obtained from spectroscopy,[18] leading to a stabilization with respect to water of 10.6 kcal./mole, in good agreement with the thermodynamic value.

Acknowledgments.—The authors wish to acknowledge the aid of D. Ebdon and D. Bullock in some of the measurements, and R. Keyes in programming the data for the IBM 704. J. E. B. wishes to express his gratitude for a research fellowship from the National Institutes of Health (CF-12, 177). We also wish to thank the University of Michigan Cancer Research Institute for partial financial support.

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[18] J. Bjerrum, C. J. Ballhausen, and C. K. Jorgensen, *Acta Chem. Scand.*, **8**, 1275 (1954).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF NEW HAMPSHIRE, DURHAM, NEW HAMPSHIRE

Metal Halide Complexes of *o*-Quinones. I. Preparation and Preliminary Characterization[1]

BY PAUL J. CROWLEY AND HELMUT M. HAENDLER[2]

Received May 7, 1962

Twenty-one representative complexes formed by the action of metal halides on phenanthrenequinone and chrysenequinone have been prepared from non-aqueous solution. The compounds are intensely colored, highly unstable in polar solvents, and occur in stoichiometric ratios of quinone:metal equal to 1:1, 2:1, and 3:1. A preliminary classification is proposed.

Introduction

Certain quinones have been reported to react with metal halides in non-aqueous solution to form intensely colored complexes. Pfeiffer[3] lists several complexes formed by various *o*-quinones and refers to the early work in this field. Meyer[4] reported the preparation of phenanthrenequinone complexes of zinc, mercury(II), iron(III), aluminum, and tin(IV) chlorides, while Knox and Innes[5] prepared phenanthrenequinone complexes containing halides of the zinc group. No further work on complexes of this sort has been reported and nothing is known of their structure and chemical nature. We intend to rectify this lack of information by a study of the electron-donor properties of these and related quinones.

The preparation of these complexes depends upon the availability of the metal halide in the pure, anhydrous form and the existence of a suitable solvent for both halide and quinone. The most practical solvent we have tested is glacial acetic acid. If anhydrous halide is available, hot, saturated solutions of the components are mixed and allowed to cool. The complex generally crystallizes rapidly. The method has a distinct disadvantage if the halide is significantly hygroscopic, as is generally the case. However, solutions of many anhydrous bromides can be prepared easily by direct bromination of the metal in methanol.[6] These solutions can be used for the preparation of the complexes by substitution of glacial acetic for most of the methanol after concentration of the latter solvent by evaporation. Addition of hot acetic acid solution to the quinone produces considerable darkening of the solution, and crystallization usually takes place at once. If not, excess solvent can be removed by boiling or, preferably, distilling under vacuum.

Four *o*-quinones were tested by these procedures: 9,10-phenanthrenequinone (I) (abbreviated phenqu), 1,2-chrysenequinone (II) (abbreviated chryqu), acenaphthenequinone (III), and 2-nitrophenanthrenequinone.

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[1] Taken from a thesis submitted to the University of New Hampshire for the degree of Doctor of Philosophy by Paul J. Crowley. Supported in part by the U. S. Atomic Energy Commission.

[2] To whom communications should be addressed.

[3] P. Pfeiffer, "Organische Molekulverbindungen," Ferdinand Enke Verlag, Stuttgart, 1927, pp. 64, 100.

[4] K. H. Meyer, *Ber.*, **41**, 2568 (1908).

[5] J. Knox and H. R. Innes, *J. Chem. Soc.*, **105**, 1451 (1914).

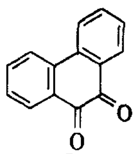
[6] (a) H. M. Haendler, F. A. Johnson, and D. S. Crocket, *J. Am. Chem. Soc.*, **80**, 2662 (1958); (b) D. S. Crocket and H. M. Haendler, *ibid.*, **82**, 4158 (1960); (c) A. E. Baker and H. M. Haendler, *Inorg. Chem.*, **1**, 127 (1962).

