The Reaction of Diphenylmethylene with the Carbon-Halogen Bond

ROBERT W. MURRAY AND ANTHONY M. TROZZOLO

Bell Telephone Laboratories, Incorporated,
Murray Hill, New Jersey

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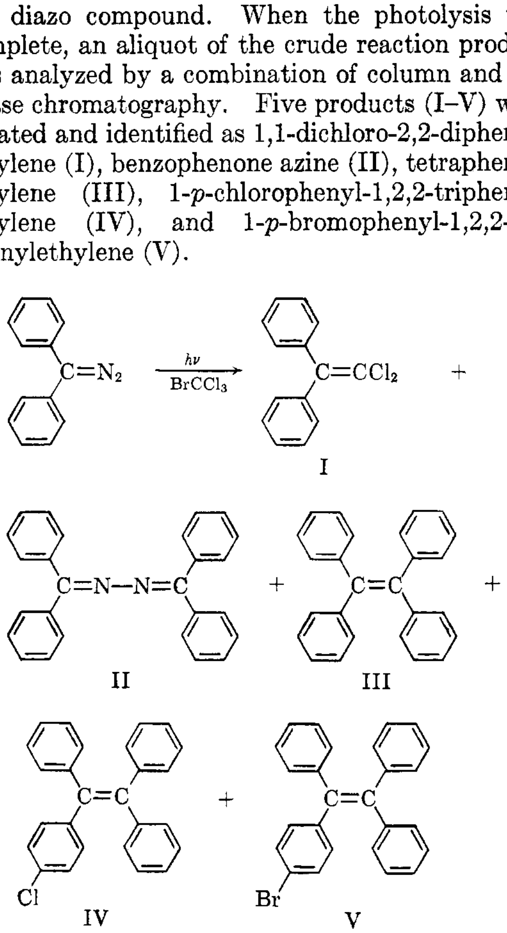
The reactions of carbenes with halogen-containing compounds have been observed by a number of workers.[1] Some of these reactions appear to be radical chain processes,[1a,b] while others appear to involve an electrophilic carbene[1g] possibly reacting through an ylid intermediate.[1e,f] Although several carbene species have been included in these studies, the reaction of diphenylmethylene with the carbon-halogen bond has not been described previously.

Diphenylmethylene has been described as a triplet species because it adds to olefins in a nonstereospecific manner.[2] Diphenylmethylene reacts with oxygen to give benzophenone,[3] unlike singlet, electrophilic carbenes which do not react with oxygen. In addition, diphenylmethylene is apparently able to abstract hydrogen atoms from a variety of substrates.[3,4] A preliminary study[1b] of the reaction of diphenyldiazomethane with bromotrichloromethane indicated that no attack of diphenylmethylene on the carbon-halogen bond had occurred, the only isolable product reported being benzophenone azine.

In view of the many reported reactions of carbenes with halogen compounds, it was felt that the reaction of diphenylmethylene with bromotrichloromethane required further investigation. Because of the reported hydrogen abstraction reactions of diphenylmethylene,[3,4] it was anticipated that this species should undergo a halogen abstraction reaction. In this study, the reaction conditions were chosen so as to minimize the formation of azine. Although even under these conditions benzophenone azine is a major product (the major product in the thermal reaction), other products are formed which indicate that diphenylmethylene can react with bromotrichloromethane. A *dilute solution* of diphenyldiazomethane in bromotrichloromethane was irradiated with two General Electric 150-watt flood lamps. The reaction flask was cooled with a stream of cold water during the lengthy photolysis period. Additional diphenyldiazomethane was added in bromotrichloromethane solution to maintain a very dilute solution of the red diazo compound. When the photolysis was complete, an aliquot of the crude reaction product was analyzed by a combination of column and gas phase chromatography. Five products (I–V) were isolated and identified as 1,1-dichloro-2,2-diphenylethylene (I), benzophenone azine (II), tetraphenylethylene (III), 1-*p*-chlorophenyl-1,2,2-triphenylethylene (IV), and 1-*p*-bromophenyl-1,2,2-triphenylethylene (V).



