Thermal Decomposition of Diphenyldiazomethane in Bromotrichloromethane.—To a solution of bromotrichloromethane (15 ml.) which had been refluxing under nitrogen for 30 min. was added slowly a solution of diphenyldiazomethane (12.6 g., 66 mmoles) in bromotrichloromethane (15 ml.). The decomposition of the diazo compound in the refluxing solution proceeded smoothly but at a slow rate. After the addition was completed, the flask contents were cooled and a portion (28.6 g.) of the crude reaction mixture was chromatographed on alumina (Woelm, neutral, number 1). Elution with 10% carbon tetrachloride–90% pentane gave 1,1-dichloro-2,2-diphenylethylene (I) (0.76 g.), identified by comparison of melting point and infrared spectrum with those of authentic material. Elution with 25% carbon tetrachloride–75% pentane gave a white solid (0.77 g.) which was identified as tetraphenylethylene (III) by comparison of its melting point, infrared spectrum, and GPC retention time with those of an authentic sample. Continued elution with 25% carbon tetrachloride–75% pentane gave a white solid (green fluorescence) which was separated by GPC to yield 1-*p*-chlorophenyl-1,2,2-triphenylethylene (IV) (0.186 g.) and 1-*p*-bromophenyl-1,2,2-triphenylethylene (V) (1.0 g.). IV and V were identified by comparison of their respective infrared spectrum and GPC retention time with those of authentic IV and V. Elution of the column with methylene chloride gave yellow crystals of benzophenone azine (II) (m.p. 164–166°).

Total yields of products: I, 4.7%; II, 24.2%; III, 7.38%; IV, 1.61%; and V, 7.67%.

1-*p*-Bromophenyl-1,2,2-triphenylethylene.—A solution of *p*-bromobenzophenone (13.05 g., 50 mmoles) and oxalyl chloride (31.8 g., 0.25 mole) in benzene (50 ml.) was refluxed for 68 hr. After the excess oxalyl chloride and benzene were removed by distillation at atmospheric pressure (under nitrogen stream), the remaining tan solid was covered with diphenylmethane (16.8 g., 0.10 mole) and the mixture was refluxed for 12 hr. A portion (4.0 g.) of the crude product was chromatographed on alumina (Woelm, neutral, number 1). Elution with pentane removed excess diphenylmethane. Continued elution with pentane and with pentane–carbon tetrachloride (70:30) mixture gave an oil (green fluorescence) which crystallized slowly. This solid was found to contain several components when it was analyzed by GPC. The component with the same retention time as the suspected 1-*p*-bromophenyl-1,2,2-triphenylethylene (V) was collected and its infrared spectrum was found to be identical with that of the suspected V.

Preparation of Chelates of Porphyrins and Phthalocyanine with "Magnesium Viologen"[1]

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Very few magnesium chelates of porphyrins or chlorins have been chemically characterized in spite of the fact that the spectra of numerous such derivatives have been recorded. Willstaetter and Forsén[2] first prepared these substances using magnesium oxide and alcoholate at 150°. For substances which would not withstand these conditions they utilized the Grignard reagent in ether at room temperature. This required precise control of concentrations to avoid over-reaction with carbonyl groups.

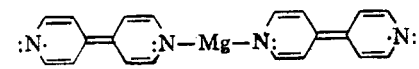
We have discovered three new reagents for the introduction of magnesium into porphyrins and chlorins. The first and most powerful of these, which we formulate as magnesium viologen, is prepared by refluxing magnesium and iodine in dry pyridine. This introduces magnesium easily into all porphyrins and chlorins tried and into phthalocyanine as well.

The second reagent is magnesium hexapyridine diiodide, prepared by a simplification of the procedure used by Spacu.[3] This is useful for all the porphyrins and chlorins tried but introduces magnesium into phthalocyanine only 1/300 as rapidly as the viologen.

The third reagent is the magnesium complex of 4,4′-dipyridyl, which was found to be present along with the viologen in the first reagent. The dipyridyl complex is the least potent for the introduction of magnesium, reacting with phthalocyanine only one third to one quarter as rapidly as the pyridine complex.

The viologens were prepared and studied by Michaelis.[4] They are monovalent radical ions prepared by the reduction of N,N′-dialkyl-4,4′-dipyridyl quaternary salts. Unsubstituted viologen can be prepared in an acid solution of 4,4′-dipyridyl by the addition of a single electron. All of these substances are highly sensitive to atmospheric oxygen.

Magnesium viologen resembles the compounds prepared by Michaelis in its sensitivity to oxygen but, because of the ease of hydrolysis of the magnesium compound, is also destroyed by water. Many canonical structures may be formulated for this hybrid, of which one is represented by formula I.



