

an increased adsorption of the yttrium as the pH value is increased: firstly, there are fewer hydrogen ions competing for sites on the carbon surface and, secondly, the aggregates may be the major adsorbing entity.

Adsorption values were read from Figs. 3, 4 and 5 at a pH value of 5.5 and a Freundlich isotherm plot which is given in Fig. 6 was obtained. From the equation determined from this plot, it was esti-

ated that the concentration of the tracer yttrium solution was about 10^{-10} or 10^{-11} M .

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Relative Stabilities of Chelate Compounds of Pyrrole Pigments¹

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The importance of dielectric constant in the determination of the relative stabilities of complexes with metals has been illustrated. From competition and exchange reactions, it was observed that increasing the electron-attracting power of methenes and porphyrins results in an increase in affinity for copper and a decrease in affinity for magnesium.

Porphyrins and closely related compounds are used in the physiological processes of plants and animals in the form of chelate compounds, usually with either magnesium or iron. While the bonding to magnesium is probably ionic² the bonding to either ferrous or ferric iron may be either ionic or covalent.³

Barnes and Dorough⁴ have compared the relative stabilities of various metalloporphyrins and found the general over-all stability to be small divalent > large divalent > alkali.

In our studies, the relative stabilities and rates of formation of the chelate compounds were considered from the following points of view: (1) influence of the medium on chelation, (2) influence of the nature of the metal to nitrogen bond (covalent or ionic) and (3) the effect of the electron-attracting power of the chelating group. Copper was chosen as an example of a metal which readily forms covalent bonds in porphyrin systems and magnesium as one which preferentially forms ionic bonds.⁵ The dipyrromethenes require two molecules for equivalence to one atom of metal, the porphyrin, one molecule to an atom. The experiments were of two kinds: (1) competition of one equivalent of each of two dipyrromethenes for one equivalent of metal and (2) exchange of metal between preformed metal-chelate and a free chelating agent. If the metal exchanges with difficulty, experiments of the first type give information about relative rates of reaction. If the metal exchanges with ease, experiments of this type give information about stabilities. To test for the ease of exchange, and hence for stabilities instead of rates, experiments of the second type were performed.

(1) Porphyrin Studies. XIII. Paper XII, W. S. Caughey and A. H. Corwin, *THIS JOURNAL*, **77**, 1509 (1955). This paper was presented at the Atlantic City Meeting of the American Chemical Society, September, 1952, and is from the doctoral dissertation of Marjorie H. Melville.

(2) J. W. Barnes and G. D. Dorough, *THIS JOURNAL*, **72**, 4047 (1950).

(3) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, p. 117.

(4) J. W. Barnes and G. D. Dorough, *THIS JOURNAL*, **72**, 4045 (1950).

(5) Ward V. Evans and R. Pearson, *ibid.*, **64**, 2867 (1942).

Discussion of Results

Effect of Medium on Relative Stability.—In their classical studies on the hydrolysis of alkyl halides, Gleave, Hughes and Ingold⁶ called attention to the fact that electron-donating alkyl groups could diminish the rate of the reaction if the transition state involved only the breaking and forming of covalent bonds, while in the case that the reaction involved ionization as the rate-determining step, electron-donating alkyl groups would speed the reaction. In only the latter case would an increase in the dielectric constant of the medium cause a marked increase in rate. Because of the numerous cases in which it can be shown that rates and equilibria are parallel,⁷ the results of the British investigators create a presumption that cases will be found in which a given type of substitution will also produce opposite effects upon stabilities, depending upon whether the bond affected is ionic or covalent. For the same reason, it also is to be presumed that cases should be found in which a change in dielectric constant should produce reversal of relative stabilities.

In the case of copper compounds, it has been pointed out earlier⁸ that the nature of the medium is of critical importance in determining the relative stabilities of bonds to oxygen and nitrogen. In a medium of low dielectric constant, oxides are more stable than nitrides, while in high dielectric constant the ammine is more stable than the hydrate.⁹ Recently, Irving¹⁰ reported that the order of stability can change with a change in solvent.

We now have found that when water and pyridine are allowed to compete for copper, the stability of the pyridine complex relative to the aquo complex in dioxane is increased by the addition of

(6) J. L. Gleave, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 238 (1935).

