

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MICHIGAN STATE UNIVERSITY, EAST LANSING, MICHIGANGroup Theory and Isomerism¹

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Polya's theorem has been used to determine the number of isomers of various types of inorganic compounds. By the introduction of the now well-known concept of a point group description of a molecule into Polya's formulation, we have been able to determine the number of both geometrical isomers and optical isomers for the first time. Cycle indices for most structures of inorganic chemistry are tabulated.

Introduction

The problem of determining the number of isomers of compounds can be approached by a brute force enumeration using drawings and models or by some analytical method of calculation. Counting isomers by means of models, referred to by Polya² as "Herumprobieren," becomes extremely difficult and subject to errors³ as the complexity of the structure increases. Applications of permutation group theory have been made by Lunn and Senior⁴ and others,⁵ who used their method. The most effective method of calculation is one devised and used by Polya^{2,6,7} for enumeration of isomers in fused aromatic systems. Polya's articles, however, are esoteric and have been largely overlooked except in one attempt by Hill⁸ to apply Polya's method to chemical isomerism in general.

Instead of employing the unfamiliar permutation group formalism, we have reformulated Polya's technique in terms of point groups. By using this more familiar approach we hope to promulgate group theoretical methods of calculating numbers of isomers.

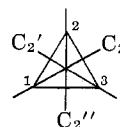
Mathematical Introduction

A permutation of degree n rearranges n distinct objects among themselves. The permutation

$$A = \begin{pmatrix} 1 & 2 & 3 & \dots & n \\ a_1 & a_2 & a_3 & \dots & a_n \end{pmatrix}$$

indicates that 1 is to be replaced by a_1 , 2 is to be replaced by a_2 , and so on. The ordered sequence $\{a_1, a_2, \dots, a_n\}$ is clearly some arrangement of the first n integers. With each element of a point group G , we can associate a permutation such that the set of all these permutations forms a so-called permutation group, G' , isomorphic to G .

The rotations which transform an equilateral triangle into itself form the point group D_3 of order 6. By means of the following diagram



one can readily write the permutation operation corresponding to each symmetry operation of D_3 .

Symmetry operation	Permutation
E	$\begin{pmatrix} 1 & 2 & 3 \\ 1 & 2 & 3 \end{pmatrix} = \begin{pmatrix} 1 \\ 2 \\ 3 \end{pmatrix} \begin{pmatrix} 2 \\ 3 \end{pmatrix} \begin{pmatrix} 3 \end{pmatrix}$
C_3^+	$\begin{pmatrix} 1 & 2 & 3 \\ 2 & 3 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 2 & 3 \\ 2 & 3 & 1 \end{pmatrix}$
C_3^-	$\begin{pmatrix} 1 & 2 & 3 \\ 3 & 1 & 2 \end{pmatrix} = \begin{pmatrix} 1 & 2 & 3 \\ 3 & 1 & 2 \end{pmatrix}$
C_2	$\begin{pmatrix} 1 & 2 & 3 \\ 1 & 3 & 2 \end{pmatrix} = \begin{pmatrix} 1 \\ 2 \\ 3 \end{pmatrix} \begin{pmatrix} 2 & 3 \\ 3 & 2 \end{pmatrix}$
C_2'	$\begin{pmatrix} 1 & 2 & 3 \\ 2 & 1 & 3 \end{pmatrix} = \begin{pmatrix} 1 \\ 2 \\ 3 \end{pmatrix} \begin{pmatrix} 2 & 3 \\ 3 & 2 \end{pmatrix}$
C_2''	$\begin{pmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \end{pmatrix} = \begin{pmatrix} 1 \\ 2 \\ 3 \end{pmatrix} \begin{pmatrix} 2 & 3 \\ 3 & 2 \end{pmatrix}$

The permutations have been expressed as a product of permutations that involve separate elements and which are called cycles. C_2 , for example, is said to consist of one cycle of length one and one cycle of length two. As suggested above, elements belonging to the same class consist of similar sets of cycles.