In this formulation, magnesium is represented as covalently bound to nitrogen. This is consistent with the behavior of magnesium in the porphyrin[5] and phthalocyanine[6] complexes. In the latter, the tendency to solvation by water is so great that Evstigneev and Krasnovskii[7] reported that crystal water could not be removed by sublimation of the

(1) Porphyrin Studies XXII. Paper XXI, A. H. Corwin and O. D. Collins, III, *J. Org. Chem.*, **27**, 3060 (1962). A portion of this work was from the doctoral dissertation of P. E. Wei, The Johns Hopkins University, 1958. The authors wish to acknowledge support by a grant from the National Institutes of Health, RG-6691.

(2) R. Willstaetter and L. Forsén, *Ann.*, **396**, 180 (1913).

(3) G. Spacu, *Soc. de Stiinte din Cluj*, **1**, 72 (1921).

(4) L. Michaelis, *Biochem. Z.*, **250**, 564 (1932); L. Michaelis and E. S. Hill, *J. Gen. Physiol.*, **16**, 859 (1933).

(5) See P. E. Wei, dissertation, The Johns Hopkins University, 1958.

(6) G. T. Byrne, R. P. Linstead, and A. R. Lowe, *J. Chem. Soc.*, 1017 (1934).

(7) V. B. Evstigneev and A. A. Krasnovskii, *Dokl. Akad. Nauk SSSR*, **58**, 417 (1947).

dye, although Putseiko and Terenin[8] disagreed to the extent of reporting that it could only be removed by sublimation. The high tendency of magnesium to solvate was noticed by Willstaetter and Forsén[2] and makes the preparation of unsolvated complexes comparable in difficulty to the preparation of unsolvated iron complexes. In our work it has been found convenient in the more difficult preparations to characterize the dipyridine complexes. By analogy to the hemochromes, these may be represented at $3sp^3d^2$ octahedral complexes.

Smith[9] found that the action of alkali metals on pyridine resulted in the formation of blue compounds similar to our magnesium viologen. This reaction proceeds without the evolution of molecular hydrogen. We attribute this to the concurrent formation of hydropyridine derivatives. On treatment with water, these blue solutions yield dipyridyls. We have found that magnesium reacts similarly, forming 4,4′-dipyridyl without the evolution of measurable amounts of hydrogen. The purpose of the iodine in the preparation is to create a reactive surface on the magnesium, since the reaction will proceed slowly in the absence of iodine.

Potassium viologen, called by him 4,4′-dipyridyl negative ion, has recently been shown by Ward[10] to possess an unpaired electron.

The blue color of the magnesium viologen can be discharged by bubbling in dry molecular oxygen. If no excess magnesium is present, the blue color does not regenerate and the power to introduce magnesium is reduced by a factor of 20.

Using these reagents, it has been found possible to prepare many new magnesium porphyrin and chlorin chelates of which two are characterized in this communication: magnesium mesoporphyrin dimethyl ester dipyridine complex and magnesium octamethylporphyrin dipyridine complex. In addition the preparation of magnesium phthalocyanine monopyridine monoaquo complex is described.

Experimental

"Magnesium Viologen."—Five hundred milligrams of magnesium turnings (20.6 mmoles) and 500 mg. of iodine (2.0 mmoles) were added to 20 cc. of very dry pyridine and refluxed under nitrogen. The iodine color disappeared in 2 min. and a green color appeared. This turned to blue as the reagent formed. This amount of reagent was sufficient for about 500 mg. of a porphyrin.

In a study of the reaction, it was performed in a 25 ml. three-necked flask fitted to a reflux condenser which led through a drying tube to a 1-l. graduated cylinder filled with water and inverted in a trough. One of the necks was fitted with a dropping funnel for the subsequent addition of water. After adding the reagents and refluxing for 10 min., the color had turned deep blue but no appreciable evolution of gas was observed. To equilibrate the volume, the reaction flask was cooled. Ten milliliters of water was added and the blue color was discharged but no gas was evolved.

When 500 mg. of magnesium was refluxed with less than 5 mg. of iodide in 10 ml. of pyridine, the blue color also formed. When equimolar amounts of iodine and magnesium were refluxed in pyridine, the iodine color did not disappear and no blue color formed after 1 hr. Instead, white magnesium iodide appeared in the flask.

In another preparation, magnesium turnings were refluxed under dry pyridine in the absence of iodine with frequent scratching of the metal. After 2 hr. the blue color of the viologen began to appear. While this method of preparation demonstrates that iodine is not a necessary reagent for the formation of the viologen, it is not a convenient one for obtaining the material.

A sample of the blue compound dissolved in pyridine was filtered under nitrogen to remove excess magnesium. Dry oxygen gas was bubbled through. The blue color was discharged, leaving a brown solution. On refluxing with phthalocyanine the soluble magnesium complex was slowly formed. The reaction was approximately one-twentieth as fast as that with the blue compound but about fifteen times as fast as that with magnesium hexapyridine diiodide.

