

The *n*-heptyldimethylchlorosilane was converted by the previously described manner to *n*-heptyltrimethylsilane in a 77.6% yield, b.p. 183.5° at 750 mm., n_D^{25} 1.4184, d_4^{25} 0.7465; found R_D 0.338, calcd. R_D 0.338.

A gas-liquid phase chromatogram of the *n*-heptyltrimethylsilane indicated only one component, and it was indistinguishable from authentic *n*-heptyltrimethylsilane. The infrared spectra of this product and authentic *n*-heptyltrimethylsilane were also indistinguishable.

1,3-Di-*n*-heptyltetramethyldisiloxane from *n*-Heptyldimethylchlorosilane.—One hundred grams (0.52 mole) of the *n*-heptyldimethylchlorosilane in 100 ml. of ether was poured over crushed ice. The organic layer was separated, washed neutral, and the solvent was removed in a vacuum. The product was distilled at reduced pressure to give 75 g. (87.5% yield) of 1,3-di-*n*-heptyltetramethyldisiloxane, b.p. 178–180° at 20 mm., n_D^{25} 1.4305, d_4^{25} 0.8170; found R_D 0.316, calcd. R_D 0.316.

Anal. Calcd. for $\text{Si}_2\text{C}_{18}\text{H}_{42}\text{O}$: Si, 17.51. Found: Si, 17.46.

1,3-Di-*n*-heptyltetramethyldisiloxane from Heptene-3 and *sym*-Tetramethyldisiloxane.—A mixture of 157 g. (1.6 moles) of heptene-3, 100.5 g. (0.75 mole) of *sym*-tetramethyldisiloxane and 0.75 ml. of a 0.1 molar alcoholic solution of chloroplatinic acid (7.5×10^{-3} mole) was refluxed for 48 hours. The mixture was distilled to give 216 g. (87.5% yield) of 1,3-diheptyltetramethyldisiloxane, b.p. 162–190° at 18 mm., n_D^{25} 1.4308–1.4302, d_4^{25} 0.8274–0.8246; found R_D 0.316, calcd. R_D 0.316.

Anal. Calcd. for $\text{Si}_2\text{C}_{18}\text{H}_{42}\text{O}$: Si, 17.51. Found: Si, 17.37.

To a dispersion of 218 g. (0.66 mole) of the 1,3-diheptyltetramethyldisiloxane in 400 ml. of concd. sulfuric acid was added 100 g. of ammonium chloride. Then dry hydrogen chloride was passed through the stirred dispersion for 2 hours. The layers were allowed to separate, and a 96.5-g. portion (0.5 mole) of the upper layer (crude heptyldimethylchlorosilane) was added slowly with stirring to a solution of 1 mole of methylmagnesium bromide in 1 l. of ether. When the addition was complete, 200 ml. of concd. hydrochloric acid was added, the organic layer was separated and the solvent was removed in a vacuum. Distillation through a 25 mm. \times 90 cm. column packed with Heli-pak resulted in 74.5 g. (86.6% yield) of heptyltrimethylsilanes, b.p. 180–183°, n_D^{25} 1.4222 to 1.4170, d_4^{25} 0.7566 to 0.7491; found R_D 0.377–0.336, calcd. R_D 0.338.

Anal. Calcd. for $\text{SiC}_7\text{H}_{15}\text{Cl}_3$: Si, 16.28. Found: Si, 16.53.

A gas-liquid phase chromatogram of a typical fraction (b.p. 180°, n_D^{25} 1.4222, d_4^{25} 0.7566) revealed that three components were present. The major component was identical with an authentic sample of *n*-heptyltrimethylsilane, and

the two minor components were identical with a mixture of authentic 3- and 4-heptyltrimethylsilanes.

Authentic *n*-Heptyltrimethylsilane.—To a vigorously stirred dispersion of 46 g. (2 moles) of sodium in 500 ml. of dry boiling toluene and 25 g. of trimethylchlorosilane was slowly added a mixture of 134 g. (1 mole) of *n*-heptyl chloride and 108.5 g. (1 mole) of trimethylchlorosilane. After the addition was complete the mixture was refluxed for 30 minutes, washed with 500 ml. of water, and the solvent was removed under reduced pressure. The residue was refluxed for 16 hours with 100 ml. of 10% alcoholic potassium hydroxide, and most of the alcohol was removed under reduced pressure. The residue was then washed with water, cold concentrated sulfuric acid and finally with water. After drying over anhydrous sodium sulfate the product was distilled through a 15 \times 800 mm. vacuum-jacketed column packed with Heli-pak to give 77.5 g. (45% yield) of *n*-heptyltrimethylsilane, b.p. 184° at 750 mm., n_D^{25} 1.4186, d_4^{25} 0.7466; found R_D 0.338, calcd. R_D 0.338.² A gas-liquid phase chromatogram of the product detected no impurities.

