[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORQUIMA S.A., SÃO PAULO]

Studies on the Coördinate Bond. II. Ferrous Complexes of α-Diimines[1]

BY P. KRUMHOLZ

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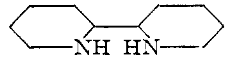
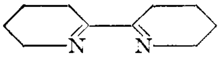
The supposed color reaction of α,α'-dipiperidyl with ferrous salts is shown to be due to an oxidation or dehydrogenation product of this base, probably α,α'-bis-Δ¹-piperideine. Based on the α-diimine structure of that compound stable ferrous complexes of glyoxal and biacetyl bis-N-methylimine have been prepared. Their absorption spectra are similar to the spectra of the ferrous complexes of α,α'-dipyridyl and o-phenanthroline. Possible relations between the structure and the color of the α-diimine complexes are briefly discussed.

In 1898, Blau[2] stated that α,α'-dipiperidyl, with ferrous salts, gives a color reaction similar to the reaction of α,α'-dipyridyl. This statement has since been quoted in numerous monographs and reviews on coördination and analytical chemistry. α,α'-Dipiperidyl may be regarded as a cyclic derivative of ethylenediamine and, as the latter is known to give only colorless and unstable[3] ferrous complexes, Blau's findings seem rather surprising. Thus we decided to reinvestigate the reaction between ferrous salts and α,α'-dipiperidyl. We found in accordance with Blau,[2] that the base prepared by reduction of α,α'-dipyridyl with sodium in alcoholic solution[2] gives a purple coloration with ferrous salts, but that maximal color intensity is produced by the addition of only a few mole per cent. of the latter. The intensity of the color reaction may be increased several times by heating the base in the presence of oxygen to 150°, whereas heating in the absence of oxygen is without a noticeable effect. Thus the color reaction with ferrous salts is probably due to the presence of an oxidation or dehydrogenation product of α,α'-dipiperidyl. This product may be separated from the latter by ether extraction of an aqueous solution at *p*H 7, the strong base α,α'-dipiperidyl being transformed completely at that *p*H into its salt. Therefore, it is probably a weak tertiary base. The ether extract gives a very intensive purple coloration with aqueous ferrous salt solutions. The complex may be precipitated from such solutions as insoluble poly-iodide, which can be transformed with sodium sulfite into the crystalline iodide. The quantity obtained was insufficient for complete analysis or for the determination of the structure of the organic component.[4] Figure 1 shows the absorption spectrum of the complex. The complex is remarkably stable in acid solution, but the absorption spectrum shifts slowly to longer wave lengths, as shown in Fig. 1. We supposed that the complex forming base from α,α'-dipiperidyl might be its partly dehydrogenated derivative α,α'-bis-Δ¹-piperideine (3,4,5,6,-3',4',5',6'-octahydro α,α'-dipyridyl). This substance may be regarded as a cyclic derivative of an α-diimine. Aliphatic imines of α-dicarbonyl compounds are so far not known. We found that on mixing alcoholic or aqueous solutions of glyoxal or biacetyl with ferrous salts and excess methylamine, a strong blue color develops, which changes slowly to a deep purple red. The blue color is destroyed by acidification, whereas the red coloration remains stable. We assumed that the red coloration is due to ferrous complexes of biacetyl-bis-N-methylimine (and of the corresponding glyoxal derivative) whereas the initial blue coloration is due to ferrous complexes of the corresponding mono-N-methylimines in analogy to the blue complexes of α-diketo monoximes.[5] We succeeded in isolating the red ferrous complexes in the form of their crystallized iodides, the analysis of which corresponds closely to the composition of tris-(biacetyl-bis-N-methylimine) ferrous iodide and tris-(glyoxal-bis-N-methylimine) ferrous iodide. The former compound crystallizes from its aqueous solution in anhydrous form, the latter as trihydrate. Both