TABLE I

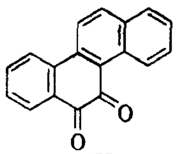
METAL HALIDE COMPLEXES OF 9,10-PHENANTHRENEQUINONE AND 1,2-CHRYSENEQUINONE

	Analysis				
Formula[a],[b]	Determination	Calcd., %	Found, %	Metal method	Color
phenqu·$MnBr_2$	phenqu	49.23	49.10		
	Mn	12.99	12.75	Anthranilate	Violet
	Br	37.79	37.70		
chryqu·$MnBr_2$	chryqu	54.60	54.72		
	Mn	11.61	11.50	Anthranilate	Black
	Br	33.79	33.56		
phenqu·$CoBr_2$	phenqu	48.76	48.75		
	Co	13.80	13.53	Anthranilate	Black
	Br	37.43	37.30		
chryqu·$CoBr_2$	chryqu	54.14	54.19		
	Co	12.36	12.30	Anthranilate	Black
	Br	33.51	33.48		
phenqu·$ZnBr_2$	phenqu	48.04	48.04		
	Zn	15.09	15.06	Anthranilate	Violet
	Br	36.88	36.84		
chryqu·$ZnBr_2$	chryqu	53.42	53.19		
	Zn	13.52	13.65	Anthranilate	Black
	Br	33.06	33.00		
phenqu·$CdBr_2$	phenqu	43.34	43.35		
	Cd	23.40	23.35	Anthranilate	Brown
	Br	33.27	33.17		
chryqu·$CdBr_2$	chryqu	48.68	48.85		
	Cd	21.19	21.08	Anthranilate	Brown
	Br	30.13	30.17		
phenqu·$InBr_3$	In	20.39	20.03	Oxide	Black
	Br	42.61	40.19		
chryqu·$InBr_3$	In	18.73	18.50	Oxide	Black
	Br	39.13	38.96		
phenqu·$SnBr_4$	Sn	18.36	18.36	Oxide	Black
	Br	49.44	49.23		
chryqu·$SnBr_4$	Sn	17.04	17.04	Oxide	Violet
	Br	45.89	45.72		
2phenqu·$NiBr_2$	Ni	9.24	9.23	Dimethylglyoxime	Violet
	Br	25.17	24.97		
2chryqu·$NiBr_2$	chryqu	70.27	70.15		
	Ni	7.99	8.08	Dimethylglyoxime	Black
	Br	21.75	21.69		
2phenqu·$HgBr_2$	phenqu	53.60	53.48		Red
2chryqu·$HgBr_2$	chryqu	58.90	59.00		Red
3phenqu·$FeBr_3$	phenqu	67.88	67.73		
	Fe	6.07	6.17	Oxide	Brown
	Br	26.05	26.05		
3chryqu·$FeBr_3$	chryqu	72.38	72.51		
	Fe	5.22	5.23	Oxide	Black
	Br	22.40	22.30		
phenqu·MoO_2Br_2	Mo	19.35	19.33	Lead molybdate	Black
phenqu·MoO_2Cl_2	Mo	23.57	23.35	Lead molybdate	Black
chryqu·MoO_2Cl_2	Mo	20.99	20.75	Lead molybdate	Violet

[a] phenqu is 9,10-phenanthrenequinone, $C_{14}H_8O_2$. [b] chryqu is 1,2-chrysenequinone, $C_{18}H_{10}O_2$.



I



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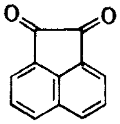

III

Phenanthrenequinone and chrysenequinone react with a much greater variety of metal halides than would be inferred from the previous literature. To date, manganese(II), cobalt(II), zinc, cadmium, indium, tin(II), nickel, mercury(II), iron (III), molybdenum(VI), titanium(IV), uranium(VI), antimony(V), and copper(II) give evidence of complex formation, although it has not been possible to isolate pure specimens of all these. The empirical formulas, the analytical data, and the colors of those definitely characterized are given in Table I. Acenaphthenequinone and 2-nitrophenanthrene appear surprisingly unreactive.