The first two of these products 1,1-dichloro-2,2-diphenylethylene (I) (4.3%) and benzophenone azine (II) (9.6%) were identified by comparing their infrared spectra and melting points with those of the authentic materials. The remaining products, tetraphenylethylene (III) (12.4%), 1-*p*-chlorophenyl-1,2,2-triphenylethylene (IV) (0.29%), and 1-*p*-bromophenyl-1,2,2-triphenylethylene (V) (5.43%), could only be separated by repeated gas phase chromatography (GPC). They were identified by comparing infrared spectra and GPC retention times with those of the authentic materials. Authentic IV was prepared by the thermal decomposition of 1,2-dichloro-1,1,2,2-tetraphenylethane (VI) as described by Norris, *et al.*[5] Authentic V was prepared by the reaction of *p*-bromophenyldichlorophenylmethane and diphenylmethane with GPC being used to separate V from the other products produced in this reaction. No hexachloro-

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(1) (a) W. H. Urry and J. R. Eiszner, *J. Am. Chem. Soc.*, **73**, 2977 (1951). (b) W. H. Urry and J. R. Eiszner, *ibid.*, **74**, 5822 (1952). (c) W. H. Urry, J. R. Eiszner, and J. W. Wilt, *ibid.*, **79**, 918 (1957). (d) W. H. Urry and J. W. Wilt, *ibid.*, **76**, 2594 (1954). (e) C. D. Gutsche and M. Hillman, *ibid.*, **76**, 2236 (1954). (f) D. D. Phillips, *ibid.*, **76**, 5385 (1954). (g) V. Franzen, *Ann.*, **627**, 22 (1959). (h) J. N. Bradley and A. Ledwith, *J. Chem. Soc.*, 1495 (1961). (i) F. Weygand and K. Koch, *Angew. Chem.*, **73**, 531 (1961). (j) W. von E. Doering, paper presented before the Division of Organic Chemistry, American Chemical Society Meeting, St. Louis, Mo., March, 1961. (k) I. A. D'Yakanow and N. B. Vinogradova, *J. Gen. Chem. USSR*, **21**, 851 (1951); **22**, 1349 (1952); **23**, 66 (1953).

(2) R. M. Etter, H. S. Skovronek, and P. S Skell, *J. Am. Chem. Soc.*, **81**, 1008 (1959).

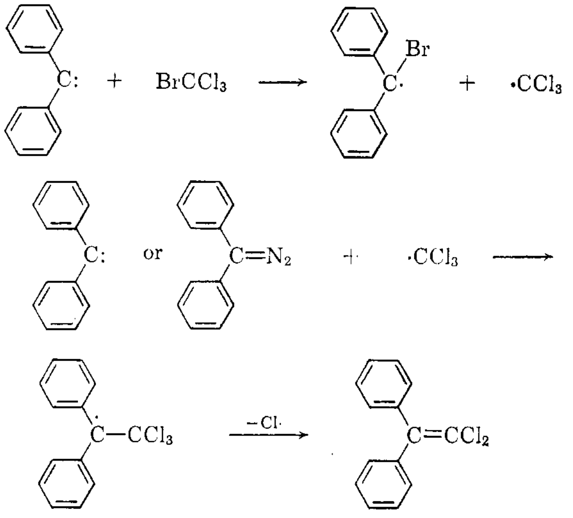
(3) W. Kirmse, L. Horner, and H. Hoffmann, *Ann.*, **614**, 19 (1958).

(4) (a) W. E. Parham and W. R. Hasek, *J. Am. Chem. Soc.*, **76**, 935 (1954). (b) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4675 (1952).

(5) J. F. Norris, R. Thomas, and B. M. Brown, *Ber.*, **43**, 2940 (1910).

ethane and no VI could be detected in the crude product of the diphenyldiazomethane–bromotrichloromethane reaction. Similar results were obtained when diphenyldiazomethane was thermally decomposed in refluxing bromotrichloromethane.

A halogen abstraction reaction of triplet[2–4] diphenylmethylene with bromotrichloromethane could proceed in either of two ways: (1) to give the chlorodiphenylmethyl radical and the bromodichloromethyl radical or (2) to give the bromodiphenylmethyl radical and the trichloromethyl radical. The first path is considered unlikely in view of previous work which indicates that abstraction reactions involving bromotrichloromethane proceed exclusively *via* bromine abstraction.[6] If the second of these possibilities had occurred, it is conceivable that I could have been produced by a reaction of diphenylmethylene or diphenyldiazomethane with the trichloromethyl radical followed by elimination of a chlorine atom.