(7) L. P. Hammett, *THIS JOURNAL*, **59**, 96 (1937).

(8) A. H. Corwin in "A Symposium on Copper Metabolism," W. C. McElroy and B. Glass, Editors, The Johns Hopkins University Press, Baltimore, Md., 1950, pp. 10-11.

(9) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. I, Oxford University Press, Oxford, 1950, p. 156.

(10) H. Irving, Discussion of a paper by H. Freiser, *The Analyst*, **77**, 841 (1952).

excess water. This seeming contradiction of the mass action effect is ascribed to the change in dielectric constant. The readier ionization of the copper to oxygen bond in the medium of higher dielectric constant leads to relative stabilization of the less ionizable copper to nitrogen bond. It also has been found that the dielectric constant influences the rate of formation of a porphyrin chelate: copper mesoporphyrin was formed after 20 minutes at 50°, in a solution of pyridine containing 50% water, while no perceptible amount of complex was formed in pyridine solution alone under the same conditions.

Opposite Effects of Substituents on Relative Stabilities of Copper and Magnesium Complexes of Dipyrromethenes.—The demonstration given above of the reversal of stabilities on going from covalent to ionic bonds can be supplemented by a similar demonstration of reversal due to changes in substituents. In the usual ionic complexes with metals, the compound containing the more strongly basic nitrogens, having higher electron densities, should provide greater electrostatic attraction for the positively charged metal ion and therefore should form the stronger bonds to the metal. If the nitrogen to metal bonds are covalent, however, the compound containing the less basic nitrogens should form the more stable bonds due to the greater attraction of the nitrogens for the bonding electrons.

In the first study designed to test this principle, three dipyrromethenes were used as the chelating compounds: methene I, 3,5,3',5'-tetramethyl-4,4'-diethyldipyrromethane; methene II, 3,5,3',5'-tetramethyl-4,4'-dicarbethoxydipyrromethene; methene III, 3,5,4'-trimethyl-3',5',4'-tricarbethoxydipyrromethene. If copper remains covalently bonded to methene nitrogens, an increase in the electron-attracting power of the methene should increase the bond strength, resulting in the stability series III > II > I. Competition experiments were performed between all three pairs of the methenes, using just sufficient copper to bond with one of the two methenes present. In these experiments (Chart I) the expected order was observed, namely, III > II > I. In the competition between I and II, it was observed that the affinities are sufficiently close that only about 2/3 of the copper goes to II and 1/3 to I. In the case of II and III, all the copper goes to III. In the pair I and III, all the copper goes to III.

CHART I
METHENE COMPETITION REACTIONS FOR COPPER

Reactants	Concentrations after reaction in moles/liter				
	I	II	III	Cu-I	Cu-II
(a) I and II				0.24	0.6
				0.6	1.0
(b) I and III	0.7		0		
(c) II and III		1.5	0		
		1.4	0.05		

To make certain that we were not dealing simply with a rate phenomenon, exchange reactions were performed (Chart II). In each case, mixing the copper complex of lower number with methene bases of higher number gave exchange of the organic

molecules on the copper, while mixing the copper complexes of higher number with methene bases of lower number gave no exchange except in the case of methene I and methene II which exchanged partially when approached from either side.

CHART II
METHENE EXCHANGE INVOLVING COPPER COMPLEXES

Reactants	Concentrations after reaction in moles/liter				
	I	II	III	Cu-I	Cu-II
(a) Cu-II and I				0.23	0.6
(b) Cu-II and III		1.2	0		
		1.4	0		
(c) Cu-I and III	0.7		0.2		

The order of relative stabilities found in the equilibration studies is the same as that found in the simple competition studies and we have established, for this small series, that increasing the electron-attracting power of a methene causes an increase in affinity for copper.

Magnesium complexes of porphyrins have been prepared and are relatively stable. Magnesium complexes of dipyrromethenes are much less stable. We have prepared and isolated magnesium complexes of methenes II and III and have subjected them to competition and exchange reactions as in the case of copper.

In chelate compounds with ionic bonds, we would expect the order of stability to be reversed from that found with covalent bonds. That is, the stability of the magnesium chelates should be II > III. In the competition experiment, methene II was found to possess the magnesium and in the exchange reaction, II took magnesium away from III, but not III from II. The expected order is that which was found experimentally and we conclude that in this case the factor which makes the stronger copper chelate makes the weaker magnesium chelate.

