[Contribution from the Chemical Laboratories of the University of Notre Dame]

Organoboron Compounds. IV. Phenyldifluoroborane and Other Aryldihalogenoboranes[1–3]

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The reaction of boron fluoride and boron chloride with trisubstituted organoboroxines has been found to be applicable within limits to the preparation of aryldihalogenoboranes. The chloro- compounds are obtainable in good yield when boron halide-sensitive groups are absent from the benzene ring, but the fluoro- compounds are obtainable only in relatively low yield. Partial cleavage of triarylboroxines occurs on reaction with boron fluoride with formation of hydrocarbon. Boron fluoride dihydrate causes complete hydrolysis of triarylboroxines or arylboronic acids to hydrocarbon. Aryldifluoroboranes are best prepared by the action of fluorinating agents such as antimony trifluoride on the aryldichloroboranes. Phenyldifluoroborane and *p*-tolyldifluoroborane have been prepared by the direct reaction of boron fluoride on the triarylboroxine and also through the chloro- compounds and have been fully characterized. The materials described in the literature as phenyl- and *p*-tolyldifluoroborane appear to contain little if any of the authentic compounds.

Aryldichloroboranes have been prepared previously by the reaction of boron chloride with arylmercury compounds[4] in sealed tubes at 100 to 300°, and phenyldichloroborane has been prepared by the high temperature, palladium-catalyzed reaction between boron chloride and benzene.[5] Neither of these methods is convenient for ordinary laboratory use and the yields are apparently not high. The use of the Grignard reagent[6,7] and zinc aryls[8] has been claimed to be successful for the preparation of phenyldifluoroborane and *p*-tolyldifluoroborane. Since the reaction of boron halides with trialkylboroxines has been found to provide an excellent method for the preparation of alkyldihalogenoboranes, its applicability to the preparation of aryldihalogenoboranes has been investigated. The results of this study are reported in the present paper.

Experimental

Arylboronic Acids.—Phenyl- and *p*-tolyl-boronic acids were prepared in yields of 80% by the method of Khotinsky and Melamed,[9] using a twofold or greater excess of methanol-free methyl borate and following the modified procedure of Bean and Johnson.[10] *p*-Anisylboronic acid was obtained in 52% yield.

Triarylboroxines.—These were prepared in various instances by thermal dehydration and by reaction of the acid with thionyl chloride.[11] The most satisfactory procedure involved the treating the reaction residue, after removal of ether, with toluene, distilling off methanol and removing the water[12] as an azeotrope with benzene. Recrystallization from carbon tetrachloride gave sharp-melting crystalline solids; triphenylboroxine, m.p. 215°, and tri-*p*-tolylboroxine, m.p. 233–244°.

Phenyldichloroborane from the Reaction of Boron Chloride with Triphenylboroxine.—Purified, powdered triphenylboroxine (208 g., 0.66 mole of trimer) was placed in a 500-ml., 2-necked flask, having an inlet tube which extended to the bottom of the flask and a water-cooled reflux condenser. A solid carbon dioxide-cooled condenser was attached to the top of the reflux condenser and led to bubbling bottles for detection of exit gases. The apparatus was flushed out with dry nitrogen. Boron chloride was passed through mercury bubbling bottles and into the reaction flask at a moderate rate, such that the gas was completely absorbed. Within a few minutes the solid began to liquefy and heat evolution was evident. After 4 hr. the mixture was completely liquid. After cooling under nitrogen, the reaction product was distilled rapidly under vacuum, with the receiver being cooled in a solid carbon dioxide-bath, until solid appeared in the condenser. The distillate was redistilled through a 60-cm., glass-helix packed column. Dissolved boron chloride was removed at atmospheric pressure and the remaining product under vacuum. Water-white phenyldichloroborane (175.2 g., 1.1 moles) was collected at 59.5–63.0° at 13–15 mm., yield 55%.