Polya's theorem is based upon a function called the cycle index. The cycle index of a group G is given by²

$$Z(G) = \frac{1}{g} \sum h_{i_1 i_2 \dots i_p} f_1^{i_1} f_2^{i_2} \dots f_p^{i_p} \quad (1)$$

where g is the order of G , p is the number of points permuted, f_1, f_2, \dots, f_p are p variables, and $h_{j_1 j_2 \dots j_p}$ is the number of permutations of G which consist of j_1 cycles of length 1, j_2 cycles of length 2, etc. The prime on the summation indicates that it is to be taken over all sets $\{j_k\}$ consistent with the condition that

$$\sum_{l=1}^p l j_l = P$$

As an example, the point group D_3 consists of one element of three cycles of length 1; two elements of one cycle of length 3; and three elements of one cycle of length 1 and one cycle of length 2. Therefore

$$Z(D_3) = 1/6(f_1^3 + 2f_3 + 3f_1 f_2)$$

(1) Supported by a research grant from the National Institute of Health.

(2) G. Polya, *Helv. Chim. Acta*, **19**, 22 (1936).

(3) See example III of text.

(4) A. C. Lunn and J. K. Senior, *J. Phys. Chem.*, **33**, 1027 (1929).(5) L. E. Marchi, W. C. Fernelius, and J. P. McReynolds, *J. Am. Chem. Soc.*, **65**, 329 (1943).(6) G. Polya, *Acta Math.*, **68**, 145 (1937).(7) G. Polya, *Krist.*, **93**, 415 (1936).(8) T. L. Hill, *J. Chem. Phys.*, **11**, 294 (1943).

TABLE I
CHOICE OF POINT GROUPS

For total no. of stereoisomers	For geometrical isomers
C _n	C _{nv}
	C _{nh}
	S _n
D _n	D _{nd}
	D _{nh}
T	T _d
O	O _h
I	I _h

The cycle index is not unique for a point group, since it also depends upon the number of points being permuted, *i.e.*, p , which for our example is 3.

Lastly, define a configuration counting series by

$$F(x_1, x_2, \dots, x_m) = \sum F_{k_1 k_2 \dots k_m} x_1^{k_1} x_2^{k_2} \dots x_m^{k_m} \quad (2)$$

where the summation is over $k_j = 0$ to ∞ for each j from 1 to m where m is the number of constituents. If $F_{k_1 k_2 \dots k_m}$ is the number of isomers when k_1 substituents of type 1, k_2 substituents of type 2, etc., are substituted into a skeletal parent compound, then Polya's theorem says that

$$F(x_1, x_2, \dots, x_m) = Z[G; f(x_1, x_2, \dots, x_m)] \quad (3)$$

where G is the point group of the skeletal parent compound and $Z[G; f(x_1, x_2, \dots, x_m)]$ denotes the polynomial obtained from $Z(G)$ by replacing f_j by $(x_1^j + x_2^j + \dots + x_m^j)$.⁹

In order to determine the number of ways of arranging two different kinds of atoms on the corners of an equilateral triangle, let $f(x_1, x_2) = x_1 + x_2$, since $m = 2$ (two different kinds of substituents), and obtain for D_3

$$F(x_1, x_2) = 1/6[(x_1 + x_2)^3 + 2(x_1^3 + x_2^3) + 3(x_1 + x_2)(x_1^2 + x_2^2)] = x_1^3 + x_1^2 x_2 + x_1 x_2^2 + x_2^3$$

The four unit coefficients, respectively, indicate that there is one way to distribute three atoms of the same kind, one way for two of the first kind and one of the second, one way for one of the first and two of the second, and only one way to distribute three of the second kind.

Choice of Point Group

In calculating the *total* number of stereoisomers, we choose the point group which corresponds to the rotations of the skeletal parent compound. This must include all the rotational symmetry elements. Enantiomorphs can then be eliminated by adding any planes or alternating axes of symmetry. Table I lists the common point groups consisting of pure rotations along with the point groups into which they transform by the addition of planes, etc. The total number of stereoisomers is calculated from the left-hand column, the number of geometrical from the right-hand column, and the number of pairs of enantiomorphs from their difference.

(9) For a proof of this theorem (in English) see G. E. Uhlenbeck and G. W. Ford, "Studies in Statistical Mechanics," J. de Boer and G. E. Uhlenbeck, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, p. 198.