Anal. Calcd. for $\text{SiC}_7\text{H}_{15}$: Si, 16.28. Found: Si, 16.37.

3- and 4-Heptyltrichlorosilane.—To a refluxing solution of 98 g. (1 mole) of heptene-3 and 406.5 g. (3 moles) of trichlorosilane was added 40 g. of a 25% solution of acetyl peroxide in dibutyl phthalate over a period of 5 days. Distillation resulted in 110 g. (47% crude yield) of the 3- and 4-heptyltrichlorosilanes. Redistillation through a 15 \times 800 mm. vacuum jacketed column packed with Heli-pak gave 3- and 4-heptyltrichlorosilane, b.p. 205–206° at 750 mm., n_D^{25} 1.4510, d_4^{25} 1.103; found R_D 0.244, calcd. R_D 0.244.

Anal. Calcd. for $\text{SiC}_7\text{H}_{15}\text{Cl}_3$: neut. equiv., 77.8; Si, 12.04. Found: neut. equiv., 80.0; Si, 11.72.

3- and 4-Heptyltrimethylsilane.—To a solution of one mole of methylmagnesium bromide in 500 ml. of ether was added slowly 58 g. (0.25 mole) of the pure 3- and 4-heptyltrichlorosilane with stirring. The product was isolated in the usual manner and distilled through a 15 \times 800 mm. vacuum jacketed column packed with Heli-pak, to give 26.0 g. (60.2% yield) of 3- and 4-heptyltrimethylsilane, b.p. 174.5–176° at 750 mm., n_D^{25} 1.4262–1.4258, d_4^{25} 0.7622–0.7620; found R_D 0.336, calcd. R_D 0.338.

Acknowledgments.—The authors wish to express their appreciation to Cynthia Ann Skelton for carrying out the chromatographic analysis and to Janet Gardner for carrying out some of the preparative work.

MIDLAND, MICHIGAN

[CONTRIBUTION NO. 457 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND Co.]

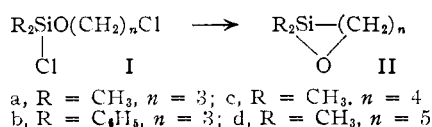
1-Oxa-2-Silacycloalkanes and their Conversion to Bis-(hydroxyalkyl)-disiloxanes

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Four 2,2-disubstituted 1-oxa-2-silacycloalkanes, members of a new class of silicon heterocycles, have been prepared by ring closure of the corresponding (chloroalkoxy)-chlorosilanes. The latter were made from dichlorosilanes and α,ω -chlorohydrins or oxacycloalkanes. The oxasilacycloalkanes were hydrolyzed readily to α,ω -bis-(hydroxyalkyl)-disiloxanes.

In studies of heterocyclic silicon chemistry, several 2,2-disubstituted 1-oxa-2-silacycloalkanes (II) have been prepared by heating the corresponding (chloroalkoxy)-chlorosilanes (I) with metallic sodium or lithium.



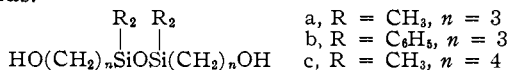
The (chloroalkoxy)-chlorosilanes were obtained by two routes. Those in which $n = 3$ were obtained from the appropriate disubstituted dichlorosilane and trimethylene chlorohydrin with triethylamine as acid acceptor. Compounds in which $n = 4$ and 5 were prepared smoothly and in good yields by heating the dichlorosilanes with tetrahydrofuran and tetrahydropyran, respectively, to 200° in an autoclave.¹ At 250°, tetrahydro-