The combined residues from the reaction and the distillation were treated with 300 ml. of water, the mixture heated to reflux, treated with decolorizing charcoal, filtered and chilled and the precipitated solid collected on a Buchner funnel. The wet solid was treated with 400 ml. of toluene and refluxed under a Stark–Dean trap until no more water came off. The residual mixture was filtered hot and the filtrate cooled. The precipitated solid was collected, washed with petroleum ether and dried in an oven for 1 hr. at 110°. Evaporation of the toluene filtrate gave additional solid which was treated similarly. The total yield of recovered triphenylboroxine was 70.2 g., m.p., after recrystallization from carbon tetrachloride, 214–215°. The yield of phenyldichloroborane based on triphenylboroxine consumed was 83%.

***p*-Tolyldichloroborane** was prepared several times in one-to-two mole quantities by the same procedure as used for the phenyldichloroborane. Actual yields ranged from 36 to 58%. In one run the unused tri-*p*-tolylboroxine was recovered. The yield in this run based on used boroxine was 91%.

In some early experiments boron halide was treated with heated, molten triarylboroxine instead of with powdered solid. In the case of the phenyl- compound some charring was observed and the yields of product were lower than when reaction was carried out without external heating. With tri-*p*-tolylboroxine the high temperature reaction resulted in extensive carbonization and the production of large amounts of toluene as a by-product. In one run the toluene was isolated, purified and weighed and found to account for 40% of the boroxine consumed.

Attempted Preparation of *p*-Anisyldichloroborane.—Tri-*p*-anisylboroxine (234 g.) was treated with boron chloride according to the procedure described above for the preparation of phenyldichloroborane. Boron chloride was absorbed readily by the powdered boroxine, and liquefaction of the mixture occurred. Upon distillation of the reaction mixture into a solid carbon dioxide-cooled receiver a considerable amount of liquid distillate was obtained, most of which, however, was boron chloride. The higher boiling product resinified into a glassy, puffy mass on attempted distillation. Only a few ml. of dark colored liquid was obtained, and this was discarded.

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(1) Paper III, P. A. McCusker, E. C. Ashby and H. S. Makowski, This Journal, **79**, 5182 (1957).

(2) The authors acknowledge with thanks helpful discussions with Professor G. F. Hennion.

(3) From the dissertation submitted by Henry S. Makowski in partial fulfillment of the requirements for the degree of Doctor of Philosophy, University of Notre Dame, 1957.

(4) A. Michaelis and E. Richter, *Ann.*, **315**, 29 (1901).

(5) R. Pace, *Atti accad. Lincei*, **10**, 193 (1929).

(6) E. Krause, German Patent 371,476 (1923); *C. A.*, **18**, 992 (1924).

(7) M. F. Lappert, *Chem. Revs.*, **56**, 1050 (1956).

(8) K. Torsell, *Acta Chem. Scand.*, **8**, 1779 (1954).

(9) E. Khotinsky and M. Melamed, *Ber.*, **42**, 3090 (1909).

(10) F. R. Bean and J. R. Johnson, This Journal, **54**, 4415 (1932).

(11) H. R. Snyder, J. A. Kuck and J. R. Johnson, *ibid.*, **60**, 105 (1938).

(12) P. A. McCusker, E. C. Ashby and H. S. Makowski, *ibid.*, **79**, 5179 (1957).