Experimental

Starting Materials.—The four quinones were prepared and purified by methods given in the literature: 9-10-phenanthrenequinone,[7] 1,2-chrysenequinone,[8] 2-nitrophenanthrenequinone,[9] and acenaphthenequinone.[10] The methanolic metal bromide solutions were prepared by direct bromination.[6] One-tenth of a mole of metal was covered with 250 ml. of anhydrous methanol. In order to ensure complete oxidation of the metal, bromine was added cautiously in small portions to slight excess. The mixtures either were allowed to stand or were refluxed gently until the reaction ceased. The resulting metal bromide solutions were filtered prior to use in the procedures below.

General Procedure for the Complexes.—Thirty ml. of the metal bromide–methanol solution was concentrated to about 5 ml. by boiling. To this was added a hot, filtered solution of 0.01 mole of quinone in 60 ml. of glacial acetic acid. The color changed immediately from orange to deep brown or black. If crystallization did not occur at once, the solution was concentrated by boiling. Precautions were taken to prevent bumping. A glass stirring rod gave the best results; boiling chips proved worthless. The crystalline product was filtered hot on a sintered glass funnel, washed several times with ligroin, and dried at reduced pressure in a vacuum desiccator. This method was used in all cases with two exceptions.

Procedure Using $MoCl_5$.—To a hot, filtered solution of 0.01 mole of quinone in 60 ml. of glacial acetic acid was added a solution of 2.7 g (0.01 mole) of molybdenum pentachloride (Climax Molybdenum Co.) in 10 ml. of glacial acetic acid. The solution darkened and black crystals formed immediately. The product was filtered, washed with ligroin, and dried at reduced pressure.

Procedure Using $TiCl_4$ or $SbCl_5$.—A solution of 0.005 mole of titanium tetrachloride (Matheson Coleman and Bell, 99.5% pure) or antimony pentachloride (Baker and Adamson, reagent grade) in 10 ml. of dry carbon tetrachloride was added to a suspension of 0.005 mole of powdered quinone in 30 ml. of dry carbon tetrachloride. The original yellow or orange color of the quinone changed to those given in Table II. The color changes took place as soon as the reagents were mixed, in all cases except the acenaphthenequinone– and 2-nitrophenanthrenequinone–titanium tetrachloride systems, for which the time required for color change was 3–5 min. and 10 days, respectively. Unfortunately, none of these products could be separated completely from the reaction mixture without undergoing considerable decomposition.

TABLE II

COLORS OF THE $TiCl_4$ AND $SbCl_5$ COMPLEXES

Quinone	Halide	
	$TiCl_4$	$SbCl_5$
9,10-Phenanthrenequinone	Black	Brown
1,2-Chrysenequinone	Brown	Black
Acenaphthenequinone	Red	Blue-green
2-Nitrophenanthrenequinone	Black	Black

Elementary Analyses.—Samples of the complexes were digested in water to give quantitative precipitation of the quinone which was filtered and weighed directly. An aliquot of the filtrate was treated with excess silver nitrate and back titrated with thiocyanate to determine halide. The metal was determined conventionally on a second aliquot. Other procedures had to be used for the molybdenum, indium, and tin complexes. When these complexes are digested in water, they yield a precipitate of quinone which is contaminated with metal oxide. Accordingly, the molybdenum complexes were decomposed completely with nitric and sulfuric acids to remove the halide and organic portions prior to determination of the metal as lead molybdate. The indium complexes were treated with dilute ammonium hydroxide to precipitate the indium and the quinone together. After filtration the quinone was removed by ignition, and indium was determined as the oxide. Halide was determined on an aliquot of the filtrate. The tin complexes were decomposed by digestion in nitric acid. The precipitate was ignited to remove the quinone, and tin was determined as the oxide. A second sample was decomposed with water and analyzed for halide as before.