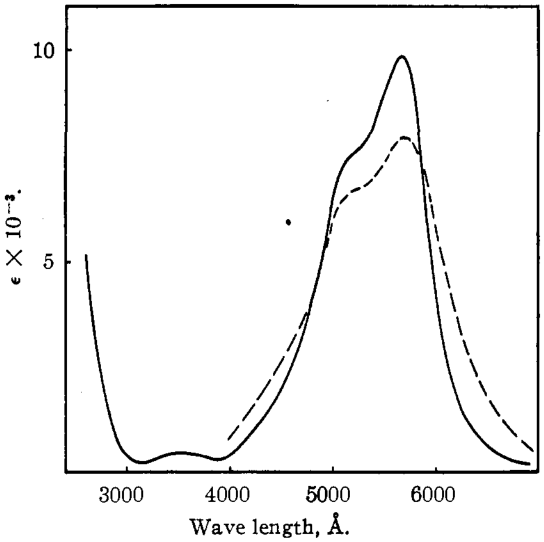


Fig. 1.—Ferrous complex prepared from oxidized α,α'-dipiperidyl: —, neutral solution; – –, solution in 0.1 *N* hydrochloric acid after 3 days of standing at 20°. ε-Values based on the iron content.

$$\begin{array}{ccc} H_3C\cdot C—C\cdot CH_3 & \qquad & HC—CH \\ \|\qquad\ \ \| & & \|\quad\ \| \\ H_3C\cdot N\quad N\cdot CH_3 & & H_3C\cdot N\quad N\cdot CH_3 \end{array}$$

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(1) For paper I, see *Anais da Acad. Bras. de Ciências*, **22**, 263 (1950).

(2) F. Blau, *Monatsh.*, **19**, 647 (1898).

(3) See J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

(4) The iron and iodine content correspond to the composition of a hexahydrate of a complex between ferrous iodide and 3 molecules of a base derived from the dipiperidyl (see later).

(5) See F. Feigl, "Chemistry of Specific, Selective and Sensitive Reactions," Academic Press, Inc., New York, N. Y., 1949, p. 209, W. Kuester, *Z. physiol. Chem.*, **155**, 157 (1926).

complexes are decomposed by boiling with alkali with the formation of methylamine, recovered in an 80 to 85% yield. The complexes are remarkably stable in acid solution. The biacetyl derivative must be boiled for more than 1 hour with 2 formal sulfuric acid for complete decomposition. From the products of acid decomposition, methylamine was recovered in almost quantitative yield and biacetyl in a yield of about 90%.

The absorption spectrum of the ferrous complex of biacetyl-bis-N-methylimine, shown in Fig. 2, is almost identical with the spectrum of the ferrous complex of the supposed α,α'-bis-Δ^1-piperideine (see Fig. 1), showing in acid solution a slow shift to longer wave lengths similar to the latter. Thus the structure proposed for the dehydrogenation product of α,α'-dipiperidyl seems to be correct.

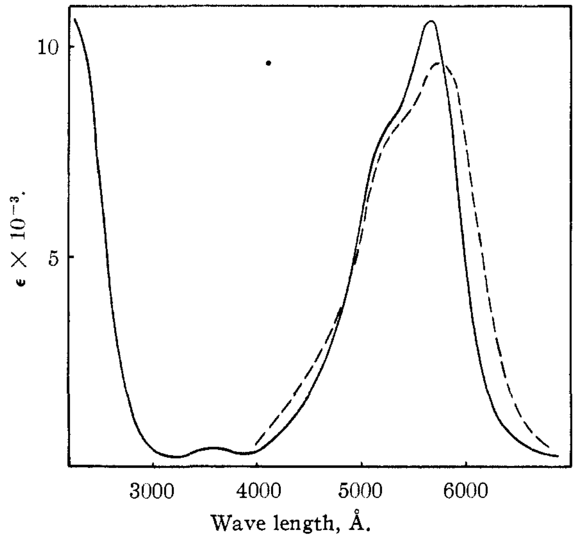

Fig. 2.—Ferrous tris-(biacetyl-bis-N-methylimine): —, neutral solution; – –, solution in 0.1 *n* hydrochloric acid after 20 days standing at 20°.

Methylglyoxal, phenylglyoxal and 1,2-cyclohexanedione can be condensed like glyoxal and biacetyl with methylamine and ferrous salts. No colored complexes could be obtained from benzil under similar conditions

Finally we found that the addition of ferrous chloride (0.25 mole) to an alcoholic solution of biacetyl-bis-anil[6] produces a rapidly fading blue coloration. The absorption spectrum consists of one broad band extending over the whole of the visible range with a maximum at about 600 mμ and a molecular extinction coefficient of about 10^3 (calculated on iron). The addition of a few per cent. of water changes the color into red, the same change being produced by an excess of ferrous chloride.