Phenyldifluoroborane from the Reaction of Boron Fluoride with Triphenylboroxine.—An attempt was made to induce reaction between boron fluoride and solid, powdered triphenylboroxine at low temperature as occurs in the case of the chloro- compound. Boron fluoride was passed through 64.8 g. of boroxine for a period of 2 hr., but no reaction occurred. Partial melting of the boroxine also failed to initiate reaction. The addition of a small amount of liquid tri-*n*-amylboroxine also failed to cause reaction. To obtain any reaction between triphenylboroxine and boron fluoride, it was necessary to maintain the boroxine well above its melting point and supply boron fluoride under careful control. This was done as follows. Triphenylboroxine (114 g., 0.37 mole of trimer) was placed in a 500-ml. distilling flask provided with an inlet tube for boron fluoride, with stopcock control to permit cutting off the flow of boron fluoride and sending the stream through a by-pass when desired. A condenser, vacuum adapter and receiver were attached to the distilling flask. The side arm of the vacuum adapter led to a 50-ml. flask cooled to solid carbon dioxide temperature, and sulfuric acid bubbling bottles were attached to permit detection of exit gases. A stopcock was inserted between the adapter and cold trap. The system was swept out thoroughly with boron fluoride and, with the exit stopcock closed, the reaction flask was heated by means of a Meker burner with access of boron fluoride to the molten triphenylboroxine. Boron fluoride was fed in for periods of 2 to 5 minutes. The entrance stopcock was then closed and the exit stopcock opened and any product formed was distilled out. If distillation was attempted in a stream of boron fluoride, triphenylboroxine was carried over in large amounts. By manipulation of the stopcocks, over a period of 7 hr., 50 g. of reaction product was obtained. This product was carefully fractionated in a 40-cm., packed column and yielded two main fractions, one at 80°, 10 g., and the other at 96°, 23 g. The 80° fraction was washed with water and base and water again. Its boiling point, density and refractive index agreed with the values for benzene, and its *m*-dinitro derivative had the proper melting point. The higher boiling fraction was characterized as described below and identified as phenyldifluoroborane, yield 16%. The dark-colored reaction residue was refluxed with two liters of water for 2 hr. The dark carbonaceous insoluble material was filtered off and the cooled filtrate extracted with ether. Evaporation of the ether gave off impure phenylboronic acid. Calculation of the yield of phenyldifluoroborane based on triphenylboroxine used was 18%. Apparently most of the triphenylboroxine underwent decomposition during reaction.

***p*-Tolyldifluoroborane from the Reaction of Boron Fluoride with Tri-*p*-tolylboroxine.**—The reaction of boron fluoride with tri-*p*-tolylboroxine was carried out in the same manner as for the phenyl- compound except that an attempt was made to achieve minimum reaction temperatures by use of molten metal-baths. The best runs gave only 10 to 15% yields of *p*-tolyldifluoroborane and about equal amounts of toluene. Sufficient *p*-tolyldifluoroborane was obtained, however, for complete characterization as described below.

Phenyldifluoroborane from Phenyldichloroborane and Antimony Trifluoride.—Phenyldichloroborane (175 g., 1.1 moles) was placed in a 300-ml., 3-necked flask fitted with sealed stirrer and reflux condenser. A 125-ml. erlenmeyer flask, containing 135 g. (0.76 mole) of resublimed, anhydrous antimony trifluoride, was attached to one neck of the reaction flask by means of wide bore rubber tubing. A thermometer suspended through the reflux condenser was placed in the liquid phenyldichloroborane. The liquid was cooled by means of an ice-bath to 7°. The antimony trifluoride was added in very small portions with stirring. Reaction was immediate, vigorous and strongly exothermic. The rate of addition of antimony trifluoride was controlled so that the reaction temperature was held close to 45°. The antimony trifluoride dissolved as it reacted and no gas evolution occurred during the addition. When the addition of antimony trifluoride was nearly complete, a large quantity of white crystals came out of solution. Addition of antimony trifluoride was completed in 30 minutes, after which the ice-bath was removed and stirring was continued for another 15 minutes. Distillation of the reaction mixture through a 60-cm., packed column resulted in evolution of considerable quantities of boron fluoride. After gas evolution ceased, 92 g. (66% yield), of phenyldifluoroborane was obtained at 94 to 96°. When the residue was heated in a simple distilling flask, the vapor temperature rose immediately to 222°, which is the boiling point of antimony trichloride.