X-Ray Measurements.—X-Ray powder diffraction photographs were taken of the phenanthrenequinone complexes of $ZnBr_2$, $CdBr_2$, $HgCl_2$, $FeBr_3$, and MoO_2Cl_2, using a Philips 57.3-mm. camera, with copper and iron radiation.

Magnetic Moment Measurements.—The magnetic susceptibilities of the manganese, iron, cobalt, and nickel complexes were measured by the conventional Gouy method, using a Newport Instrument Model C electromagnet with a Varian power supply. The apparatus was calibrated with $Hg[Co(SCN)_4]$ and checked with $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$.

Visible Spectra.—The spectrum of the phenanthrenequinone complex of zinc bromide was measured in glacial acetic acid by a differential method, using a phenanthrenequinone solution as the referent, and a Beckman DU spectrophotometer.

Infrared Spectra.—The spectra of the complexes and the parent quinone were obtained from Nujol and Halocarbon mulls, with the Perkin–Elmer Model 21 spectrophotometer.

Thermogravimetric Decomposition.—The thermal decomposition of the zinc bromide complex of phenanthrenequinone was studied on a recording balance constructed here by David Kingston.

Molecular Weight.—Attempts to determine molecular weights by cryoscopic and ebullioscopic methods were unsuccessful. The complexes are too highly dissociated in solutions of practical concentrations.

Discussion

The variety of complexes formed by phenanthrenequinone and chrysenequinone indicates the

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(7) R. Wendland and J. LaLonde, *Org. Syn.*, **34**, 76 (1954).

(8) C. Graeber and F. Honigsberger, *Ann.*, **311**, 262 (1900).

(9) A. Werner, *Ber.*, **37**, 3083 (1904).

(10) C. F. H. Allen and J. A. Van Allen, *Org. Syn.*, **24**, 1 (1944).

general nature of the reaction. Several complexes of those metal chlorides which are readily available in anhydrous form also have been prepared, but not as completely characterized. It is probable that other electron-pair acceptors also will react.

The failure of acenaphthenequinone and 2-nitrophenanthrenequinone to form complexes was unexpected. Apparently, the six-membered quinoidal ring fits the stereochemical requirements for complex formation better than does the five-membered ring of acenaphthenequinone. The structure of acenaphthenequinone has not yet been determined, and that of acenaphthene itself seems somewhat in doubt. The C–C distance in the CH_2–CH_2 configuration in acenaphthene has been variously reported between 1.60 and 1.86 Å., with 1.64 Å. accepted as a reasonable assessment.[11]

The corresponding distance in phenanthrene, and presumably in chrysene, is estimated to be about 1.40 Å.[12] The two quinone oxygen atoms thus may be too far apart for complex formation in acenaphthene, or there may even be a distortion of the ring so that the oxygens are not coplanar with the remainder of the molecule and thus out of position. The failure of 2-nitrophenanthrenequinone can be rationalized on the basis of an electron-withdrawing effect exerted by the nitro group on the quinone oxygens. It would be of interest to compare the behavior of 4-nitrophenanthrenequinone.

Carbon tetrachloride solutions of titanium tetrachloride and antimony pentachloride reacted with all four of the quinones. However, the complexes are so unstable and hygroscopic that they could not be separated from the reaction mixtures without appreciable decomposition. Unfortunately, the copper complex has given some trouble also and has not been isolated as yet. The regular procedure is of little value in this case since the copper tends to come out much more readily as the acetate. Other solvents such as chloroform and acetone were tried and found to be unsatisfactory. Some darkening of the solution occurred, indicating complex formation, but it was not possible to isolate any product.