Copper and Magnesium Complexes of Porphyrins and a Chlorin.—It is well known that multidentate chelates are increasingly stable as the number of coordination centers in the molecule increases. The present work furnishes a new example of this rule. Etioporphyrin II, 1,4,5,8-tetramethyl-2,3,6,7-tetraethylporphyrin, designated as compound IV, reacts with copper more readily than methene III in a competition reaction. The porphyrin also removes either copper or magnesium from the methene complex in an exchange reaction, whereas no exchange takes place from the porphyrin complex to the methene.

We should expect similar results from a reaction between methene III and etiochlorin II, compound V. We found that, at the boiling point of dioxane, the chlorin reacted more readily with copper in a competition. The chlorin also removed either copper or magnesium from the methene-copper complex in an exchange.

Two porphyrins were chosen for comparison in this study: etioporphyrin II, compound IV, and 1,3,5,7-tetracarbethoxy-2,4,6,8-tetramethylporphyrin, compound VI. We reasoned that if the results obtained in the methene series were applied to porphyrins, then we should expect the more

electron-attracting tetracarboxyporphyrin to form the more stable complex with copper.

When the competition reaction was performed, the expected order was found; that is, the more electron-attracting porphyrin, compound VI, reacted with all of the copper. Since no exchange of copper was found to take place in dioxane, the competition reaction was, in this case, measuring relative rates alone. Because the removal of copper from a porphyrin requires a strong acid, it is not surprising that no exchange took place in dioxane. Exchanges were attempted in glacial acetic acid without success. Formic acid, 98%, was tried and was found to be so strong that copper complexes were not even formed in it. Due to the fact that the groups involved in the change from compound IV to compound VI are on the periphery of the porphyrin ring and are far removed from the center of reaction, parallelism would be expected between rates and equilibria. However, it is not possible to conclude at present that stabilities parallel rates in this instance because, as indicated above, the attempted exchanges were not successful.

In a competition between porphyrin IV and VI for magnesium, compound IV bonded completely with the magnesium present. As in the methane series, the difference in the nature of the metal to nitrogen bond was observed to cause a reversal in the velocities of formation of the copper and magnesium complexes. We may infer that the same stability relationships observed in the dipyrromethenes probably hold for the porphyrins as well; that is, the more electron-attracting porphyrin forms the more stable covalent chelate and the less electron-attracting porphyrin forms the more stable ionic chelate. No exchange of magnesium was observed. The general stability of porphyrin chelates toward metallic exchange reactions has been pointed out earlier.^{4,11}

Considering the exchange of copper between compound IV, etioporphyrin II and compound V, etiochlorin II, there are more possible resonance structures for the porphyrin copper complex than for the chlorin complex. This should result in greater stability of the porphyrin complex. A competition reaction in dioxane solution between compound IV and compound V showed that half of the copper bonded with IV and half with V. No exchange reactions were found to take place. Other conditions were tried for the competition reaction to see if any differences in velocity would appear. Nitrobenzene, having a higher dielectric constant and higher boiling point than dioxane was tried as a solvent. The results again indicated that 50% of the copper bonded with each chelating group. A competition reaction performed in glacial acetic acid, in an atmosphere of hydrogen, to prevent oxidation of the chlorin to porphyrin, at room temperature, showed that the porphyrin reacted with all of the copper present. At the boiling point of glacial acetic acid, the same result was obtained.

Exchange reactions were tried, but no exchange was found to occur between either the copper complex of IV and compound V or between the copper

complex of V and compound IV. These exchange reactions were tried at the boiling point of glacial acetic acid.

In a competition reaction for magnesium, after heating just to boiling, the spectrum showed the formation of the magnesium complex of compound V, etiochlorin II. After continued boiling, the spectrum showed the formation of the magnesium complex of the porphyrin, compound IV. This indicates that the chlorin complex formed first and then an exchange took place from the chlorin complex to the porphyrin with the final formation of the more stable porphyrin-magnesium complex.