***p*-Tolyldifluoroborane from *p*-Tolyldichloroborane and Antimony Trifluoride.**—When antimony trifluoride was added to *p*-tolyldichloroborane under exactly the same conditions as described above for the preparation of phenyldifluoroborane, boron fluoride was evolved during reaction. On attempted distillation very large quantities of boron fluoride were evolved and only a very small amount of *p*-tolyldifluoroborane was obtained. The reaction conditions were modified so that the temperature was held close to 20°. Reaction was begun just above 28°, the melting point of *p*-tolyldichloroborane, and as reaction proceeded the temperature was lowered by ice-bath control. Under these conditions no gas evolution occurred. When addition of antimony trifluoride was complete, the mixture was distilled at 20 mm. into a receiver cooled to solid carbon dioxide temperature. Distillate was collected between 40 and 100° and then redistilled at atmospheric pressure in a 60-cm., packed column. From 184 g. (1.06 moles) of phenyldichloroborane and 129 g. (0.73 mole) of antimony trifluoride was obtained 108 g. of *p*-tolyldifluoroborane, b.p. 122–128°, yield 73%.

Reaction of Phenylmagnesium Bromide with Excess Boron Fluoride Etherate.—To 0.74 mole of boron fluoride etherate, cooled to solid carbon dioxide temperature, was added 0.45 moles of phenylmagnesium bromide in 450 ml. of ether. Addition required 2.5 hr. and stirring was continued for an additional 0.5 hr. The mixture was allowed to warm to room temperature and the ether was removed through a 30-cm. Vigreux column. After removal of the ether, distillation was continued until a pasty solid remained and evident decomposition set in with evolution of gas. The small amount of distillate obtained was redistilled and a few ml. of a fraction boiling from 75 to 78° was collected. This fraction contained 13.6% fluorine; calculated for phenyldifluoroborane, F, 30.18.

Physical Properties and Analyses.—Properties were measured and analyses carried out as previously described.[1,13] The molecular weight of phenyldifluoroborane was obtained cryoscopically in purified cyclohexane.

Results and Discussion

The aryldihalogenoboranes prepared in this work were purified by fractional distillation to give fractions of constant boiling point, index of refraction and density. The properties of purified samples of these compounds are listed in Table I.

TABLE I

PROPERTIES OF ARYLDIHALOGENOBORANES

Compound	B.p. °C.	B.p. Mm.	n^{25}D	d^{25}	Halogen, % Calcd.	Halogen, % Obsd.
$C_6H_5BCl_2$	36	2	1.5445	1.203	44.6	43.9
	177	748				
p-$CH_3C_6H_4BCl_2$	42	0.2	1.5452[b]	1.160[b]	41.0	40.5
	205	747				
$C_6H_5BF_2$[a]	97.8	747	1.4441	1.087	30.2	29.4
p-$CH_3C_6H_4BF_2$	127.8	747	1.4535	1.055	27.2	27.6

[a] Calcd., mol. wt., 126; obsd., mol. wt., 122; m.p. −36.2°. [b] Taken at 30°.

The aryldihalogenoboranes are, like the alkyldihalogenoboranes, fuming liquids which hydrolyze very rapidly in water. None of the aryl compounds show pyrophoric character at room temperature. The lowest boiling of these compounds, phenyldifluoroborane, can be exposed repeatedly to air without spontaneous combustion, while cyclohexyldifluoroborane, whose boiling point is only a few degrees lower, is extremely pyrophoric. The apparently lower electrophilic character of boron in phenyldifluoroborane, as compared to cyclohexyldifluoroborane which has only a slightly lower

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(13) P. A. McCusker and L. J. Glunz, THIS JOURNAL, **77**, 4523 (1955).

boiling point, probably results from contributions of quinoid structures in the case of the aryldifluoroborane. The compounds can all be distilled at atmospheric pressure without undergoing any disproportionation. When heated in the presence of antimony halides, however, the conversion of aryldifluoroboranes to boron fluoride was observed. It is not clear, however, whether this represents a disproportionation of the aryldifluoroborane, catalyzed by the antimony salts, or resulted from a shift of the phenyl group from boron to antimony. The other reaction products were not identified.