Isolation of 4,4′-Dipyridyl.[9]—The liquid fractions from several runs of the viologen were combined and evaporated to dryness. The residue was dissolved in ether, and a small amount of water was added to precipitate the resins which formed. The ether was decanted, dried over potassium hydroxide, and the product crystallized twice; m.p. 113–114°; Mixed m.p. with authentic sample of 4,4′-dipyridyl, 114°.

Anal. Calcd. for $C_{10}H_8N_2$: C, 76.90; H, 5.16. Found: C, 76.86; H, 5.06.

Magnesium Hexapyridine Diiodide.[8]—Three hundred milligrams of magnesium powder and 1 g. of iodine were dissolved in 20 ml. of dry ether in a three-necked flask provided with a condenser and nitrogen inlet. The mixture was refluxed under nitrogen for about 1 hr. until the color disappeared. The solution, still under nitrogen, was filtered through sintered glass and the solvent removed under vacuum. A 20-ml. sample of dry pyridine was added. This formed a voluminous precipitate that went into solution when heated.

To prepare porphyrin chelates with this reagent, the porphyrin was added at this point and refluxed for 15 to 30 min. until the free porphyrin absorption lines disappeared. With highly insoluble compounds like phthalocyanine the reaction was much slower.

The magnesium viologen reagent introduced magnesium into phthalocyanine about 300 times as fast as the magnesium hexapyridine diiodide, as could be ascertained from following the absorption peaks with a Beckman DK-2 spectrophotometer. The magnesium hexapyridine reagent has, however, proved to be a more practical one for the introduction of magnesium when analytical samples are desired, since the resulting chelates are easier to purify than those prepared with the viologen.

Magnesium Complex of 4,4′-Dipyridyl.—In the process of studying the magnesium-viologen reaction, it was found that one of the main products formed was 4,4′-dipyridyl. By adding an excess of magnesium iodide to 4,4′-dipyridyl dissolved in a 50–50 mixture of benzene and ether, the magnesium complex precipitated. This was removed by filtration and washed with the solvent. It was then dissolved in pyridine, the desired porphyrin added and refluxed until the free porphyrin absorption lines were absent from the spectrum. Although the magnesium was introduced, the reaction went about one-third to one-quarter as fast as with the magnesium hexapyridine diiodide.

Magnesium Mesoporphyrin IX Dimethyl Ester Dipyridine Complex.—The preparation was made with magnesium hexapyridine diiodide, as described above. A 70-mg. sample of mesoporphyrin IX dimethyl ester was added to the solution and refluxed for 20 min. when the free porphyrin lines had disappeared from the spectrum. The reaction mixture was cooled, filtered, and poured into 200 ml. of water. The

(8) E. K. Putseiko and A. N. Terenin, *Zh. Fiz. Khim.*, **30**, 1019 (1956).

(9) C. R. Smith, *J. Am. Chem. Soc.*, **46**, 414 (1924).

(10) R. L. Ward, *ibid.*, **83**, 3623 (1961).

precipitate was removed by filtration and dried in a vacuum. The solid was chromatographed over 80% Magnesol–20% cellulose, using 10:20:3 ethylene dichloride–hexane–methanol. The eluate was filtered on Whatman No. 50 paper and evaporated to dryness. It was then crystallized from hot pyridine, isoöctane and dried in a vacuum at room temperature for 12 hr.

Spectrum in pyridine—λ_{max} (mμ) α: I, 585; II, 557; III, 425; IV, 413. ϵ: I, 8.76×10^3; II, 1.91×10^4; III, 3.02×10^5; IV, 3.00×10^5.

Anal. Calcd. for $C_{36}H_{40}O_4N_4Mg \cdot 2(C_5H_5N)$: C, 71.27; H, 6.50. Found: C, 71.34; H, 6.55.

Acid treatment regenerated a compound having the spectrum of Mesoporphyrin IX.

Magnesium Octamethyl Porphyrin Dipyridine Complex.—For the preparation of this chelate the magnesium viologen reagent was used. After adding the octamethyl porphyrin, the solution was refluxed for 1 hr., then cooled, filtered, and poured into 200 ml. of water. The precipitate was allowed to settle for 1 hr. and then filtered off and dried in a vacuum. The magnesium complex was chromatographed over 80% Magnesol–20% cellulose using a 2:1 mixture of chloroform–pyridine. The eluate was evaporated to dryness in a vacuum and washed first with boiling hexane, then with a 1:2 mixture of acetone and water. Finally, it was crystallized from boiling pyridine and dried in a vacuum.