The formation of the less stable chlorin-magnesium complex first might be attributed to the difference between the chlorin nitrogens and the porphyrin nitrogens. Conant, Chow and Dietz¹² measured basicities of various porphyrins and chlorins. Their results showed that while the porphyrins contain two strongly basic groups, the chlorins have only one strongly basic group and one of intermediate basicity. It is possible that a stepwise chelation process could take place between the chlorin and magnesium involving less activation energy than a one-step process involving all four equivalent nitrogens in the porphyrin. A similar idea has been suggested previously by Ruben, Kamen, Allen and Nahinsky¹¹ for the dissociation of metal complexes. Differences between velocity and stability relationships have been observed by other investigators.^{13,14}

No exchange of magnesium was found to take place from the porphyrin-magnesium complex to the chlorin.

To summarize the results of the chlorin-porphyrin reactions, in competition for copper, the porphyrin reacted with copper preferentially. No exchange of copper took place in either direction between the porphyrin and the chlorin. In the case of magnesium, the chlorin reacted first with the magnesium and then the porphyrin removed the magnesium from the chlorin. No exchange reaction took place from the porphyrin complex to the chlorin.

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Experimental

Formation of Pyridine Complex of Cupric Acetate in Dioxane and Dioxane-Water Solutions.—One gram of cupric acetate was added to 50 ml. of purified dioxane at room temperature and allowed to stand overnight. The solution was filtered. To 2 ml. of the filtered solution was added 2 ml. of water. Two drops of pyridine formed the deep blue complex color. To another 2 ml. of the filtered solution was added 2 ml. of dioxane instead of water. Ten to twelve drops of pyridine were required to develop the same color intensity.

Chart I. Methene Competition Reactions for Copper (a).—In 3 ml. of freshly distilled purified dioxane was dissolved 5.21 mg. of methene I (2×10^{-5} mole) and 6.88 mg. of methene II (2×10^{-5} mole). Two mg. (1×10^{-5} mole) of cupric acetate monohydrate dissolved in several drops of dioxane was treated with pyridine dropwise to form the

(12) J. B. Conant, B. F. Chow and E. M. Dietz, *ibid.*, **56**, 2185 (1934).

(13) J. B. Conant and P. D. Bartlett, *ibid.*, **54**, 2881 (1932).

(14) K. W. Doak and A. H. Corwin, *ibid.*, **71**, 159 (1949).

(11) S. Ruben, M. D. Kamen, M. B. Allen and P. Nahinsky, *THIS JOURNAL*, **64**, 2298 (1942).

pyridine complex. The cupric-pyridine acetate was added to the solution of the methenes and heated to boiling. After cooling, one drop of the solution was placed on a paper strip for chromatographic separation. Whatman No. 1 filter paper was cut in strips 12" × 1". A capillary pipet delivering a drop equal to 0.02 ml. was used to place a drop of the reaction mixture to the paper strip. Using the usual cylinder and trough arrangement for paper strip chromatography, isoctane was used to develop the spot and a separation was achieved. The orange copper complex region was cut away from the yellow methene region and dissolved in 3 ml. of dioxane for spectral analysis.

Molar extinction coefficients are

	At 500 m μ	At 520 m μ
Cu-I	$= 0.48 \times 10^6$	$= 0.66 \times 10^6$
Cu-II	$= 1.0 \times 10^6$	$= 0.38 \times 10^6$

Analysis of the mixture was performed by the solution of simultaneous equations.¹⁵

		moles/liter × 10 ⁴
e_{500}	0.445	Copper-methene I 0.24
e_{520}	.245	Copper-methene II 0.60
e_{600}	.470	Copper-methene I 0.6
e_{620}	.265	Copper-methene II 1.0

(b) and (c).—The same general method was used for these competition reactions as that described in a. In b and c the methene band was analyzed spectrophotometrically rather than the copper complex band as in a. (b) 5.21 mg. of methene I (2×10^{-6} mole), 8.04 mg. of methene III (2×10^{-6} mole) and 2 mg. of cupric acetate monohydrate (1×10^{-6} mole) were used.

e_{420}	0.167	Methene I 0.7×10^{-3} mole/liter
e_{450}	0.223	Methene III 0

(c) 3.44 mg. of methene II (1×10^{-6} mole), 4.02 mg. of methene III (1×10^{-6} mole) and 1 mg. of cupric acetate monohydrate (0.5×10^{-6} mole) were used.

e_{430}	0.094	Methene II	1.5×10^{-3} mole/liter
e_{460}	.134	Methene III	0
e_{430}	.42	Methene II	1.4×10^{-3} mole/liter
e_{460}	.54	Methene III	0.05×10^{-3} mole/liter

Chart II. Methene Exchange Reactions Involving Copper Complexes.—The procedure used for the methene exchange reactions was the same as that used for the competition reactions with only a change in the addition of the cupric acetate. The pyridine complex of cupric acetate was added to one methene to form the desired complex before the addition of the second methene. The amounts of methenes I, II and III used for the exchanges were the same as those used in the competition reactions.