TABLE II
ISOMERS OF OCTAHEDRAL COMPLEXES

Formula	Stereoisomers	Geometrical	Pairs of enantiomorphs
Ma ₆	1	1	0
Ma ₅ b	1	1	0
Ma ₄ b ₂	2	2	0
Ma ₃ b ₃	2	2	0
Ma ₄ bc	2	2	0
Ma ₃ bcd	5	4	1
Ma ₂ bcde	15	9	6
Mabcdef	30	15	15
Ma ₂ b ₂ c ₂	6	5	1
Ma ₂ b ₂ cd	8	6	2
Ma ₃ b ₂ c	3	3	0

Calculation and Discussion

The examples which follow illustrate the use of the preceding method of calculating stereoisomers—geometrical and enantiomorphs.

(I) **Tetrahedral.**—The total number of stereoisomers is given by considering the point group T, whose cycle index for degree four is

$$Z(T) = 1/12[f_1^4 + 8f_1 f_3 + 3f_2^2]$$

In order to consider from one to four different substituents or ligands, replace f_j by $(x_1^j + x_2^j + x_3^j + x_4^j)$. All the coefficients in this expansion are unity except for the coefficient of $x_1 x_2 x_3 x_4$ which is 2.

The number of geometrical isomers alone is given by using the point group T_d, whose cycle index for degree four is

$$Z(T_d) = 1/24(f_1^4 + 8f_1 f_3 + 3f_2^2 + 6f_1^2 f_2 + 6f_4)$$

Replacing f_j by $x_1^j + x_2^j + x_3^j + x_4^j$ gives a polynomial, all of whose coefficients are unity. The difference in the coefficients of $x_1 x_2 x_3 x_4$ equals one, indicating the well-known pair of enantiomorphs.

(II) **Square-Planar.**—The cycle index for the dihedral group D₄ for degree four is

$$Z(D_4) = 1/8(f_1^4 + 3f_2^2 + 2f_1^2 f_2 + 2f_4)$$

Using D_{4h}

$$Z(D_{4h}) = 1/16(2f_1^4 + 6f_2^2 + 4f_1^2 f_2 + 4f_4)$$

The identity of these two cycle indices clearly indicates the lack of enantiomorphs, or optical isomers, for square-planar complex ions. To calculate the numbers of geometrical isomers, replace f_j by $x_1^j + x_2^j + x_3^j + x_4^j$. The coefficients of x_1^4 , $x_1^3 x_2$, $x_1^2 x_2^2$, $x_1^2 x_2 x_3$, and $x_1 x_2 x_3 x_4$ are, respectively, 1, 1, 2, 2, 3. These correspond to *cis* and *trans* isomers for the forms Ma₂b₂ and Ma₂bc. Mabcd exists in three different, well-known isomeric forms.

(III) **Octahedral.**—For octahedral molecules we immediately write

$$Z(O) = 1/24(f_1^6 + 8f_3^2 + 3f_1^2 f_2^2 + 6f_2^3 + 6f_1^2 f_4)$$

$$Z(O_h) = 1/48(f_1^6 + 8f_3^2 + 7f_2^3 + 6f_1^2 f_4 + 9f_1^2 f_2^2 + 8f_6 + 3f_1^2 f_2 + 6f_1 f_2^2)$$

The results of the expansions are tabulated in Table II. These results agree with an enumeration by use of models¹⁰ in every case except for Ma₃bcd for which we

(10) R. F. Trimble, *J. Chem. Educ.*, **31**, 176 (1954).