One of the more striking characteristics of the complexes is their color. Nearly all of them are dark violet or jet black in appearance. The complexes are stable enough to be handled in the open air, but they should be stored under dry conditions as a precaution. They are readily decomposed by water and other polar solvents into the original components. For example, the phenanthrenequinone–zinc bromide complex yields a precipitate of phenanthrenequinone and an aqueous solution of zinc bromide when treated with water. This fact has simplified the problem of elementary analysis quite admirably. The complexes are nearly insoluble in non-polar solvents such as chloroform, benzene, and toluene. They are insoluble in ligroin. It seems that any solution that does occur takes place *via* decomposition. When a sample of phenqu·$ZnBr_2$ was treated with dry benzene, a small amount dissolved and produced a light yellow color similar to that of phenanthrenequinone itself. An aqueous extract of the benzene gave a negative test for bromide. Repeated treatments of the sample with fresh benzene showed no decrease in the intensity of the yellow color. The solvent removed the quinone from the complex and left the bromide behind. The only thing that seems to retard this process is the fairly low solubility of the quinone in benzene.

Based on the ratio of quinone to metal, there are three types of complexes, corresponding to ratios of 1:1, 2:1, and 3:1. The nature of these complexes is of considerable interest, and some preliminary observations have been made. The X-ray powder patterns of several of the complexes have been observed to be unique. Differential spectral analysis of the zinc bromide–phenanthrenequinone complex in acetic acid, as compared to quinone in the same solvent, shows a sharp absorption peak at 513 mμ. The quinone itself absorbs at 415 and 320 mμ. The shift in absorption to longer wave lengths for the complex indicates increased delocalization of quinone electrons into orbitals binding the complex. Absorption in this region is not characteristic of highly stable complexes.

Preliminary results of a thermogravimetric analysis of the decomposition of the phenqu·$ZnBr_2$ complex indicates that the components are not bound together in a simple one-to-one ratio. The plot of weight *vs.* temperature showed a break corresponding to the loss of just 50% of the quinone. This suggests that this 1:1 complex may actually be of the type

$$[Zn(phenqu)_2]ZnBr_4$$

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[11] A. J. C. Wilson, ed., "Structure Reports," Vol. 12, International Union of Crystallography, 1949, p. 408.

[12] Based upon reported structure of pyrene, "Structure Reports," Vol. 11, 1947–1948, p. 700.

Table III

Infrared Absorption Frequencies of the Phenanthrenequinone Series in the 1700–1500 cm.$^{-1}$ Region

Compound	Range (cm.$^{-1}$)			Decrease in carbonyl frequency
	1700–1600	1600–1575	1575–1500	
phenqu	1674 s	1594 s		0
phenqu·$MnBr_2$	1629 s	1586 s		45
phenqu·$CoBr_2$	1611 m	1582 s		63
phenqu·$ZnBr_2$	1626 ms	1587 s		48
phenqu·$CdBr_2$	1639 ms	1586 s		35
phenqu·$InBr_3$	1656 ms	1589 s		18
phenqu·$SnBr_4$			1560 s	114
2phenqu·$NiBr_2$	1610 m	1582 s		64
2phenqu·$HgBr_2$	1661 s	1591 s		13
3phenqu·$FeBr_3$	1665 m (broad)	1587 s		9
phenqu·MoO_2Br_2	1613 ms	1581 s		61
phenqu·MoO_2Cl_2	1626 m	1585 s	1552 s	48

If this is the case, the intermediate [Zn(phenqu)-Br_2], or [Zn(phenqu)]$ZnBr_4$, should be an interesting compound.

The 2:1 complexes could be represented simply as [Ni(phenqu)$_2$]Br_2, and the iron(III) complex as [Fe(phenqu)$_3$]Br_3. The most probable arrangement of ligands around the iron would be that in which each quinone acts as a bidentate ligand, occupying two adjacent octahedral sites. The iron complex then should exist in optically active forms. Comparison of the two quinones leads to interesting possibilities, also. Phenanthrenequinone presumably would be a symmetrical molecule, chrysenequinone unsymmetrical. With tetrahedral metal atoms, therefore, chrysenequinone complexes would be asymmetric, if the above formulation is correct, and there should be two forms, *d*- and *l*-.