A number of differences exist between the reaction of boron chloride and boron fluoride on aryl boronic acids and triarylboroxines and on the corresponding alkyl compounds. One of the fundamental differences results from the fact that the carbon–boron link in the aromatic compounds is susceptible to hydrolytic fission under the influence of acids,[14] while in the alkyl compounds the carbon–boron bond is completely resistant to hydrolysis. This difference is responsible for the fact that while the direct reaction of boron fluoride with alkylboronic acids is the most convenient method for the preparation of alkyldifluoroboranes, an attempt to apply this procedure to the arylboronic acids results in complete conversion of the aryl compound to hydrocarbon. The strongly acid boron fluoride dihydrate, formed in the reaction, causes complete hydrolysis of the arylboronic acid and no aryldifluoroborane is formed. When phenylboronic acid was left in contact with boron fluoride dihydrate containing excess dissolved boron fluoride for several days the only isolable product formed was benzene. Likewise any hydrogen fluoride present as an impurity in the boron fluoride used or any water retained in the triarylboroxine would result in the production of hydrocarbon rather than aryldifluoroborane. In the case of the chloro- compounds the presence of any hydrogen chloride in the boron chloride used may also cause the formation of hydrocarbon.

While the reaction of boron fluoride with trialkylboroxines occurs readily even at room temperature, no reaction can be observed between triarylboroxines and boron fluoride at low temperatures. Even at temperatures above the melting point of the triarylboroxine, reaction with boron fluoride is extremely slow. Before any reaction can be made to take place the temperature must be high enough so that some carbonization of the triarylboroxine occurs. Hydrogen is apparently released in the decomposition and the carbon–boron bond is broken and hydrocarbon formed. As a method for the preparation of aryldifluoroboranes the reaction of boron fluoride with triarylboroxines is extremely tedious and capable of giving yields of only about 15%. By this method, however, the first authentic aryldifluoroborane was prepared.

Differences between the reaction of boron chloride with alkyl- and arylboroxines are not as great. The reaction can be made quantitative in either case. With the aryl- compounds the temperature must be maintained low to avoid the formation of hydrocarbon. The tendency for the *p*-tolyl- compound to undergo decomposition and form hydrocarbon as a product is apparently much greater than that of the phenyl-compound.

A characteristic difference in the behavior of boron fluoride and boron chloride with triarylboroxines must exist to account for the differences in the reactivities of the boron halides with triarylboroxines. If the initial reaction step is assumed to be the formation of a coördinate bond between the oxygen of the boroxine and the boron of the halide, the lower acceptor character of the boron fluoride[15] may cause this first step in the reaction to occur less readily. This would imply that the oxygen in the triarylboroxine was less effective as a donor atom than in the alkyl- compounds. While there is apparently no data upon which to base a comparison of the relative donor strengths of aryl and alkyl boroxines, it seems probable that such an explanation would account for the observed differences in reactivity.

A general limitation to the use of the reaction of boron halides with organoboroxines for the preparation of organodihalogenoboranes, which applies to both the alkyl and aryl series, is set by the presence of other groups in the molecule with which the boron halide may react. In the present work, this is illustrated by the failure of the reaction to produce *p*-anisyldichloroborane, although the compound has been prepared[16] by the use of mercury aryls. The boron halide presumably attacks the methoxy group and causes the production of fragments which polymerize readily to a resinous mass from which no *p*-anisyldichloroborane could be isolated.