Preparation of the Magnesium Complex of Methene II.—Into a 50-ml. 3-necked flask equipped with a source of dry nitrogen, a dropping funnel for the Grignard reagent and an escape valve was added 10 ml. of dry benzene containing 3.44 mg. of methene II (1×10^{-6} mole). The solution was agitated with a magnetic stirrer. Two drops of methylmagnesium iodide solution in ether (1 M) were added from a dropping funnel with a capillary tip delivering one drop equal to 0.01 ml. An orange precipitate formed which was filtered with suction in an atmosphere of dry nitrogen. The spectrum of the orange solid was taken in dioxane solution, λ_{\max} 470 m μ . On the addition of water to a dioxane solution of the magnesium complex, the color changed from orange to yellow and the spectrum showed the formation of methene II.

Quantitative Hydrolysis of the Magnesium Complex of Methene II.—The magnesium complex was prepared in dry benzene as described in the preparation. After the formation of the orange precipitate, the flask was warmed to dissolve the complex in benzene. The contents of the flask were filtered by gravity in an atmosphere of dry nitrogen. A dry air-box was used for handling the magnesium complex. The benzene was pumped off and some of the remaining solid was placed in a boat and the boat put into a pig for drying

in a specially constructed vacuum drying apparatus.¹⁶ After weighing the sample of the complex, it was dissolved in 10 ml. of purified dioxane and one drop of distilled water was added to hydrolyze the complex. The spectrum was taken to determine the concentration of methene formed. On hydrolysis, one mole of methene-magnesium complex should yield two moles of methene free base.

Wt. of magnesium complex, mg.	0.853; 0.875
Mole of magnesium complex	1.2×10^{-6} ; 1.23×10^{-6}
Mole of methene after hydrolysis	2.2×10^{-6} ; 2.3×10^{-6}

Preparation of the Magnesium Complex of Methene III.—Using 4.02 mg. of methene III (1×10^{-6} mole) and the procedure described for the formation of the complex of methene II, a red gelatinous precipitate was obtained which absorbed at 500 m μ . On the addition of water, the methene was regenerated. Quantitative hydrolysis of the magnesium complex gave

Weight of magnesium complex, mg.	0.848; 0.873
Moles of magnesium complex	1.03×10^{-6} ; 1.06×10^{-6}
Moles of methene after hydrolysis	1.9×10^{-6} ; 1.85×10^{-6}

Competition Reaction Between Methene II and Methene III for Magnesium.—The method used for the competition reaction is the same as the method described for the preparation of the individual magnesium complexes. A mixture of 8.02 mg. of methene III (2×10^{-6} mole) and 6.88 mg. of methene II (2×10^{-6} mole) was dissolved in 10 ml. of dry benzene. On the addition of two drops of one molar Grignard solution, an orange precipitate formed which indicated the magnesium complex of methene II, since the magnesium complex of methene III is red. The precipitate was filtered in an atmosphere of dry nitrogen. The spectrum in dry dioxane showed an absorption maximum at 470 m μ , which is the maximum for the magnesium complex of methene II.