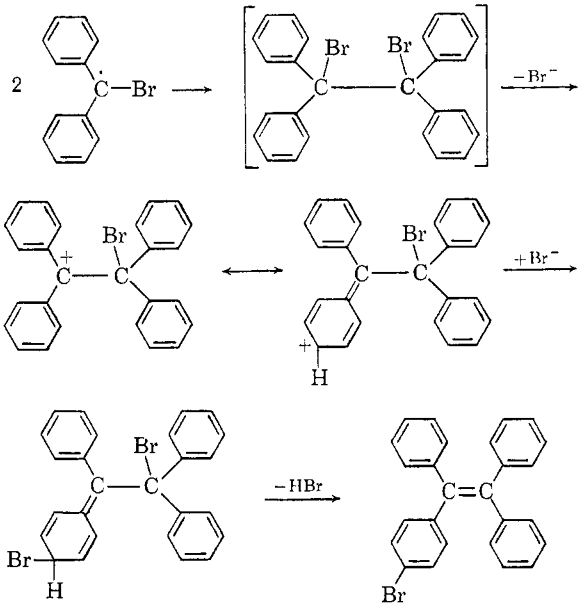


I

Dimerization of the bromodiphenylmethyl radicals, produced in this scheme, to give the unknown 1,2-dibromo-1,1,2,2-tetraphenylethane as an unstable intermediate, followed by loss of hydrogen bromide could explain the formation of V.

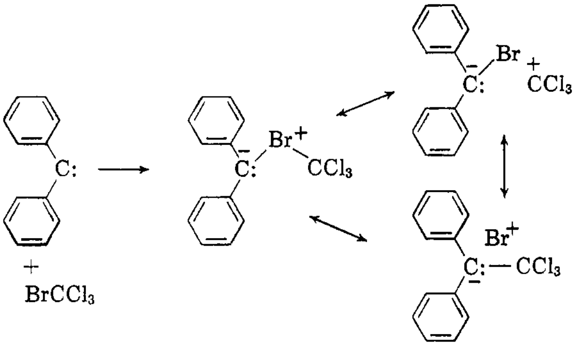
A similar path involving the chlorodiphenylmethyl radical would then explain the formation of IV. The much smaller yield of IV would be consistent with the expected smaller concentration of chlorodiphenylmethyl radicals. The production of IV in the thermal decomposition of 1,2-dichloro-1,1,2,2-tetraphenylethane, presumably by the mechanism given here, has been described by Norris *et al.*[5]

It is also interesting to consider the possibility that I is produced in a reaction between singlet diphenylmethylene and bromotrichloromethane.



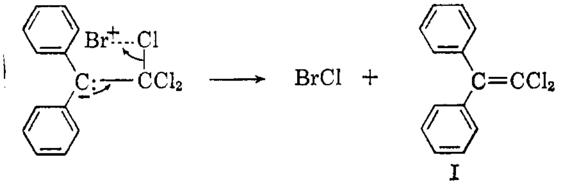
V

This reaction could lead to the formation of a transition state VII.



VII

This onium type transition state could then eliminate bromine chloride to give I.



I

Transition state VII is similar to that invoked by Doering and Knox (in the insertion reaction of biscarboethoxycarbene)[7] and by Franzen.[1g] (A similar intermediate may be responsible for the 1,1-dibromoethylene produced in the reaction of methylene with carbon tetrabromide.)[1c] The bromine chloride produced in this process could add to III to give an intermediate VIII which would be expected to be unstable and could be the precursor of IV and V by the same mechanism invoked above in the

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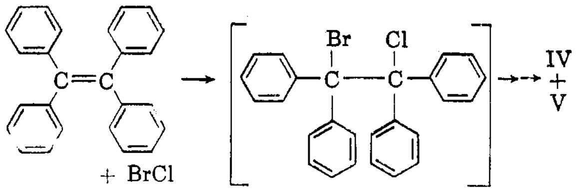
(6) M. S. Kharasch, O. Reinmuth, and W. H. Urry, *J. Am. Chem. Soc.*, **69**, 1105 (1947).