(1) W. I. Patnode and R. O. Sauer, U. S. Patents 2,381,137 (August

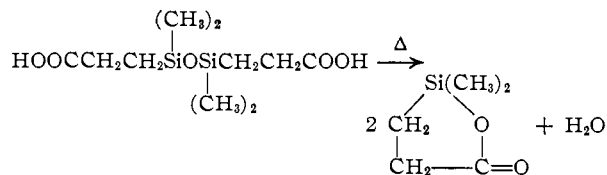
uran and dimethyldichlorosilane react to give good yields of 1,4-dichlorobutane and a dimethylpolysiloxane.²

Compounds IIa and IIc, which have five- and seven-membered rings, respectively, spontaneously formed low molecular weight polymers from which the monomers could be recovered on heating. Compound IIc, which has a six-membered ring, did not polymerize spontaneously, while IIb, a solid melting at 161.5–162°, did so only when heated above its melting point.³

Hydrolysis of IIa, IIb and IIc gave the corresponding α,ω -glycols, IIIa, IIIb and IIIc, in good yields.



Bis-(hydroxymethyl)-tetramethyldisiloxane, the only compound of this type that previously has been reported,⁴ is described as an unstable liquid which resinifies on standing. In contrast, IIIa, IIIb and IIIc are quite stable at room temperature. However, the distillation behaviors of IIIa and IIIc are anomalous. It would be expected that the boiling point of IIIa would approximate that of its diacetate which is reported⁵ to be 207° (39 mm.). Instead, IIIa distills at 75° (20 mm.). Possibly the glycol on heating reverts to a mixture of its precursors, Ia and water, and these reform the glycol on cooling. A similar observation has been made⁶ with 4,4,6,6-tetramethyl-5-oxa-4,6-disilanonane-1,9-dioic acid which, on heating, is converted to a mixture of lactone and water.



During attempted distillation of IIIc, ebullition was observed at 40° (0.13 mm.), but no distillate was condensed by the cold water condenser at the column head. However, IIIc slowly accumulated in an attached trap cooled in solid carbon dioxide. Apparently, the glycol was thermally degraded to its precursors and reformed in the cold trap.

The glycol IIIa reacted with toluene diisocyanate to form a polyurethane.

Experimental

3-Chloropropoxydimethylchlorosilane (Ia).—Dimethyldichlorosilane (252 g., 2 moles) and trimethylene chlorohydrin

7, 1954) and 2,381,138, have reported a similar reaction of halosilanes with ethylene oxide at room temperature.

(2) R. O. Sauer, U. S. Patent 2,534,149 (December 12, 1950).

(3) R. H. Krieble and C. A. Burkhard, *THIS JOURNAL*, **69**, 2689 (1947), have studied a somewhat similar ring system, the dimethylpolymethylenedioxyasilanes. Attempts to prepare a monomeric 5-membered ring compound by reaction of dimethyldichlorosilane or dimethyldiethoxysilane with ethylene glycol gave, instead, a 10-membered ring dimer. The homologous 6-membered ring compound, dimethyl-(trimethylene-1,3-dioxy)-silane, was apparently stable, similar to IIc above. They could not prepare a 7-membered ring or a polymer thereof, but did report that the corresponding 8-, 10- and 11-membered ring compounds underwent a reversible spontaneous polymerization similar to that of IIa and IIc.

(4) J. L. Speier, *et al.*, *THIS JOURNAL*, **71**, 1474 (1949).

(5) L. H. Sommer, *et al.*, *ibid.*, **77**, 2485 (1955).

(6) L. H. Sommer, U. S. Patent 2,589,446 (March 18, 1952).

(94 g., 1 mole) were mixed in 250 ml. of anhydrous ether, and triethylamine (101 g., 1 mole) was added with stirring and cooling in an ice-bath. After addition was complete, stirring was continued for 5 minutes and the mixture was filtered under nitrogen. Distillation of the filtrate gave 99.7 g. (53% yield) of 3-chloropropoxydimethylchlorosilane, b.p. 72° (16 mm.).

Anal. Calcd. for $\text{C}_6\text{H}_{12}\text{Cl}_2\text{OSi}$: C, 32.08; H, 6.42; Cl, 37.97. Found: C, 32.28; H, 6.59; Cl, 37.75.