Application of the method of continuous variation[7] to the system ferrous chloride–biacetyl-bis-anil at 600 mμ indicates the formation of a partly dissociated 1:2 compound. Substitution of the N-methyl by N-phenyl groups thus completely changes the behavior of the α-diimines against ferrous salts.

Structural Considerations

The absorption spectra of the ferrous α-diimine complexes show not only a great mutual similarity, but, as demonstrated in Fig. 3, at least with respect to the principal band in the visible, show a similar resemblance to the spectra of the ferrous complexes of α,α'-dipyridyl and *o*-phenanthroline.

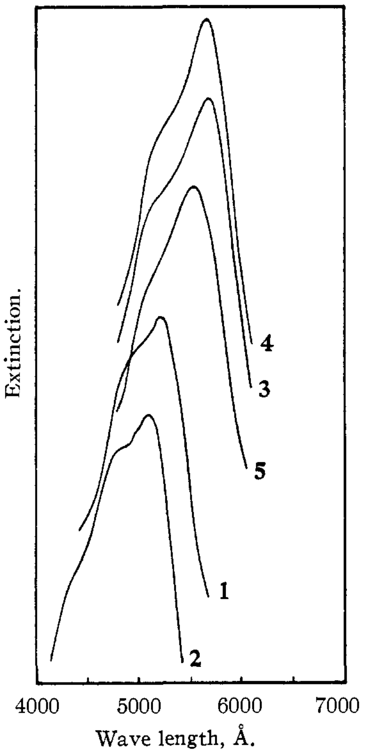

Fig. 3.—Absorption spectra of the ferrous complexes of: 1, α,α'-dipyridyl; 2, *o*-phenanthroline; 3, α,α'-bis-Δ^1-piperideine; 4, biacetyl-bis-N-methylimine; 5, glyoxal-bis-N-methylimine. The spectra are drawn in the same scale but displaced vertically.

The values of the extinction coefficients of the principal band are, as shown in Table I, not very different.

TABLE I

	Coördinated base	λ_{max}, mμ	$\epsilon_{max} \times 10^{-3}$
1	α,α'-Dipyridyl	522	8.7
2	*o*-Phenanthroline	510	11.5
3	α,α'-Bis-Δ^1-piperideine	568	10
4	Biacetyl-bis-N-methylimine	568	10.7
5	Glyoxal-bis-N-methylimine	554	8.8

The typical double structure of this band is maintained in the ferrous complexes of methyl substituted α,α'-dipyridyls[8] and *o*-phenanthrolines[9] and similarly in the ruthenium[10] and osmium[11] complexes of α,α'-dipyridyl.

Thus it is probable that all the complexes under discussion have a common structural element and that their intensive and anomalous color is related to the presence of the "chromophoric" chelate system

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[6] H. v. Pechmann, *Ber.*, **21**, 1412 (1888).

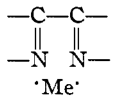
[7] P. Job, *Ann. chim.*, **11**, 97 (1936).

[8] F. Wm. Cagle and G. F. Smith, THIS JOURNAL, **69**, 1860 (1947).

[9] G. F. Smith and W. W. Brandt, *Anal. Chem.*, **21**, 948 (1949).

[10] W. W. Brandt and G. F. Smith, *ibid.*, **21**, 1313 (1949).

[11] F. H. Burstall, F. P. Dwyer and E. C. Gyarfas, *J. Chem. Soc.*, 953 (1950).



It seems to be of secondary importance as to whether or not the $-\overset{|}{C}{=}\overset{|}{N}$ group belongs to a heterocyclic ring.[12]

K. Sone[13] recently advanced similar ideas regarding the color of metal chelates and related this color with the possibility of resonance of the π-electrons over the non-metallic atoms, composing the chelate ring. This conception can be applied to the entire chelate ring, assuming that d-electrons of the metal are involved in the formation of the coördinate bond[14] and that structures such as

contribute to the state of the molecules.[15] The visible absorption of the complexes under discussion, which does not appear in their components, can now be related, in a formal way at least with an increased mobility of the π-electrons of the chelate ring, as compared with the π-electrons of the free diimine.

A contribution of the "d-bonded" structures to the ground state of the molecules may explain the unusual stability of the α-diimine complexes.

It may be mentioned that similar "d-bonded" structures may be written for most of the abnormally colored chelates.