(7) W. von E. Doering and L. H. Knox, *ibid.*, **83**, 1989 (1961).

case of the decomposition of the intermediate 1,2-dibromo-1,1,2,2-tetraphenylethane.



VIII

Experimental

Melting points and boiling points are uncorrected. Melting points were determined on a Kofler hot stage. Infrared spectra were obtained on a Perkin-Elmer Infracord spectrophotometer. Gas phase chromatograms were taken on an F&M Model 500 gas phase chromatograph with temperature programming. Ultraviolet spectra were recorded on a Beckman DK-2 spectrophotometer. Bromotrichloromethane (Matheson, Coleman and Bell reagent grade) was redistilled (b.p. 104°) shortly before use.

Diphenyldiazomethane.—Benzophenone hydrazone (13.0 g., 66 mmoles) was oxidized with yellow mercuric oxide (35 g., 160 mmoles) by the procedure described by Miller[8] to yield sticky red crystals of diphenyldiazomethane (12.2 g., 63 mmoles, 95.2%).

Photochemical Decomposition of Diphenyldiazomethane in Bromotrichloromethane.—The photolysis vessel was a 100-ml., round-bottom, three-necked flask equipped with a dropping funnel and a condenser with a Drierite guard. Stirring was accomplished by bubbling nitrogen through the solution. Two General Electric 150-watt flood lamps were used to irradiate the flask, which was cooled by flowing cold water over its exterior surface.

To the irradiated flask containing bromotrichloromethane (15 ml.) was added dropwise a solution of diphenyldiazomethane (12.2 g., 63 mmoles) in bromotrichloromethane (15 ml.) at a rate to maintain a *pale* red color in the reaction flask. As the reaction proceeded, it became necessary to add more bromotrichloromethane to the reaction flask. The total amount of bromotrichloromethane used was 50 ml. and the total photolysis time was 91 hr. At this time the flask contents were light brown and some suspended solid was present. A portion (15.7 g.) of the crude reaction mixture was then chromatographed on a column of Woelm number 1, neutral alumina (*ca.* 400 g.). Elution with 5% benzene–95% pentane gave a colorless oil (I) which solidified to white crystals when scratched. This solid was recrystallized twice from absolute ethanol and sublimed twice to give white, stocky needles of 1,1-dichloro-2,2-diphenylethylene (0.513 g.; 3.41%; m.p. 79–80.5°; mixed m.p. 79–80.5°). The infrared spectrum of I was identical to that of authentic 1,1-dichloro-2,2-diphenylethylene.

Anal. Calcd. for $C_{14}H_{10}Cl_2$: C, 67.5; H, 4.0. Found: C, 67.5; H, 4.3.

Elution of the column with 10% benzene–90% pentane gave a yellowish solid which had a purple-green fluorescence. This fraction was analyzed by gas phase chromatography using a four foot, 20% silicone gum rubber column and temperature programming beginning at 160° and heating at 2.9° per minute. This procedure gave almost complete resolution of this fraction into three separate peaks (III–V). Two of the peaks (III and V) accounted for most of this total fraction. Samples of each of these materials were collected in glass collection tubes. The first fraction (III), which had a purple fluorescence, had m.p. 225–225.5° and mixed m.p. with authentic tetraphenylethylene, 225–225.5°. Its infrared spectrum and GPC retention time were identical to those of authentic tetraphenylethylene. The remaining two fractions (IV and V) slowly solidified in the collection tubes to white solids which had a greenish fluorescence. The first of these (IV) had m.p. 165–168°. It had mixed m.p. with authentic 1-*p*-chlorophenyl-1,2,2-triphenylethylene of 155–160°. Its infrared spectrum and GPC retention time were identical to those of authentic 1-*p*-chlorophenyl-1,2,2-triphenylethylene. Solid V (m.p. 160–161°) had an ultraviolet spectrum which was very similar to that of tetraphenylethylene. It was identified as **1-*p*-bromophenyl-1,2,2-triphenylethylene** by comparison of its infrared spectrum and GPC retention time with those of authentic material.

Anal. Calcd. for $C_{26}H_{19}Br$: C, 75.9; H, 4.66; Br, 19.4. Found: C, 75.6; H, 4.98; Br, 19.5.