TABLE III
CYCLE INDICES OF INORGANIC STRUCTURES

Coordination no.	Structure	Point group	Cycle index
2	Linear
3 ^a	Triangular	D_3	$\frac{1}{6}[f_1^3 + 3f_1f_2 + 2f_3]$
		D_{3h}	$\frac{1}{12}[2f_1^3 + 6f_1f_2 + 4f_3]$
4 ^a	Square-planar	D_4	$\frac{1}{8}[f_1^4 + 3f_2^2 + 2f_1^2f_2 + 2f_4]$
		D_{4h}	$\frac{1}{16}[2f_1^4 + 6f_2^2 + 4f_1^2f_2 + 4f_4]$
	Tetrahedral	T	$\frac{1}{12}[f_1^4 + 8f_1f_3 + 3f_2^2]$
		T_d	$\frac{1}{24}[f_1^4 + 8f_1f_3 + 3f_2^2 + 6f_1^2f_2 + 6f_4]$
5 ^a	Trigonal bipyramid	D_{3h}	$\frac{1}{6}[f_1^5 + 2f_1^2f_3 + 3f_1f_2^2]$
		D_3	$\frac{1}{12}[f_1^5 + 2f_1^2f_3 + 3f_1f_2^2 + 4f_1^2f_2 + 2f_3f_2]$
	Tetragonal pyramid	C_4	$\frac{1}{4}[f_1^5 + 2f_1f_4 + f_1f_2^2]$
		C_{4v}	$\frac{1}{8}[f_1^5 + 2f_1f_4 + 3f_1f_2^2 + 2f_1^2f_2]$
6 ^a	Octahedral	O	$\frac{1}{24}[f_1^6 + 8f_3^2 + 3f_1^2f_2^2 + 6f_2^3 + 6f_1^2f_4]$
		O_h	$\frac{1}{48}[f_1^6 + 8f_3^2 + 7f_2^3 + 6f_1^2f_4 + 9f_1^2f_2^2 + 8f_6 + 3f_1^2f_2 + 6f_1f_2]$
7	Pentagonal bipyramid	D_5	$\frac{1}{10}[f_1^7 + 4f_3f_1^2 + 5f_1f_2^3]$
		D_{5h}	$\frac{1}{20}[f_1^7 + 4f_3f_1^2 + 5f_1f_2^3 + f_1^2f_2 + 4f_3f_2 + 5f_1^2f_2^2]$
8 ^b	Archimedean antiprism	D_4	$\frac{1}{8}[f_1^8 + 2f_4^2 + 5f_2^3]$
		D_{4d}	$\frac{1}{16}[f_1^8 + 2f_4^2 + 5f_2^3 + 4f_1^2f_2^3 + 4f_8]$
8	$K_4Mo(CN)_8$ dodecahedron	D_{2d}	$\frac{1}{8}[f_1^8 + 3f_2^4 + 2f_1^4f_2^2 + 2f_8]$
		D_2	$\frac{1}{4}[f_1^8 + 3f_2^4]$
12	Icosahedron	I	$\frac{1}{60}[f_1^{12} + 24f_1^2f_5^2 + 20f_3^4 + 15f_2^6]$
		I_h	$\frac{1}{120}[f_1^{12} + 24f_1^2f_5^2 + 20f_3^4 + 16f_2^6 + 24f_2f_{10} + 20f_6^2 + 15f_1^4f_2^4]$

^a Results agree with Lunn and Senior. ^b Results agree with Marchi, Fernelius, and McReynolds.

find a pair of enantiomorphs. This one example serves to illustrate the power of this method. Also concerning octahedral complexes, it has been stated¹¹: "Optical isomers can occur in nonchelate complexes with three or more different kinds of ligands and no more than two of any one kind." However, in addition to three *trans* forms of Ma_3bcd , one can easily show an optically active pair for the *cis* form for the calculated total of five isomers, four of which are geometrical. The enantiomorphs are



(IV) Other Common Inorganic Structures.—Table III presents a comprehensive list of cycle indices of commonly occurring inorganic structures.

Application to a Complicated Dimeric Case.—As a final example, we shall calculate the number of isomers

(11) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1962, p. 155. See also J. Lewis and R. G. Wilkins, "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960, p. 180; R. B. Heslop and P. L. Robinson, "Inorganic Chemistry," Elsevier Publishing Company, Amsterdam, 1960, p. 519.

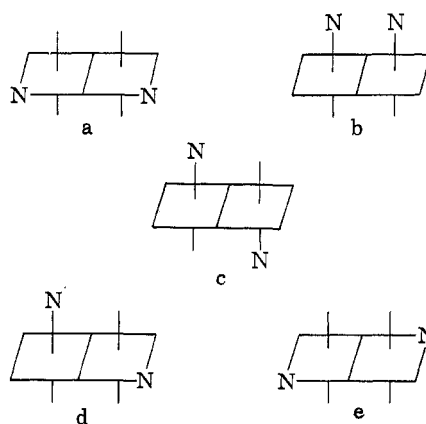


Fig. 1.—N represents nitrogen of pyridine.

