for 45 min. completely destroyed the biological activity. After decolorizing, the solution was taken to a small volume and methanol and ethanol were added, yielding crystalline 1,3-diamino-4,5,6-trihydroxycyclohexane dihydrochloride (desoxystreptamine).[9] *Anal.* Calcd. for $C_6H_{14}N_2O_3 \cdot 2HCl$: C, 30.66; H, 6.86; N, 11.93; Cl, 30.17; neut. eq., 117.5. Found: C, 30.76; H, 6.99; N, 11.36; Cl, 29.6; neut. eq., 118.7. The compound showed no optical activity in acid or alkaline aqueous solution.

The dihydrochloride was converted to desoxystreptamine by dissolving in water, treating with Amberlite IR 410 ($\overline{OH}$),[3] concentrating, and crystallizing with ethanol. *Anal.* Calcd. for $C_6H_{14}N_2O_3$: C, 44.4; H, 8.70. Found: C, 44.66; H, 8.86.

A portion was converted to the dihydrobromide by crystallization from dilute aqueous HBr with methanol. It gave an infrared spectrum identical with that of an authentic sample of 1,3-diamino-4,5,6-trihydroxycyclohexane dihydrobromide isolated from neomycin.[10] The desoxystreptamine was additionally characterized by acetylation in pyridine and acetic anhydride to give pentaacetyl-1,3-diamino-4,5,6-trihydroxycyclohexane. *Anal.* Calcd. for $C_{16}H_{24}N_2O_8$: C, 51.6; H, 6.48; N, 7.53. Found: C, 51.7; H, 6.98; N, 7.30. Selective de-O-acetylation with Amberlite IR 410 ($\overline{OH}$)[3] in water yielded N,N′-diacetyl-1,3-diamino-4,5,6-trihydroxycyclohexane. *Anal.* Calcd. for $C_{10}H_{18}N_2O_5$: C, 48.77; H, 7.37. Found: C, 48.82; H, 7.73.

Other products of the acid hydrolysis shown to be present by paper chromatography include two ninhydrin-positive reducing materials, accounting for the major portion of the material left after removal of desoxystreptamine, and several minor components. These data allow speculation that kanamycin is a trisaccharide-like molecule, composed of two aminosugar moieties glycosidically linked to desoxystreptamine.

[9] D. A. Kuehl, Jr., M. N. Bishop and K. Folkers, THIS JOURNAL, **73**, 881 (1951).

[10] Supplied by Dr. H. E. Carter, University of Illinois.

RESEARCH DEPT.
BRISTOL LABORATORIES, INC.
SYRACUSE 1, NEW YORK

M. J. CRON
D. L. JOHNSON
F. M. PALERMITI
Y. PERRON
H. D. TAYLOR
D. F. WHITEHEAD
I. R. HOOPER

RECEIVED JANUARY 2, 1958

THE RESOLUTION OF A HEXACOVALENT SILICON (IV) COMPLEX

Sir:

The possibility of six-coördinate silicon(IV) has been discussed by Stone and Seyferth[1] who described the availability of d-orbitals for bonding in silicon(IV) compounds. West[2] described the infrared spectra of $[Si(acac)_3]Cl \cdot HCl$ (I) and other β-diketones of silicon(IV), and from a comparison of these spectra with that of free acetylacetone concluded that the ligands of I behave as bidentate chelating agents.

Consequently, it appears highly probable that the cation of I should have an octahedral configuration,[3,4] which leads to the conclusion that it should be asymmetric. A resolution of racemic $[Si(acac)_3]^+$ into its optical enantiomers[5] would offer conclusive evidence for its octahedral configuration.

Optical Resolution Studies.—Racemic $[Si(acac)_3]Cl \cdot HCl$ was prepared by a modification of the method of Dilthey[6] and its resolution was attempted by treatment with sodium (−)-dibenzoyl-*d*-tartrate,[7-9] according to the equation[10]

$$2\text{D,L-}[Si(acac)_3]Cl \cdot HCl + d\text{-}(-)\text{-}Na_2C_{18}H_{12}O_8 \longrightarrow \text{L-}[Si(acac)_3]d\text{-}(-)\text{-}HC_{18}H_{12}O_8 + \text{D-}[Si(acac)_3]Cl \cdot HCl + 2NaCl \quad (1)$$