2,2-Dimethyl-1-oxa-2-silacyclopentane (IIa).—3-Chloropropoxydimethylchlorosilane (80 g., 0.43 mole) in 50 ml. of decane was added slowly to a rapidly stirred refluxing mixture of sodium (19 g., 0.83 mole) in 500 ml. of decane. After addition was complete, heating was discontinued and stirring was continued for 30 minutes. The condenser was replaced by a Vigreux column and the solution was rapidly distilled until the head temperature reached 171°. The distillate was refractionated to give 16.1 g. (31% yield) of product, b.p. 97–100°. Within an hour after the distillation, the distilled fractions had increased noticeably in viscosity. The most viscous fraction was found to have a molecular weight of 2340. A typical sample was analyzed.

Anal. Calcd. for $\text{C}_6\text{H}_{12}\text{OSi}$: C, 51.72; H, 10.34; Si, 24.14; mol. wt., 116. Found: C, 51.81; H, 10.22; Si, 24.18; mol. wt., 756.

A small sample of polymer was heated in a flask connected to a micro distilling column. The entire sample distilled as a clear, fluid liquid, b.p. 95°, n_D^{20} 1.4170. Immediate analysis indicated it to be monomeric 2,2-dimethyl-1-oxa-2-silacyclopentane.

Anal. Calcd. for $\text{C}_6\text{H}_{12}\text{OSi}$: C, 51.72; H, 10.34; mol. wt., 116. Found: C, 51.52; H, 10.32; mol. wt., 122.

3-Chloropropoxydiphenylchlorosilane (Ib).—Diphenyldichlorosilane (506 g., 2.0 moles) and triethylamine (101 g., 1.0 mole) were dissolved in benzene (300 ml.). Trimethylene chlorohydrin (94 g., 1.0 mole) was added with rapid stirring over a two-hour period. The addition of ether (400 ml.) caused the separation of triethylamine hydrochloride which was removed by filtration. After washing the solid with ether, the filtrate was distilled to obtain 107 g. (34% yield) of 3-chloropropoxydiphenylchlorosilane, b.p. 126–130° (0.13 mm.).

Anal. Calcd. for $\text{C}_{13}\text{H}_{16}\text{Cl}_2\text{OSi}$: C, 57.88; H, 5.15; Cl, 22.83. Found: C, 55.11; H, 5.06; Cl, 23.36.

2,2-Diphenyl-1-oxa-2-silacyclopentane (IIb).—3-Chloropropoxydiphenylchlorosilane (106 g., 0.34 mole) in 45 ml. of toluene was added over a 2.5-hour period to a rapidly stirred refluxing mixture of sodium (15.7 g., 0.68 mole) in 800 ml. of toluene. Stirring and refluxing were continued for 30 minutes. Filtration gave a purple-colored, fine suspension which was clarified by centrifuging. Distillation gave 28.7 g. (35% yield) of 2,2-diphenyl-1-oxa-2-silacyclopentane, b.p. 122° (0.23 mm.). This material solidified on cooling and was recrystallized from decane, m.p. 155–157°. Recrystallization from acetone raised the melting point to 161.5–162°.

Anal. Calcd. for $\text{C}_{15}\text{H}_{16}\text{OSi}$: C, 75.00; H, 6.67; Si, 11.67; mol. wt., 240. Found: C, 74.38; H, 6.68; Si, 11.23; mol. wt., 250.

When this oxasilacyclopentane was heated at 180° for 10 minutes under a stream of nitrogen, the molecular weight increased to about 800.

4-Chlorobutoxydimethylchlorosilane (Ic).—Dimethyldichlorosilane (129 g., 1.00 mole) and tetrahydrofuran (36 g., 0.50 mole) were mixed and heated to 200° for 4 hours in a stainless steel autoclave. Distillation gave 90.7 g. (90% yield) of 4-chlorobutoxydimethylchlorosilane, b.p. 64° (4.2 mm.).

Anal. Calcd. for $\text{C}_6\text{H}_{14}\text{Cl}_2\text{OSi}$: C, 35.82; H, 6.97; Si, 13.93. Found: C, 35.87; H, 7.09; Si, 14.20.

In a second run, due to mechanical failure, the reaction temperature went to at least 275°. None of the desired product was found. Instead, a 65% yield of 1,4-dichlorobutane and a non-distillable liquid, presumably a dimethylpolysiloxane, were obtained.²

2,2-Dimethyl-1-oxa-2-silacyclohexane (IIc).—4-Chlorobutoxydimethylchlorosilane (118 g., 0.59 mole) was added slowly to a rapidly stirred mixture of sodium (27.6 g., 1.2 moles) in 400 ml. of refluxing decane. The mixture was distilled rapidly until the head temperature reached 171°.