Methene Exchange Reactions with Magnesium.—Due to the general instability of the methene-magnesium complexes, conditions were sought under which the magnesium complexes could be formed and exchanges tried without precipitation and filtration of the complexes. 4-Methyl-1,3-dioxane was prepared according to the directions of Carlin and Smith¹⁷ and proved to be a satisfactory solvent for magnesium complexes of methene II and methene III. A solution of 3.44 mg. of methene II (1×10^{-6} mole) in 10 ml. of 4-methyl-1,3-dioxane was placed in the reaction flask described in the preparation of the individual complexes. One drop of 1 M methylmagnesium iodide solution was added while dry nitrogen was passed through the flask. The solution became orange on the addition of the Grignard solution. To the solution was added with stirring, 4.02 mg. of methene III (1×10^{-6} mole). After methene III dissolved, the solution was heated to boiling on a hot-plate and, after cooling, the spectrum was taken. An absorption maximum at 470 m μ and no maximum at 500 m μ indicated that no exchange of magnesium took place from methene II to methene III. The same procedure was used for the second exchange reaction with the change that methene III-magnesium complex was formed first and then methene II was added. After heating to boiling and cooling, the spectrum showed that methene II-magnesium complex had formed, indicating an exchange from methene III to methene II.

Competition Reaction between Compound IV and Methene III for Copper.—The course of the competition reaction between etioporphyrin II (compound IV) and methene III was followed using a hand spectroscope. A mixture of 4.02 mg. of methene III (1×10^{-6} mole) and 2.39 mg. of compound IV (0.5×10^{-6} mole) was dissolved in about 5 ml. of dioxane. One mg. of cupric acetate monohydrate (0.5×10^{-6} mole) was dissolved in pyridine and added to the solution of the porphyrin and the methene. The reaction mixture was heated to boiling. The hand spectroscope showed

(16) The authors wish to express their appreciation to Mr. Joseph Walter for the construction of the vacuum drying apparatus used in these determinations.

(17) R. B. Carlin and L. O. Smith, Jr., *THIS JOURNAL*, **69**, 2007 (1947).

(15) See R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 29.

etioporphyrin II-copper complex bands and no unreacted etioporphyrin II.

Exchange Reactions between Compound IV and Methene III.—(a) Using the same general procedure described in the competition reaction for copper, the copper complex of compound IV was formed first and then the methene was added to the solution. The reaction mixture was boiled for 5 minutes and, after cooling, the hand spectroscopy showed no formation of etioporphyrin II, compound IV. (b) Using the same procedure, the copper complex of methene III was formed and compound IV was then added to the solution. After boiling, the hand spectroscopy showed formation of the copper complex of compound IV.

Competition and Exchange Reactions between Compound V and Methene II for Copper.—The same general method was used for the competition and exchange reactions between compound V and methene III for copper as that described for compound IV and methene III.

Exchange Reaction between Compound IV and Methene II and Magnesium.—The procedure used for this exchange reaction is the same as that described for the exchange reactions of methene II and methene III and magnesium, using 4-methyl-1,3-dioxane as the solvent, 1.72 mg. of methene II, 1.2 mg. of compound IV and 1 drop of 1 *M* Grignard reagent.

Competition between Compound IV and Compound VI for Copper.—In 4 ml. of pyridine was dissolved 2.39 mg. of compound IV (0.5×10^{-6} mole), and 3.27 mg. of compound VI (0.5×10^{-6} mole) was dissolved in 5 ml. of pyridine. The two porphyrin solutions were mixed. One mg. of cupric acetate monohydrate (0.5×10^{-6} mole) was added to the porphyrin solution and the mixture heated to boiling and boiled 5 minutes. For spectra, the solution was diluted 1:10 and then 5:10 with pyridine:

- | | | | | |
|-----|------------------|-------|------------------|----------------------------|
| (1) | ϵ_{620} | 0.163 | Etioporphyrin II | 0.48×10^{-6} mole |
| (2) | ϵ_{620} | 0.127 | Etioporphyrin II | 0.46×10^{-6} mole |

Exchange Reactions with Copper between Compound IV and Compound VI.—The procedure used in the competition reaction was tried for an exchange reaction.

Competition and Exchange Reactions with Magnesium, Compound IV and Compound VI.—The procedure described for the methene-magnesium reactions was used for the reactions between these two porphyrins and magnesium.

Competition and Exchange Reactions between Compound V and Compound IV for Copper.—(a) 2.39 mg. of compound IV (0.5×10^{-6} mole) and 2.40 mg. of compound V (0.5×10^{-6} mole) were dissolved in 19 ml. of glacial acetic acid. One mg. of cupric acetate monohydrate (0.5×10^{-6} mole) dissolved in 1 ml. of glacial acetic acid was added to the solution at room temperature with stirring and in a hydrogen atmosphere. After 10 minutes the spectrum was taken and absorption bands appeared at 520, 560 and 620 $m\mu$. (b) Exchange reactions were performed using the same general procedure described for the competition reaction in a.