The diastereoisomer $\text{L-}[Si(acac)_3]d\text{-}(-)\text{-}HC_{18}H_{12}O_8$ is less soluble than the other diastereoisomer and precipitates from solution. For $\text{L-}[Si(acac)_3]d\text{-}(-)\text{-}HC_{18}H_{12}O_8$, a 0.0088% solution showed α_{obs} to be $-0.068 \pm 0.003°$; $[\alpha]^{23}D -773°$. The optical rotation of the diastereoisomer decreased (became more positive) with time as the asymmetric silicon complex ion racemized, and, after six hours, the observed rotation decayed to a constant value (−0.008°) due to the asymmetric monohydrogen dibenzoyl-*d*-(−)tartrate anion. In order to replace the resolving anion with chloride, the diastereoisomer was treated with an anion-exchange resin in the chloride form (Dowex 1-X8), which gave $\text{L-}[Si(acac)_3]Cl \cdot HCl$. A 0.0311% solution of this enantiomer showed α_{obs} to be $-0.300 \pm 0.003°$; $[\alpha]^{23}D -965°$. The observed rotation decreased (became more positive) as the compound racemized, and decayed to zero degrees in six hours with a half-life of one hour. By extrapolation, the specific rotation, $[\alpha]^{23}D$ at zero time is found to be −1,300°. In order to determine whether the anion-exchange resin removed the negative rotating monohydrogen (−)-dibenzoyl-*d*-tartrate anion quantitatively from the diastereoisomer, an experiment was performed in which a sample of sodium monohydrogen (−)-dibenzoyl-D-tartrate was treated with resin under similar conditions; the filtrate showed no optical rotation, indicating that essentially complete removal of the asymmetric anion had been achieved.

The optical rotation of the filtrate from reaction 1 was found to be strongly dextrorotatory. It was treated with the chloride form of an anion-exchange resin (Dowex 1-X8) in order to remove the monohydrogen (−)-dibenzoyl-D-tartrate anion, and its rotation was measured. A 0.1164% solution showed $\alpha_{obs} = 0.790 \pm 0.03°$; $[\alpha]^{23}D +679°$. The observed rotation of this solution of the *dex-*

---

[1] F. G. A. Stone and D. Seyferth, *J. Inorg. Nuclear Chem.*, **1**, 112 (1955).

[2] R. West, Abstr. of Papers, 132nd Meeting, Am. Chem. Soc., 11-N (1957), THIS JOURNAL, in press.

[3] A. Werner, *Ber.*, **47**, 3087 (1914).

[4] J. C. Bailar, Jr., Ed., "Chemistry of the Coördination Compounds," Reinhold Publishing Co., New York, N. Y., 1956, pp. 274 ff.

[5] acac = acetylacetonate anion, $C_5H_7O_2^-$. This cation is also named tris-(2,4-pentanediono)-silicon(IV) cation.

[6] W. Dilthey, *Ber.*, **36**, 932, 1595 (1903).

[7] S. Kirschner, Dissertation, University of Illinois, 1954, p. 43.

[8] C. L. Butler and L. H. Cretcher, THIS JOURNAL, **55**, 2605 (1933).

[9] F. Zetzsche and M. Hubacher, *Helv. Chim. Acta*, **9**, 291 (1926).

[10] "D" and "L" indicate dextrorotatory and levorotatory complex ions, respectively; the "*d*-(−)-" prefix for dibenzoyltartrate indicates a negative rotating anion derived from dextrorotatory tartaric acid.

tro enantiomer decayed to zero degrees with a half-life of one hour at 23°, which is the same half-life observed for the *levo* isomer. The lower specific rotation of the *dextro* isomer is due to the presence of some *levo* isomer in a relatively large quantity of *dextro* isomer.

Resolution of the complex cation D,L-$[Si(acac)_3]^+$ into its optical enantiomers indicates that the silicon(IV) is six-coördinate in this complex, and that the cation is octahedral. The possibility of seven-coördination (coördination by the chloride ion) is remote in view of the conductivity of the complex in anhydrous chloroform solution. Additional details of the resolution of this and other six-coördinate silicon(IV) complexes will appear in a forthcoming publication.

The authors wish to express their sincere appreciation to the Union Carbide Corporation for a research fellowship grant which contributed significantly to the progress of this investigation.

