 (1959).

$+7.1°$) gives $\equiv$ Si*Cl ($[\alpha]$D $+14.1$), which furnished $\equiv$Si*H ($[\alpha]$D $-6.4°$). For the new system in which R = ethyl, $\equiv$Si*H ($[\alpha]$D $+0.76°$) gives $\equiv$Si*Cl ($[\alpha]$D $+2.0°$) which upon reduction gives $\equiv$Si*H ($[\alpha]$D $-0.75°$). The parallel behavior of the four systems in these cycles leaves little doubt that for the new systems, as for the original system, chlorination proceeds *via* retention and reduction by inversion of configuration.[8]
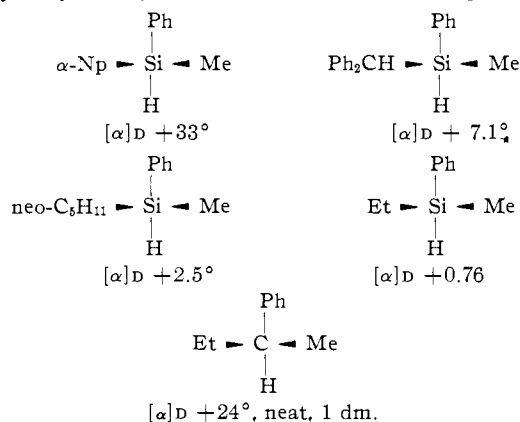
For the chlorosilanes having R = neopentyl or ethyl, coupling with α-naphthyllithium in ether gave back the α-NpPhMeSi*R derivatives which were enantiomers of the starting compounds. Since a high degree of conservation of optical activity obtains for these four-reaction sequences, it follows that the reactions involved are highly stereospecific.

$$\alpha\text{-NpPhMeSi*R} \xrightarrow[\text{inversion}]{Br_2} PhMeRSi*Br \xrightarrow[\text{inversion}]{LiAlH_4} PhMeRSi*H$$

I

$$\xrightarrow[\text{retention}]{Cl_2} PhMeRSi*Cl \xrightarrow[\text{inversion}]{\alpha\text{-NpLi}} \alpha\text{-NpPhMeSi*R}$$

II

For R = neopentyl, I had $[\alpha]$D $+23.2°$ whereas II had $[\alpha]$D $-18.6°$. For R = ethyl, I had $[\alpha]$D $-4.16°$ whereas II had $[\alpha]$D $+3.36°$. For R = benzhydryl, probably due to the presence of active hydrogen in this group, the cycle was less stereospecific; I had $[\alpha]$D $+15.5°$ whereas II had $[\alpha]$D $-7.1°$. The designated assignments of stereochemistry to each of the four reactions are in accord with previous stereochemical studies on the α-naphthylphenylmethylsilyl system,[1,2,5] and are also in accord with an assigned course of inversion of configuration for the cleavage of α-NpPhMeSi*C$_6$H$_4$-p-(OCH$_3$) with bromine[6] to give α-NpPhMeSi*Br.

The above Walden cycles, previous determination of the stereochemistry of reactions of α-NpPhMeSi*-compounds, and the recent rigorous determination of the absolute configuration of $(-)$-α-NpPhMeSi*H by the X-ray method,[9] lead to assignment of absolute configuration for compounds containing four organosilicon systems. This is done below for the dextrorotatory $\equiv$Si*H compounds.

The absolute configuration of the carbon analog[10] of phenylethylmethylsilane is included for comparison.

Ph
|
α-Np ◄ Si ◄ Me
|
H
$[\alpha]$D $+33°$

Ph
|
Ph₂CH ◄ Si ◄ Me
|
H
$[\alpha]$D $+7.1°$

Ph
|
neo-C₅H₁₁ ◄ Si ◄ Me
|
H
$[\alpha]$D $+2.5°$

Ph
|
Et ◄ Si ◄ Me
|
H
$[\alpha]$D $+0.76$

Ph
|
Et ◄ C ◄ Me
|
H
$[\alpha]$D $+24°$, neat, 1 dm.