Spectrum in pyridine—λ_{max} (mμ): I, 584; II, 557; III, 425; IV, 412. ϵ: I, 6.44×10^3; II, 1.63×10^4; III, 2.85×10^5; IV, 1.93×10^5.

Anal. Calcd. for $C_{28}H_{28}N_4Mg \cdot 2(C_5H_5N)$: C, 75.68; H, 6.35. Found: C, 75.75; H, 6.09.

Magnesium Phthalocyanine Monopyridine Monoaquo Complex.—The preparation was performed with the magnesium viologen reagent. After adding the insoluble phthalocyanine, the suspension was refluxed for 0.5 hr., filtered, precipitated with water, filtered, and dried. The magnesium chelate was then dissolved in pyridine and precipitated by adding an excess of benzene. This precipitate was chromatographed over alumina using pyridine as the solvent. The pyridine was removed under vacuum and the product washed first with hot hexane and then with a mixture of 1:2 acetone–water. It was then crystallized from hot pyridine.

Spectrum in pyridine—λ_{max}(mμ): I, 680; II, 651; III, 614; IV, 588 (minor peak); V, 519 (minor peak). ϵ: I, 2.71×10^5; II, 3.71×10^4; III, 4.32×10^4.

Anal. Calcd. for $C_{32}H_{16}N_8Mg \cdot C_5H_5N \cdot H_2O$: C, 70.11; H, 3.66. Found: C, 69.93, 70.38; H, 3.70, 3.69.

Syntheses and Reactions of Methyl Triphenylpyrrolecarboxylates[1]

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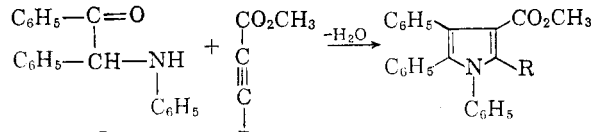
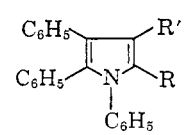
As part of a study of the reactions of sodium β-formyl-β-keto-α-nitropropionate,[4,5] it became necessary to synthesize several heretofore unknown, vicinally substituted triphenylpyrroles as intermediates for further investigations. On examination of Fisher-Hirschfelder molecular models of these compounds, it was apparent that none of the phenyl groups could lie coplanar with the pyrrole nucleus without interfering with a neighboring phenyl substituent. Therefore, it was of interest to investigate the possible existence of this type of molecular arrangement of substituted pyrroles.

A convenient synthesis of substituted pyrroles is the recently reported[6] Michael condensation of the hydrochloride of an α-(primary)amino ketone and dimethyl acetylenedicarboxylate (IIa) in the presence of sodium acetate. As a test of the applicability of the reaction to the synthesis of N-substituted pyrroles, the hydrochloride of desylaniline (I) was condensed with IIa in the presence of sodium acetate to give a 39% yield of dimethyl 1,4,5-triphenylpyrrole-2,3-dicarboxylate (IIIa). However, by a slight modification of the described procedure, IIIa was obtained in 79% yield from the condensation of desylaniline and IIa alone. Similarly, by the condensation of I and methyl propiolate (IIb), methyl 1,4,5-triphenylpyrrole-3-carboxylate (IIIb) was obtained in 70% yield. The mechanism proposed[6] is consistent with our observations that in the condensation of I and IIb the product formed is the 3-carbomethoxypyrrole IIIb, and not the isomeric 2-carbomethoxypyrrole.



I IIa. R = CO_2CH_3 b. R = H IIIa. R = CO_2CH_3 b. R = H

In no instance, however, were the corresponding intermediate hydroxypyrrolines[6] isolated in the formation of IIIa and IIIb. Hydrolysis of IIIa and IIIb in alcoholic potassium hydroxide followed by acidification gave the corresponding acids, 1,4,5-triphenylpyrrole-2,3-dicarboxylic acid (VI) and 1,4,5-triphenylpyrrole-3-carboxylic acid (VII), respectively. Decarboxylation of VII proceeds smoothly in quinoline with copper chromite catalyst to give 1,2,3-triphenylpyrrole (VIII).



VI. R, R′ = CO_2H
VII. R = H; R′ = CO_2H
VIII. R, R = H

The orientation of the condensation reaction of I and IIb to give IIIb was established as shown by

(1) Supported in part by Research Grant No. CY-2240 of the National Institutes of Health, U.S. Public Health Service.

(2) United States Steel Foundation Fellow 1960–1962.

(3) To whom inquiries should be addressed.

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(5) P. E. Fanta, R. M. W. Rickett, and D. S. James, *J. Org. Chem.*, **26**, 938 (1961).

(6) J. B. Hendrickson and R. Rees, *J. Am. Chem. Soc.*, **83**, 1250 (1961).