Since it seemed probable that the bonding between the metal halide and the quinone involved the carbonyl groups, a survey was made of some spectra in the 1700–1500 cm.$^{-1}$ region. The infrared spectrum of 9,10-phenanthrenequinone contains two strong, sharp bands in the 1700–1500 cm.$^{-1}$ region. The first absorption, at 1674 cm.$^{-1}$, is the carbonyl band. The second is an aromatic band, and it occurs at 1595 cm.$^{-1}$. While both absorptions are strong, the aromatic band has a slightly lower intensity. The spectra of the 9,10-phenanthrenequinone complexes are characterized by a decrease in the frequency of the carbonyl band and an increase in the intensity of the aromatic band. In nearly all cases the aromatic band becomes so strong that its intensity is greater than that of the carbonyl band. This effect does not create any complications in the 9,10-phenanthrenequinone series since the carbonyl bands are well defined in most cases and can be assigned frequency values without any trouble. For example, phenqu·$ZnBr_2$ absorbs at 1626 and 1587 cm.$^{-1}$. The latter band is the stronger. Except as noted below, the spectra of the other complexes in this series are similar in appearance. The frequencies of the carbonyl and aromatic bands are given in Table III. The last column shows the difference between the carbonyl absorption of the complex and that of the parent quinone. Shifts ranging from 9 to 114 cm.$^{-1}$ were observed.

3phenqu·$FeBr_3$ gives a rather poor spectrum. There is a broad band between 1675 and 1635 cm.$^{-1}$, the most intense absorption occurs at 1665 cm.$^{-1}$, and the aromatic band occurs at 1587 cm.$^{-1}$. The phenqu·$SnBr_4$ spectrum contains only one band in the 1700–1500 cm.$^{-1}$ region. It occurs at 1560 cm.$^{-1}$ and probably is a combination of the carbonyl and aromatic absorptions. This is the largest shift observed for any of the complexes, a decrease of 114 cm.$^{-1}$. In phenqu·MoO_2Cl_2 a third band appears at 1552 cm.$^{-1}$. It is not present in the corresponding bromide.

The fact that the frequency of the carbonyl band of 9,10-phenanthrenequinone differs from those of the complexes supports the contention that the carbonyl groups are directly involved in the bonding. It is expected that coördination through the quinone oxygens will result in a reduction of the double bond character of the carbonyl groups and shift the carbonyl band to a lower frequency. This is analogous to the well known behavior of carbonyl groups subjected to hydrogen bonding or chelation.

The magnetic data for several complexes are presented in Table IV. These measurements indicate that the four complexes have weak field

TABLE IV

MAGNETIC DATA FOR THE PHENANTHRENEQUINONE SERIES

Complex	$\mu_{\text{obs.}}$	$\mu_{\text{calcd.}}$	n	Reported range[a]
phenqu·$MnBr_2$	5.84	5.92	5	5.65–6.10
	5.85			
3phenqu·$FeBr_3$	5.83			
	6.16	5.92	5	5.70–6.0
	5.94			
phenqu·$CoBr_2$	4.71			
	4.74	3.88	3	4.30–5.20
2phenqu·$NiBr_2$	3.22			
	3.26	2.83	2	2.80–3.50

[a] J. Lewis and R. G. Wilkins, ed., "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960, pp. 400–454.

bonding, with the oxygen to metal bonds oriented in sterically favored directions. This orientation results in a tetrahedral configuration for the manganese(II) and cobalt(II) complexes, an octahedral configuration for iron(III), and either a tetrahedral or octahedral configuration for nickel(II).

The above results suggest an expanded classification of these complexes, as shown in Table V.