Redistillation gave 51 g. (67% yield) of 2,2-dimethyl-1-oxa-2-silacyclohexane, b.p. 122–125°, n_D^{25} 1.4260.

Anal. Calcd. for $C_8H_{14}OSi$: C, 55.38; H, 10.77; Si, 21.54; mol. wt., 130. Found: C, 55.61; H, 10.83; Si, 21.30; mol. wt., 133.

5-Chloropentoxymethylchlorosilane (Id).—Tetrahydropyran (42 g., 0.49 mole) and dimethyldichlorosilane (129 g., 1.0 mole) were mixed and heated at 200° for 4 hours under autogenous pressure. Distillation gave 53.5 g. (51% yield) of 5-chloropentoxymethylchlorosilane, b.p. 57° (0.6 mm.).

Anal. Calcd. for $C_7H_{16}Cl_2OSi$: C, 39.07; H, 7.45; Cl, 33.02. Found: C, 39.36; H, 7.57; Cl, 32.88.

An attempt to combine tetrahydropyran and dimethyldichlorosilane at reflux temperature in the presence of anhydrous zinc chloride was unsuccessful.

2,2-Dimethyl-1-oxa-2-silacycloheptane (IId).—5-Chloropentoxymethylchlorosilane (50.3 g., 0.23 mole) was added slowly to a stirred mixture of lithium (3.25 g., 0.47 mole) in 300 ml. of refluxing decane. Refluxing and stirring were continued overnight, resulting in complete disappearance of the lithium. The reaction mixture was filtered and distilled to give 7.1 g. (21% yield) of product, b.p. 143–146°. Analysis of this product after it had been allowed to stand for several days showed it to be a polymer of 2,2-dimethyl-1-oxa-2-silacycloheptane.

Anal. Calcd. for $C_7H_{16}OSi$: C, 58.33; H, 11.11; Si, 19.44; mol. wt., 144. Found: C, 56.81; H, 10.8; Si, 19.18; mol. wt., 537, 524.

A freshly distilled sample has a molecular weight of 248, indicating that the ring-opening polymerization is fairly rapid. Comparison of the boiling point of this material with those of its homologs strongly suggests that it distills as the seven-membered ring compound and not as a dimer.

The 4,4,6,6-Tetramethyl-5-oxa-4,6-disila-1,9-nonanediol (IIIa).—2,2-Dimethyl-1-oxa-2-silacyclopentane (50 g., 0.45 mole) was distilled into a solution of 9 ml. of water and 0.5 ml. of hydrochloric acid in 250 ml. of acetone. This mixture was allowed to stand for four days. Removal of the acetone and distillation of the residue gave 40.6 g. (75% yield) of 4,4,6,6-tetramethyl-5-oxa-4,6-disila-1,9-nonanediol, b.p. 75° (20 mm.), n_D^{25} 1.4470.

Anal. Calcd. for $C_{10}H_{26}O_3Si_2$: C, 48.00; H, 10.40; Si, 22.40; mol. wt., 250. Found: C, 48.24; H, 10.52; Si, 22.47; mol. wt., 248.

Condensation of Toluene Diisocyanate with 4,4,6,6-Tetramethyl-5-oxa-4,6-disila-1,9-nonanediol.—The diol (2.2 g.) and toluene diisocyanate (1.65 g.) were mixed with three drops of triethylamine. An exothermic reaction took

place and the product was heated on a steam-bath for 1.5 hours to give a hard, clear yellow solid which was leached with chloroform. The chloroform solution was filtered and the polymer was precipitated by adding the filtrate to petroleum ether. The polymer became insoluble before its molecular weight could be determined.

Anal. Calcd. for $(C_{19}H_{32}O_3N_2Si_2)_x$: C, 53.78; H, 7.55; Si, 13.28. Found: C, 54.58; H, 7.62; Si, 13.14.