Competition and Exchange of Magnesium between Compound V and Compound IV.—The procedure used in the methene-magnesium competition and exchange reactions also were used for the chlorin-porphyrin reactions with magnesium.

Formation of Copper Mesoporphyrin in Pyridine and Pyridine-Water Mixture.—(a) To 1 ml. of a pyridine solution of mesoporphyrin 5×10^{-4} *M* was added 1 ml. of pyridine and 5 drops of a pyridine solution of cupric acetate monohydrate 0.012 *M*. (b) To 1 ml. of the same mesoporphyrin solution was added 1 ml. of distilled water and 5 drops of cupric acetate monohydrate in pyridine (0.012 *M*). Solutions a and b were placed in a water-bath at 50° for 20 minutes. The spectrum of the two solutions after that time was taken with a hand spectroscopy. Solution a showed no copper-mesoporphyrin spectrum, while b showed the formation of the copper complex of mesoporphyrin.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF TORONTO]

Dipole Moments of Phenylmercurials

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The dielectric constant of solid diphenylmercury has been found to be 2.87, showing that the atomic polarization is normal. Thus the observed polarization apparently is due to orientation, so that diphenylmercury is not linear. Also non-linearity in the C-Hg-X bond is confirmed by dipole moment studies of several substituted phenylmercuric halides. The included angle of these mercurial linkages seems to be 130–150°.

There is doubt about the valence angle which mercury assumes when it is bonded to carbon or to carbon and halogen. Smyth¹ and Oesper² assumed an angle of 180° in calculation of the electric moment of benzylmercuric chloride. This assumption is validated by evidence from Raman spectra,^{3–5} electron diffraction⁶ and X-ray diffraction⁷ that mercuric chloride is linear, at least in the vapor state. Indeed the valence electrons of mercury (II), occupying 6s² orbitals might be expected in compound formation to assume sp orbitals which, from symmetry considerations, are diametrically opposed.

However other studies have indicated that the C-Hg-X bond in organomercurials is angular.

- (1) C. P. Smyth, *J. Org. Chem.*, **6**, 421 (1941).
- (2) P. F. Oesper and C. P. Smyth, *THIS JOURNAL*, **64**, 173 (1942).
- (3) K. W. F. Kohrausch, "Der Smekal-Raman Effekt," Verlag von Julius Springer, Berlin, 1931, pp. 182–184.
- (4) P. Krishnamurti, *Ind. J. Phys.*, **5**, 113 (1930).
- (5) H. Braune and G. Engelbrecht, *Z. physik. Chem.*, **10B**, 1 (1930); **11B**, 409 (1931).
- (6) H. Braune and S. Knoke, *ibid.*, **23B**, 163 (1933).
- (7) H. Braune and R. Linke, *ibid.*, **31B**, 12 (1935).

Curran⁸ assigned a non-linear bonding in the arylmercuric bromides to explain the moments of 3.06, 3.39 and 1.57 *D* obtained, respectively, from phenyl-, *p*-tolyl- and *p*-chlorophenylmercuric bromides. This angularity cannot be ascribed to coordination with the solvent, dioxane, because the moments determined in benzene solution are about the same.⁹ Curran assumed the C-Hg moment to be about zero, the over-all H-C₆H₄-Hg moment to be 0.3, the *p*-CH₃-C₆H₄ moment to be 0.4 and the -HgBr moment to be 2.75. Then if the difference between the C-Cl and C-H dipoles is 1.6 Curran's calculation shows that the C-Hg-Br angle varies with the aryl group; it is 140° for the *p*-tolylmercurial and 167° for the *p*-chlorophenylmercurial. However these results should be regarded only qualitatively since a difference of 0.1 *D* in these highly degenerate *para*-substituted benzenes would vitiate the calculated differences.

Earlier Hampson¹⁰ had presented evidence for

- (8) B. C. Curran, *THIS JOURNAL*, **64**, 830 (1942).
- (9) B. C. Curran, *ibid.*, **57**, 2162 (1935).
- (10) G. C. Hampson, *Trans. Faraday Soc.*, **30**, 877 (1934).