DEPARTMENT OF CHEMISTRY S. K. DHAR
WAYNE STATE UNIVERSITY VERA DORON
DETROIT 2, MICHIGAN STANLEY KIRSCHNER

RECEIVED DECEMBER 19, 1957

DEUTERIUM EXCHANGE OF DECABORANE WITH DEUTERIUM OXIDE AND DEUTERIUM CHLORIDE

Sir:

We wish to report the results of a series of deuterium exchange experiments which illustrate the exchange of as many as eight hydrogen atoms of decaborane by deuterium and which further illustrate either the existence of two types of exchangeable hydrogens (bridge or terminal) or the dioxane catalyzed migration of bridge deuterium to terminal positions.

TABLE I

RESULTS OF D_2O–$B_{10}H_{14}$ EXCHANGE EXPERIMENTS IN DIOXANE SOLUTION AT ROOM TEMPERATURE

Equilibration time, hr.	Initial concn., mole/l.		B–D infrared absorption	Deuterium/mole
	$B_{10}H_{14}$	D_2O		
0.15	0.083	3.10	Bridge + extremely weak terminal	2.3
0.15	0.167	6.20	Bridge + very weak terminal	4.6
2.00	0.167	6.20	Bridge + weak terminal	5.2
36.0	0.083	3.10	Bridge + moderate terminal	6.2
72.0	0.120	1.55	Bridge + strong terminal	7.5

TABLE II

EXCHANGE OF $B_{10}H_{14}$ WITH DCl

Solvent	Exchange time, hr.	Initial quantities, moles		B–D infrared absorption	Deuterium/mole
		DCl	$B_{10}H_{14}$		
Dioxane	114	0.036	0.0024	Bridge + strong terminal	6.2
Dioxane	96	.032	.0016	Bridge + strong terminal	5.9
Methylene chloride	93	.0384	.0024	Identical with $B_{10}H_{14}$	0

Perdeuterodecaborane was prepared by the pyrolysis (100°) of perdeuterodiborane. This material gave B–D stretching absorptions in the infrared at 5.25 μ (terminal-d_{10}) and 7.30 μ (bridge-d_4). The latter absorption is characterized by a broad band and weak intensity. With normal decaborane the corresponding absorptions are found at 3.8 and 5.25 μ, respectively. All spectra were determined in carbon disulfide solution.

Partially deuterated samples of decaborane (prepared as described below) were sublimed, weighed and analyzed for hydrogen and deuterium by the quantitative pyrolytic decomposition of this material to boron and hydrogen–deuterium at 900° followed by mass spectrometric measurements of the H/D ratio.

Table I sets forth the infrared absorptions and deuterium analyses of several samples of decaborane which were equilibrated with deuterium oxide in dioxane solution for varying periods of time at room temperature.

As seen in Table I the first detectable deuterium which enters the decaborane molecule enters the bridge positions but longer equilibration times produce appreciable exchange at terminal positions. Furthermore the equilibration of a sample of $B_{10}H_{10}D_4$ (bridge-d_4) in pure dioxane produces after one day at room temperature appreciable amounts of absorption at 5.25 μ as a sharp band characteristic of terminal B–D bonds. Similar rearrangement of deuterium in $B_{10}H_{10}D_4$ (bridge-d_4) decaborane does not occur in methylene chloride solution under identical conditions of time and temperature.

Table II presents the results of three exchange experiments carried out with decaborane and deuterium chloride in sealed bulbs at room temperature. It is to be noted that methylene chloride solvent does not produce exchange.

These results clearly point to the fact that the four bridge hydrogens of decaborane are rapidly removed by bases (water, dioxane, etc.) and are easily replaced by acids (hydronium ion, hydrogen chloride, etc.). Furthermore, less rapid but appreciable exchange involving terminal positions appears to occur only in the presence of basic solvents such as dioxane or diethyl ether by what may be a base-catalyzed internal rearrangement of bridge deuterium to terminal positions or a base-catalyzed process involving another type of $B_{10}H_{13}^-$ anion formed by direct removal of a terminal proton. That this latter terminal hydrogen exchange process is not as rapid as bridge exchange is apparent from the above results.

REDSTONE ARSENAL RESEARCH
DIV. OF ROHM AND HAAS CO. M. FREDERICK HAWTHORNE
HUNTSVILLE, ALABAMA JOHN J. MILLER

RECEIVED JANUARY 2, 1958