It is noteworthy that the above first comparison of analogous compounds containing asymmetric silicon and asymmetric carbon indicates the same sign of $[\alpha]$D for the same configuration, and much smaller optical

(8) The new systems differ from the original system in that $\equiv$Si*H and $\equiv$Si*Cl having the same sign of $|\alpha|$D have the same configuration in the new systems. This is also true of the original systems for rotations measured below 340 mμ. Discussion of these aspects is deferred to a later paper.

(9) T. Oshida, R. Pepinsky, and Y. Okaya, Abstracts, International Union of Crystallography Congress, Rome, Italy, September, 1963. These results are in accord with a less rigorous determination utilizing Cram's rule of asymmetric induction and some reasonable assumptions: A. G. Brook and W. W. Limburg, *J. Am. Chem. Soc.*, **85**, 832 (1963).

(10) D. J. Cram and J. Allinger, *ibid.*, **76**, 4518 (1954).

rotation for the silicon compound. In the phenylethylmethyl systems, methyl and ethyl must have nearly the same polarizability, and the lower rotation of the silicon analog may reflect, at least in part, lower selectivity in conformation distribution due to the larger size of Si.

All three α-NpPhMeSi*R compounds (rotations given above for I) were prepared by treatment of $(-)$-α-NpPhMeSi*Cl with RLi in ether. Syntheses of $\equiv$Si*R, R = benzhydryl[3] or ethyl,[4] have been reported using this procedure. Cleavage of the α-naphthyl group was performed in benzene with equimolar bromine (*ca.* 2 *M* bromine) for 20 minutes at room temperature for R = neopentyl or ethyl and in carbon tetrachloride for 1 hr. for R = benzhydryl. Without isolation, the optically active bromosilanes were reduced to $\equiv$Si*H and the latter purified by fractional distillation in all cases, and also by subsequent recrystallization for the benzhydryl compound. All three silanes were dextrorotatory (rotations given above); two were liquids and the benzhydryl compound had m.p. 55–56°. Chlorination in carbon tetrachloride gave a dextrorotatory $\equiv$Si*-Cl compound (rotations given above) in all three cases; again, only the benzhydryl compound was crystalline and had m.p. 66–68°. Coupling of the dextrorotatory chlorides with α-naphthyllithium gave optically active α-NpPhMeSi*R compounds (rotations given above for II) which were purified by fractional distillation. Infrared spectra and analyses for the new compounds were all in accord with the assigned structures. Further work on the new optically active systems is in progress.

On the Stereochemistry of Homoenolization

Sir:

Recent work demonstrated that hydrogens beta to a carbonyl can be abstracted by alkali to produce homoenolate ions.[1] We have now studied the stereochemistry of the reverse process, the protonation of homoenolic species, and have found a high degree of stereospecificity whose mechanistic course depends on the medium. The results shed light on the stereochemistry of homoenolization and provide examples of electrophilic substitutions that proceed by inversion of configuration.

On mild treatment with alkalies, 1-acetoxynortricyclene[2] (I) yielded ion II, which collapsed to norbornan-2-one by protonation at either of the equivalent homoenolic carbons C-5 or C-6. In deuterated medium this homoketonization produced 6-deuterionorbornan-2-one with an *exo* deuterium (IIIa) or with an *endo* deuterium (IIIb) according to whether cleavage occurred with inversion or retention of configuration, respectively.[3] The 6-deuterionorbornan-2-one was converted to 2-deuterionorbornane (IV) by Wolff–Kishner reduction,[4] and the *exo/endo* ratio of deuterium in the hydrocarbon was determined by infrared spectroscopic comparison with authentic *exo-2d*-norbornane (IVa) and *endo-2d*-norbornane (IVb), which were separately synthesized as follows.

(1) A. Nickon and J. L. Lambert, *J. Am. Chem. Soc.*, **84**, 4604 (1962).

(2) Prepared as reported by H. Hart and R. A. Martin, *J. Org. Chem.*, **24**, 1267 (1959); *J. Am. Chem. Soc.*, **82**, 6362 (1960).

(3) Any deuterium subsequently incorporated at the enolizable position (C-3) in norbornan-2-one was removed after every run by repetitive treatment with potassium hydroxide in methanol–water.

(4) Deuterium analyses showed that no deuterium was lost during the Wolff–Kishner reduction.