Experimental Part

α,α′-Dipiperidyl.—To a solution of 1.56 g. (0.01 mole) of α,α′-dipyridyl, m.p. 70.5°, in 100 ml. of ethanol, 6 g. of metallic sodium was added while stirring. As the reaction became sluggish, the mixture was heated under reflux. After cooling, the mixture was brought to *p*H 4 with hydrochloric acid, filtered from the sodium chloride and the liquid evaporated at reduced pressure. The residue was dissolved in 10 ml. of water, neutralized to *p*H 7 and extracted with ether until all non-reacted α,α′-dipyridyl was removed (color reaction with ferrous salts). After the addition of an excess of sodium hydroxide the aqueous layer was extracted four times with 40 ml. of ether. After evaporation of the latter, the residue was distilled at 0.05 mm. and about 60°, yielding 0.7 to 1 g. of α,α′-dipiperidyl in the form of an almost colorless, very hygroscopic, oily liquid.

α,α′-Bis-Δ^1-piperideine (?) and Its Ferrous Complex.—0.3 g. of α,α′-dipiperidyl was heated for 15 min. to 150° while blowing a slow stream of dry air over the surface of the liquid. The base turned yellow and then brown. Three charges were dissolved in 5 ml. of water, the solution neutralized to *p*H 7 and extracted four times with 30 ml. of ether. The ether solution was extracted with 10 ml. of a 0.05 *m* solution of ferrous chloride, which turned into an intensive purple. On addition of a solution of potassium poly-iodide, a dark brown precipitate was obtained, which was filtered and dissolved in 5 ml. of water, using the least necessary quantity of sodium sulfite. After addition of 2 g. of potassium iodide and keeping for several hours at 5°, the black iodide was collected, recrystallized from a few ml. of water and dried over calcium chloride; yield about 50 mg. For iron determination the iodide was decomposed with concentrated sulfuric acid, ignited, dissolved in hydrochloric acid and iron determined by colorimetry with α,α′-dipyridyl.[16] For iodine determination the substance was decomposed by boiling with sodium hydroxide and hydrogen peroxide, the filtered solution acidified after addition of some sodium sulfite with sulfuric acid, then heated to boiling and iodine determined by potentiometric titration with 0.01 *n* silver nitrate.

Anal. Calcd. for $\mathrm{FeI_2{\cdot}(C_{10}H_{16}N_2)_3{\cdot}6H_2O}$: Fe, 6.72; I, 30.5. Found: Fe, 6.6, 6.55, 6.65; I, 30.6.

Tris-(biacetyl-bis-N-methylimine) Ferrous Iodide.—4.15 g. (0.05 mole) of biacetyl dissolved in 75 ml. of ethanol was mixed with 20 ml. of a 7.5 *m* aqueous solution of methylamine (0.15 mole) and maintained during 15 min. at 25°. Then 20 ml. of a molar solution of ferrous chloride (0.02 mole), freshly reduced by shaking with iron powder was added, the deep blue mixture shaken during 10 minutes and finally heated for 20 minutes to 40°. The blue color changed into a deep purple. Excess methylamine and solvent was evaporated under reduced pressure at a temperature not exceeding 40° until the volume was reduced to 25 ml. The solution was filtered and, after addition of 10 to 15 g. of potassium iodide, kept for several hours at 5°. The collected iodide was recrystallized twice from about 5 times its weight of water. From the collected filtrates the remaining complex was precipitated as poly-iodide, the tarry precipitate dissolved in a solution of sodium sulfite and reprecipitated as poly-iodide. The latter was dissolved in 10 ml. of water using the least necessary amount of sodium sulfite and the filtered solution after addition of 5 g. of potassium iodide crystallized at 5°. The total yield was 4 to 5 g. of almost black crystals with a metallic luster, readily soluble in water.

By slow evaporation of a diluted aqueous solution the iodide crystallized in the form of purple microscopic hexagonal plates. Iron and iodine were determined as described before, iron alternatively after decomposition with boiling hydrochloric acid by double precipitation as hydroxide. Nitrogen was determined by the Kjeldahl method.

Anal. Calcd. for $\mathrm{FeI_2(C_6H_{12}N_2)_3}$: Fe, 8.64; I, 39.3; N, 13.01. Found: Fe, 8.73, 8.85, 8.65; I, 39.0, 39.3, 39.0; N, 13.1, 13.25.