TABLE IV
ISOMERS OF THE RESTRICTED FORM OF $Nb_2Cl_2(C_2H_5O)_6(C_5H_5N)_2$

Structure (Fig. 1)	Point group	Cycle index	No. of geom. isomers
a	C_{2v}	$\frac{1}{4}(f_1^8 + 2f_1^2f_2^3 + f_1^4f_2^2)$	11
b	C_{2v}	$\frac{1}{4}(f_1^8 + f_2^4 + 2f_1^2f_2^3)$	10
c	C_{2h}	$\frac{1}{4}(f_1^8 + f_2^4 + 2f_1^2f_2^3)$	10
d	C_1	f_1^8	28
e	C_{2h}	$\frac{1}{4}(f_1^8 + 2f_2^4 + f_1^4f_2^2)$	11

of $Nb_2Cl_2(C_2H_5O)_6(C_5H_5N)_2$.¹² This compound is an example of octahedral coordination in which two coordination positions are common to each of the two metal ions (see Fig. 1). Either the chloride or ethoxide ligands but not the pyridines may occupy the bridge positions.

We shall treat this differently and calculate the number of isomers in steps. Consider the bridging ligands to be the same. The point group is D_{2h} , and for degree eight (we are excluding the bridge positions since they are fixed) the cycle index is

$$Z(D_{2h}) = \frac{1}{8}(f_1^8 + 5f_2^4 + 2f_1^4f_2^2)$$

Let $f_j = x_1^j + x_2^j + x_3^j$, where x_1 is for chloride, x_2 for ethoxide, and x_3 for pyridine. If both chlorides serve as the bridge, the number of geometrical isomers is 8, the coefficient of $x_2^6x_3^2$. If two of the ethoxides occupy the bridge positions, then the number of geometrical isomers is 68, the coefficient of $x_1^2x_2^4x_3^2$.

In the case where the bridge positions consist of one chloride and one ethoxide, the point group is C_{2v} , whose cycle index for degree 8 is

$$Z(C_{2v}) = \frac{1}{4}(f_1^8 + f_1^4f_2^2 + 2f_2^4)$$

Again, we let $f_j = x_1^j + x_2^j + x_3^j$ since there are three kinds of substituents. The number of geometrical isomers in this case is 47, the coefficient of $x_1x_2^5x_3^2$. The total number of geometrical isomers is therefore the sum for the above three cases, *viz.* 123.

We now recalculate the number of geometrical isomers with the added restriction that each of the pyridine molecules must be bonded to a different niobium atom. The five distinguishable ways to put one pyridine on each niobium ion are illustrated in Fig. 1. The

(12) This problem was the stimulus for the present program: R. A. D. Wentworth and C. H. Brubaker, Jr., *Inorg. Chem.*, **3**, 47 (1964).

calculations are summarized in Table IV. The total number of geometrical isomers of $\text{Nb}_2\text{Cl}_2(\text{C}_2\text{H}_5\text{O})_6(\text{C}_5\text{H}_5\text{N})_2$, with the restrictions that (1) each niobium is surrounded octahedrally by ligands, (2) each niobium is bonded to only one pyridine molecule, and (3) pyridine molecules cannot act as bridging ligands, is 70.

Calculation of the total number of geometrical isomers by considering the eight distinguishable ways to distribute two pyridines on the eight nonbridging positions¹³ separately yields 123. This agrees with our preceding result.

(13) The number eight was calculated from the cycle index for the D_{2h} point group.

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Scrambling of Methoxyl, Dimethylamino, and Chloro Groups on Silicon¹

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By means of gas chromatography, quantitative data were obtained on ester interchange between tetramethyl and tetraethyl silicates (1) $\text{Si}(\text{OCH}_3)_4$ vs. $\text{Si}(\text{OC}_2\text{H}_5)_4$. H^1 nuclear magnetic resonance was used to investigate the systems: (2) $\text{Si}(\text{OCH}_3)_4$ vs. SiCl_4 and (3) $\text{Si}[\text{N}(\text{CH}_3)_2]_4$ vs. SiCl_4 . The equilibria for the esters (system 1) are close to those expected for ideal random interchange. However, the mixed species are greatly favored in the exchanges involving silicon tetrachloride. The deviation from ideal random behavior is larger in the case of exchange of dimethylamino groups with chlorines than in the case of alkoxy groups with chlorines. This is similar to the situation found with the analogous phosphorus compounds. Measurements are presented on the rates of exchange of chlorine for either methoxyl or dimethylamino groups.