The 4,4,6,6-Tetraphenyl-5-oxa-4,6-disila-1,9-nonanediol (IIIb).—2,2-Diphenyl-1-oxa-2-silacyclopentane (5 g., 0.021 mole) was dissolved in 50 ml. of dioxane. Water was added until the cloud point was reached. Five drops of concentrated hydrochloric acid was added and the solution was clarified by the addition of dioxane. The solution was heated on a steam-bath for 1.5 hours and allowed to stand for two days after which the volatile liquids were removed at 20 mm. pressure. The residue, a light straw-colored, viscous liquid, was heated at 65° for 10 minutes at 0.3 mm. Trituration in petroleum ether caused solidification. Recrystallization from cyclohexane gave 2.2 g. of 4,4,6,6-tetraphenyl-5-oxa-4,6-disila-1,9-nonanediol, m.p. 104–108°. A second recrystallization from cyclohexane raised the melting point to 110–111°. Infrared analysis supported the assigned structure.

Anal. Calcd. for $C_{30}H_{34}O_3Si_2$: C, 72.29; H, 6.83; mol. wt., 498. Found: C, 72.25; H, 6.77; mol. wt., 485.

5,5,7,7-Tetramethyl-6-oxa-5,7-disila-1,11-undecanediol (IIIc).—2,2-Dimethyl-1-oxa-2-silacyclohexane (30.5 g., 0.23 mole) and water (4.4 ml., 0.25 mole) were mixed and stirred. An exothermic reaction took place which caused a temperature rise to 50°. To ensure completion of the reaction, 10 ml. of acetone, 3 drops of hydrochloric acid and another 1 ml. of water were added. After standing two days, the acetone was removed from the clear, colorless solution at a pressure of 15 mm. To remove the excess water, the crude product was heated to 40° (0.13 mm.). Under these conditions, ebullition occurred and the product slowly vaporized. The vapors were not condensed by cold water but could be trapped at solid carbon dioxide temperature. The distillation was interrupted and the condensed liquid, A, n_D^{25} 1.4492, and the distillation residue, B, n_D^{25} 1.4495, were analyzed separately. The infrared spectra of A and B were identical and were in agreement with the proposed structure.

Anal. Calcd. for $C_{12}H_{30}O_3Si_2$: C, 51.81; H, 10.79; Si, 20.14; mol. wt., 278. Found for A: C, 51.24; H, 10.90; Si, 20.06; mol. wt., 320. Found for B: C, 51.60; H, 10.87.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SAGA UNIVERSITY]

Some Addition Compounds of Bis-salicylaldehyde-ethylenediimine-copper. Part II

BY TSUGUO TANAKA

RECEIVED DECEMBER 30, 1957

The absorption spectra of bis-salicylaldehyde-ethylenediimine-copper in various solvents were measured. The absorption maxima of band II can be correlated with the formation of addition compounds. Three 5,5'-disubstituted bis-salicylaldehyde-ethylenediimine-coppers were prepared, and their formation of addition compounds with propionic acid and phenol was investigated; the methyl substituent facilitates the formation of an addition compound, while the chloro and nitro substituents retard it.

The description of Pfeiffer, *et al.*,¹ of the color of bis-salicylaldehyde-ethylenediimine-copper in various solvents led to the isolation of the addition compounds of the complex with acids and phenols.² Attempts were then made to correlate the absorption spectrum in a given solvent with the formation of an addition compound between the complex and the solvent, and to ascertain the nature of the bond between the acid (or phenol) and the complex.

(1) P. Pfeiffer, E. Breith, E. Lübke and T. Tsumaki, *Ann.*, **503**, 85 (1933).

(2) T. Tanaka, *Bull. Chem. Soc. Japan*, **29**, 93 (1956).

The absorption spectra of bis-salicylaldehyde-ethylenediimine-copper in methyl alcohol and in absolute ethyl alcohol were reported by Tsumaki³ and Kiss, *et al.*,⁴ respectively, but their data do not agree. According to Tsuchida and Tsumaki,^{5,6} band I (566 m μ) is due to excitation of the 3 d electron of the copper atom, band II (357 m μ) to the

(3) T. Tsumaki, *ibid.*, **13**, 252 (1938).

(4) A. v. Kiss, P. Csokan and G. Nyiri, *Z. physik. Chem., Abt. A.*, **190**, 65 (1942).

(5) R. Tsuchida, "The Colors and the Structures of the Metal Complexes," Zoshindo, Osaka, 1947, p. 160; T. Tsumaki and R. Tsuchida, *Bull. Chem. Soc. Japan.*, **13**, 527 (1938).