For determination of the decomposition products about 0.1 g. of the iodide was distilled with 50 ml. of 15% sulfuric acid, maintaining a constant volume by dropwise addition of water to the distillation flask. About 1 hour boiling was necessary for complete decomposition. The distillate (about 50 ml.) was collected in an ice-cooled flask and the biacetyl determined as nickel dimethylglyoxime, by warming with nickel salt, hydroxylamine hydrochloride and sodium acetate.[17] Up to 93% of the theoretical amount of biacetyl could be recovered. The acid solution was mixed with an excess of sodium hydroxide, the methylamine distilled into 0.1 *n* hydrochloric acid and determined by potentiometric titration. The titration curve was practically identical with one obtained by titration of an authentical sample of methylamine and quite different from the titration curve of ammonia. The recovery of methylamine was practically quantitative.

Decomposing the iodide by boiling with *n* sodium hydroxide yielded 80 to 85% of the expected amount of methylamine.

Tris-(glyoxal-bis-N-methylimine) Ferrous Iodide.—Ten ml. of a commercial 30% solution of glyoxal (0.052 mole) diluted with the equal volume of water was mixed with 20 ml. of *m* ferrous chloride (0.02 mole) and 20 ml. of 7.5 *m* aqueous methylamine (0.15 mole). The mixture turned blue almost immediately, changing the color slowly to a deep red. After one hour standing at 25° the reaction mixture was treated as described above for the biacetyl complex. The crude iodide was recrystallized from water and finally from 0.01 *n* hydrochloric acid. The total yield including that obtained from the poly-iodide was 1.5 to 2 g.

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[12] This disproves, at least in respect to the band under discussion' our previous statement (P. Krumholz, *Nature*, **167**, 570 (1951)) that the visible absorption of ferrous tris-α,α′-dipyridyl is due to electronic transitions involving the entire polynuclear chelate system, that is the dipyridyl molecule as such.

[13] K. Sone, *Bull. Chem. Soc. Japan*, **25**, 1 (1952).

[14] See L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1944; J. Chatt, *J. Chem. Soc.*, 3340 (1949); J. Chatt and A. A. Williams, *ibid.*, 3061 (1951).

[15] M. Calvin and K. W. Wilson, THIS JOURNAL, **67**, 2003 (1945), were the first to discuss structures involving double bonds with the metal atom for chelates (of 1,3-diketones).

[16] F. Feigl, P. Krumholz and H. Hamburg, *Z. anal. Chem.*, **90**, 199 (1933).

[17] See J. M. Johlin, THIS JOURNAL, **37**, 892 (1915).

The iodide crystallized as trihydrate of almost black color, very soluble in water.

Anal. Calcd. for $FeI_2(C_4H_8N_2)_3 \cdot 3H_2O$: H_2O, 8.77. Found: H_2O, 8.45. Dried over calcium chloride *in vacuo* to constant weight.

Anal. Calcd. for $FeI_2(C_4H_8N_2)_3$: Fe, 9.94; I, 45.15; N, 14.95. Found: Fe, 10.08, 10.05; I, 45.0, 45.2; N, 14.55, 14.7.

Absorption Spectra.—The absorption spectra were determined with a Unicam Spectrophotometer. 5×10^{-5} to 10^{-4} molar solutions of the diimine complexes at an optical depth of 10 mm. were used. Measurements were reproducible within ±1%.

For the ultraviolet measurements the iodides were transformed to the chlorides by shaking the 10^{-3} *m* aqueous solutions of the former with silver chloride. The concentration of the chloride solutions was checked by comparison of the visible absorption with that of the pure iodide.

The photometric measurements on the very unstable complexes of the biacetyl-bis-anil were made in the following way: 2 ml. of a 0.01 *m* solution of the bis-anil[6] in absolute ethanol was mixed in an absorption cell of 5 mm. optical depth with 0.5 ml. of a solution prepared by dilution of 0.1 ml. of a 2.5 *m* aqueous solution of ferrous chloride with 25 ml. of absolute ethanol and the absorption measured within 10 to 15 seconds after the mixing. Fresh solutions were prepared for measurements at different wave lengths.

For the continuous variation measurements the 10^{-2} *m* alcoholic solutions of the bis-anil and of ferrous chloride, were mixed in variable proportions and the extinction measured at 600 mμ. The reproducibility of these measurements was about ±3%.