Although there is a considerable body of literature³ on the redistribution reactions of alkoxy groups, halogens, and amino groups on silicon, it is very difficult to determine from this literature whether or not equilibrium was reached. In studies of redistribution reactions, it is important to obtain the equilibrium values, since large deviations from the equilibria corresponding to random sorting may be the cause of unusually high or low yields in preparative chemistry. Such deviations are also important to the understanding of the chemistry of these compounds, as explained in the Discussion section of this paper.

Unlike the previous authors, we took special care in this study to separate rate phenomena from the equilibria. As a result, it is now possible to determine whether the data reported in the previous literature correspond to partial or complete equilibration. By treating the equilibria in terms of deviations of the corresponding free energies from those expected for completely random exchange, we have been able to compare on a logical basis the results obtained on compounds of silicon with those found for analogous compounds of phosphorus.

Experimental

Tetramethyl silicate, tetraethyl silicate, and silicon tetrachloride were re-purified by careful distillation in a dry atmosphere from commercial samples obtained from the Anderson Chemical Company. The tetrakis(dimethylamino)silane (*i.e.*, octamethylsilanetetramine) was prepared⁴ from silicon tetrachloride and was also carefully purified by fractionation. In all cases, middle cuts having a constant boiling point were taken from a fractionating column with *ca.* 20 theoretical plates.

Ester Interchange.—The substituent-exchange reaction between tetramethyl silicate and tetraethyl silicate was carried out in sealed glass tubes at 150°. Analyses were performed by gas chromatography using a Perkin-Elmer vapor fractometer, Model 154D, with a printing integrator. A 2-m. column containing C-22 firebrick supporting 10% of Tween 80 was employed at a temperature of 80°. The retention times of tetramethyl silicate and tetraethyl silicate were identified through runs on the pure samples, and assignment of the chromatographic peaks due to the mixed esters was made from their sequence and checked by material-balance calculations. The retention times were found to increase more than linearly with substitution of ethyl for methyl.

Redistribution between the tetramethyl and tetraethyl silicates was found to reach equilibrium within *ca.* 4 days at 150°. The data reported here correspond to 10 days at that temperature.

Exchanges with SiCl_4 .—Equilibrium measurements for the reactions between silicon tetrachloride and either tetramethyl silicate or tetrakis(dimethylamino)silane were made at room temperature on samples heated in sealed glass tubes at 120° for 200 hr. in the case of the first system and 18 hr. for the second. These heating times were chosen on the basis of rate studies. However, because of fast re-equilibration at room temperature (see Fig. 5-7) the equilibrium data on the system $\text{Si}[\text{N}(\text{CH}_3)_2]_4$ vs. SiCl_4 correspond to a temperature between 25 and 37°, since the samples stood overnight at room temperature and the n.m.r. measuring probe operates at 37°. Contrary to the data of Kumada,³ samples with low SiCl_4 content took somewhat longer

(1) Presented in part at the 141st National Meeting of the American Chemical Society, Washington, D. C., March 22, 1962.

(2) On leave of absence from the Inorganic Chemicals Division of Monsanto, July, 1961-1962.

(3) D. F. Peppard, W. G. Brown, and W. C. Johnson, *J. Am. Chem. Soc.*, **68**, 73 (1946); M. Kumada, *J. Inst. Polytech. Osaka City Univ. Ser. C*, **2**, 139 (1952) [*Chem. Abstr.*, **48**, 11303g (1954)]; Yu N. Vol'nov, *J. Gen. Chem. USSR*, **17**, 1428 (1947); K. Schaarschmidt, *Z. anorg. allgem. Chem.*, **310**, 69 (1961). Also, for example, F. C. Boye and H. W. Post, *J. Org. Chem.*, **17**, 1389 (1952), and K. A. Andrianov, S. A. Golubtsov, and N. P. Lobusevich, *Zh. Obshch. Khim.*, **26**, (1956); *J. Gen. Chem. USSR*, **26**, 207 (1956). For reviews of the chemistry studied here, see C. Eaborn, "Organosilicon Compounds," Butterworth, London, 1960, and R. Fessenden and J. S. Fessenden, *Chem. Rev.*, **61**, 361 (1961).

(4) H. Breederveld and H. I. Waterman, *Research (London)*, **5**, 537 (1952).