TABLE V

CLASSIFICATION OF THE COMPLEXES

Type	Empirical formula	Suggested formulation
I	phenqu·$ZnBr_2$	$[Zn(phenqu)_2]ZnBr_4$
II	phenqu·$InBr_3$	$[In(phenqu)Br_2]Br$
III	phenqu·$SnBr_4$	$[Sn(phenqu)Br_2]Br$[a] $[Sn(phenqu)Br_4]$[b]
IV	2phenqu·$NiBr_2$	$[Ni(phenqu)_2]Br_2$[a] $[Ni(phenqu)_2Br_2]$[b]
V	3phenqu·$FeBr_3$	$[Fe(phenqu)_3]Br_3$
VI	phenqu·MoO_2Cl_2	...

[a] If tetrahedral. [b] If octahedral.

The unique nature of the molybdenum complex probably results from the reductive action of $MoCl_5$ in the quinone, similar to the action of $MoCl_5$ on $(C_6H_5)_3PO$ reported by Horner and Tyree.[13]

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(13) S. M. Horner and S. Y. Tyree, Jr., *Inorg. Chem.*, **1**, 122 (1962).

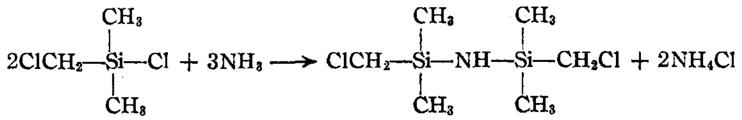
CONTRIBUTION FROM THE INSTITUT FÜR ANORGANISCHE CHEMIE
DER UNIVERSITÄT MARBURG, MARBURG, GERMANY

A New Heterocycle Containing Sulfur and Silicon

BY MAX SCHMIDT AND MARKUS WIEBER

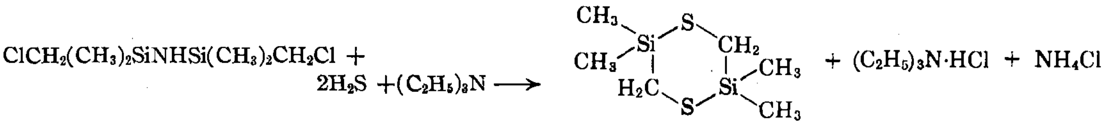
Received October 9, 1961

The reaction of chloromethyldimethylchlorosilane with ammonia yields the new 1,3-bis-(chloromethyl)-tetramethyldisilazane



$$2ClCH_2-\underset{CH_3}{\overset{CH_3}{Si}}-Cl + 3NH_3 \longrightarrow ClCH_2-\underset{CH_3}{\overset{CH_3}{Si}}-NH-\underset{CH_3}{\overset{CH_3}{Si}}-CH_2Cl + 2NH_4Cl$$

Both the original chloromethyldimethylchlorosilane and the new 1,3-bis-(chloromethyl)-tetramethyldisilazane react with H_2S in the presence of triethylamine to give a new ring compound, 2,2,5,5-tetramethyl-1,4-dithia-2,5-disilacyclohexane.



The properties of the new compound are described. The reaction with water gives 1,3-bis-(mercaptomethyl)-tetramethyldisiloxane, which is converted into the corresponding silver mercaptide by silver nitrate. Dry hydrogen chloride converts the ring molecule into mercaptomethyldimethylchlorosilane, ethyl alcohol into mercaptomethyldimethylethoxysilane. The latter mercaptan reacts with disulfur dichloride in a condensation reaction and forms a sulfane derivative, 2,2′-bis-(ethoxydimethylsilane)-dimethyltetrasulfane.

Introduction

The preparations of 2,2,6,6-tetramethyl-1-oxa-2,6-disila-4-thiacyclohexane and the corresponding selenium compound have been reported recently by members of this Laboratory.[1] The appropriate equations are

(1) M. Schmidt and M. Wieber, *Ber.*, **94**, 1426 (1961).