SÃO PAULO, BRAZIL

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF CORNING GLASS WORKS AND THE DOW CORNING CORPORATION]

Silanol Derivatives of the Dimethyl Substituted Organosilicon Compounds

BY J. F. HYDE

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Dimethylsilanediol and the next member of the series, tetramethyldisiloxane-1,3-diol, have been isolated and characterized. They are relatively stable materials in the absence of acidic or alkaline dehydration catalysts.

One of the striking contrasts between organosilicon chemistry and organic chemistry has been the existence of compounds in which two hydroxyl groups are attached to a single silicon atom. The relatively stable character of such compositions was demonstrated by Kipping's extensive studies of diphenylsilanediol and its condensation products.[1]

These same studies further emphasized the polymeric character of the condensation products and disclosed the apparent inability of silicon–oxygen double bonds to form from the hydroxy-compounds by loss of water.

More recently a number of dialkylsilanediols have been reported.[2]

During the preparation of this manuscript a note by Lucas and Martin has appeared describing the tetramethyldisiloxane-1,3-diol, and its preparation by another method.[3]

The dimethylsilanediol had become increasingly conspicuous by its absence from the literature. It holds a position of some general interest from both a theoretical and a practical point of view, since it is the monomeric parent of a whole series of industrially important polymeric products.

The ready isolation of the dimethylsilanediol, and its behavior suggest that it is inherently no less stable under normal conditions than the diphenylsilanediol. It does appear to be more sensitive to the catalytic effect of traces of acid or base in causing dehydration, and these catalysts must be strictly excluded for a successful preparation.

The indications are that the dimeric diol is more stable toward dehydration than the monomeric diol. This might be expected on the basis of a greater separation of the hydroxyl groups. It is possible also that an intermolecular association of the hydroxyl groups could add a further stabilizing effect in both compounds. In the case of the dimeric diol, intramolecular hydrogen bridging could produce a six-membered ring of added stability.

This relatively stable character of the diols indicates that other factors besides the nature of the attached groups are involved. Presumably the same fundamental factors which oppose any tendency to form doubly bonded oxygen structures would favor the formation of stable diols. One of these factors could be polarizing effects due to the over-all positive nature of the ($R_2Si<$) grouping.

Experimental Part

Preparation of Dimethylsilanediol.—A 74.0-g. (0.5 mole) portion of $Me_2Si(OEt)_2$ (freshly distilled from potassium carbonate) was mixed with 34 g. (2 moles) of distilled H_2O in a Vycor brand erlenmeyer flask. After 24 hours at 25° with intermittent shaking, two liquid phases were still present. The mixture became homogeneous after 30 hours and the odor of ester was gone in 48 hours. After 8 hours on the water vacuum at 25° a semi-crystalline mass remained. Several hours on a Hyvac were necessary to remove the remaining water completely and leave 42.3 g. of a fluffy dry mass of flaky crystals (yield 92%). The density, determined by pycnometer with octamethylcyclotetrasiloxane as the immersion fluid, was found to be 1.097 ± 0.002.

Anal. Found: OH, 32.8 (Zerewitinoff); Si, 30.79. Calcd.: OH, 36.9; Si, 30.45.

Samples could be further purified by rinsing with low boiling petroleum ether, dissolving in benzene by heating to 60°, and cooling. The melting point of the platelets thus formed was 96–98°. The molecular weight determined cryoscopically in benzene was 94 (calcd. 92).

The diol is soluble in water to the extent of 245 g./100 g. of H_2O. The compound is sensitive to condensation

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(1) (a) W. Dilthey and F. Eduardoff, *Ber.*, **37**, 1139 (1904); (b) R. Robison and F. S. Kipping, *J. Chem. Soc.*, **93**, 439 (1908); (c) F. S. Kipping, *ibid.*, **101**, 2108 (1912); (d) **101**, 2125 (1912).

(2) (a) Diethylsilanediol. P. A. DiGiorgio, L. H. Sommer and F. C. Whitmore, THIS JOURNAL, **68**, 344 (1946). (b) Organosilicon Compounds. Dialkylsilanediols. P. A. DiGiorgio, Abstract of a Paper presented at the Atlantic City Meeting of the American Chemical Society, April, 1946. (c) Di-*t*-butylsilanediol. Abstract of a Paper presented at the Atlantic City Meeting of the American Chemical Society, September, 1949, L. J. Tyler, L. H. Sommer and F. C. Whitmore.

(3) G. R. Lucas and R. W. Martin, THIS JOURNAL, **74**, 5225 (1952).