Yields of these three solids as determined from gas chromatogram peak areas were 11.04% (III), 0.26% (IV), and 4.88% (V). Elution ofthe column with methylene chloride gave at pale yellow solid (II). This was recrystallized twice from ethanol to give pale yellow, fluffy needles, m.p. 162–166°, mixed m.p. with authentic benzophenone azine, 161–165°. Its infrared spectrum was identical to that of authentic benzophenone azine. Yield was 1.07 g. (9.6%).

1,1-Dichloro-2,2-diphenylethylene.—Alcoholic potassium hydroxide was prepared (*ca.* 0.5 *N*) and allowed to stand for 24 hr. The mixture was then filtered to remove carbonate. A 100-ml. round-bottom flask was charged with 2.86 g. (0.01 moles) of 1,1-diphenyl-2,2,2-trichloroethane and 50 ml. of alcoholic potassium hydroxide and the solution refluxed for 4 hr. The reaction mixture was allowed to cool and water was added. The reaction mixture was extracted with methylene chloride, the extracts dried ($MgSO_4$), and the methylene chloride evaporated to give orange-colored needles. This solid was recrystallized from ethanol to give pale orange needles which were sublimed to white needles, m.p. 79–80.5°, lit. m.p. 80°.[9]

Benzophenone Azine.—To a mixture of benzophenone hydrazone and 30 ml. of 95% ethanol was added, dropwise, concentrated sulfuric acid until the solution remained acid to pH paper. After standing for 22 hr. the flask contained a white precipitate. The flask contents were heated to boiling, filtered hot, and the ethanol evaporated to give a pale yellow solid. This solid was recrystallized from absolute ethanol to give pale yellow, stocky needles, m.p. 164–166°, lit., m.p. 164°.[10]

1,2-Dichloro-1,1,2,2-tetraphenylethane.—Tetraphenylethylene (3.32 g., 0.01 mole) was dissolved in a minimum amount of chloroform and dry chlorine gas bubbled into the solution for 5 hr. At the end of this time the reaction mixture was allowed to stand for an additional 3 hr. The chloroform was then evaporated to give white crystals of the chloroform complex of 1,2-dichloro-1,1,2,2-tetraphenylethane, m.p. 157–159° dec., lit., m.p. 160–162° dec.[11]

Thermal Decomposition of 1,2-Dichloro-1,1,2,2-tetraphenylethane.—The chloroform complex, prepared as described above, was recrystallized from ether and the resulting solid was placed in a pear-shaped flask which was immersed in an oil bath. The flask contents were kept under a stream of nitrogen. The flask was slowly heated with evolution of hydrogen chloride beginning at *ca.* 150°. The flask was heated to 180° and heating was continued until hydrogen chloride evolution had ceased (*ca.* 35 min. at 180°). The crude product had a purple fluorescence. This material was analyzed by gas phase chromatography using a 4-ft. 20% column and temperature programming. The crude material was found to be composed of two fractions. The first fraction had the same retention time as tetraphenylethylene. The second and smaller fraction was collected. It was a white solid with a greenish fluorescence, m.p. 168.5–169.5°; lit., m.p. for 1-*p*-chlorophenyl-1,2,2-triphenylethylene, 166–167°.[5]

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(8) J. B. Miller, *J. Org. Chem.*, **24**, 560 (1959).

(9) A. Baeyer, *Ber.*, **6**, 220 (1873).

(10) H. H. Szmant and C. McGinnis, *J. Am. Chem. Soc.*, **72**, 2890 (1950).

(11) J. F. Norris, *ibid.*, **38**, 707 (1916).

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]

Peter Entien Wei, Alsoph H. Corwin,
and Roberto Arellano

The Johns Hopkins University, Baltimore 18, Maryland

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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.

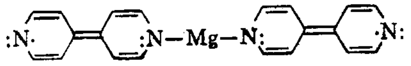
We have discovered three new reagents for the introduction of magnesium into porphyrins and chlorins. The first and most powerful of these, which we formulate as magnesium viologen, is prepared by refluxing magnesium and iodine in dry pyridine. This introduces magnesium easily into all porphyrins and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

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[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).