The reaction of antimony trifluoride and presumably other similar fluorinating agents with aryldichloroboranes provides the best method for the preparation of aryldifluoroboranes. The reaction is rapid and yields are high. This reaction combined with the high-yield reaction of boron chloride with triarylboroxines affords the best route to this new class of compounds. Boron fluoride does not effect halogen exchange with triaryldichloroboranes. When boron fluoride was passed for long periods through phenyldichloroborane at room temperature and at higher temperature, no absorption of gas occurred, and the phenyldichloroborane was recovered unchanged.

The material previously described by Krause[6] as phenyldifluoroborane, obtained by the reaction of boron fluoride with the Grignard reagent, evidently contains little or none of the authentic compound. Krause reports a boiling point of 75 to 78°, which is 20° lower than the value observed in this work. No other constants were reported by Krause and no analyses apparently made. Others[8] have reported that the method has failed in their hands. In view of the results previously obtained,[13] which indicated that monoalkylation of boron fluoride could not be achieved with alkyl Grignard reagents, it is probable that aryl Grignard reagents also fully alkylate boron fluoride. The product obtained by Krause[6] also was obtained in very

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[14] A. D. Ainley and F. Challenger, *J. Chem. Soc.*, 2171 (1930).

[15] H. C. Brown and R. B. Holmes, THIS JOURNAL, **78**, 2173 (1956).

[16] A. Michaelis, *Ann.*, **315**, 19 (1901).

small yield in this work. Its fluorine content was found to be only 13.6% compared to a theoretical of 30.2% for phenyldifluoroborane. A possible explanation of the source of this 75–80° boiling product is afforded by our observation that ether–boron fluoride can undergo extensive decomposition on fractional distillation to give ethylene and other incompletely characterized products,[17] one of which boils sharply at 78°. Benzene is also a possible product in this reaction since it also has been observed that partially decomposed ether–boron fluoride is strongly acidic. It is probable that the product obtained by Krause from the reaction of boron fluoride with phenylmagnesium bromide contains benzene and one of the decomposition products of ether–boron fluoride. It is also possible that appreciable amounts of toluene may be present in the material reported by Krause[6] as *p*-tolyldifluoroborane (b.p. 95–97) along with decomposition products of ether–boron fluoride.

The reaction of zinc diphenyl with distilled ether–boron fluoride recently has been reported[8] to yield phenyldifluoroborane in 46% yield. In this case the product is again uncharacterized and is reported as having a boiling point of 82 to 85° at 730 mm. The product is reported as obtained by repeated distillations of the reaction product through a column. Under such conditions ether–boron fluoride could produce material boiling at that temperature and again benzene may be present due to the action of partially decomposed ether–boron fluoride on the zinc diphenyl. The action of zinc alkyls on boron chloride has been shown to result in complete alkylation.[18]

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[17] P. A. McCusker and L. J. Glunz, unpublished work.

[18] H. J. Becher, *Z. physik. Chem., Frankfurt*, **2**, 276 (1954).

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Organoboron Compounds. V. Electric Moments of Some Alkyl- and Aryldihalogenoboranes in Benzene and Dioxane[1-3]

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The electric moments of organodihalogenoboranes in benzene reveal a strong resonance involving structures of the type $^+C_6H_5{=}^-BX_2$ which make a greater contribution to the chloro- than to the fluoro- compounds. The moments in dioxane indicate that the chloro- compounds are practically completely solvated and the fluoro- compounds only partially solvated. Carbon is negative with respect to boron in the dioxanates.

Electric moments of alkyldihalogenoboranes are of interest in determining the relative importance of resonance involving halogen-to-boron double bond character in the fluoro, chloro, bromo and iodo compounds. The present study is limited to fluorides and chlorides. The moments of the aryldihalogenoboranes offer a direct measurement of the effect of π-electron delocalization on the overall polarity of the molecules. Of all elements, trivalent boron appears most likely to have large contributions of resonance structures of the type $^+C_6H_5{=}^-MX_2$ because of its unsaturated character and its position in the top row in the periodic table. Evidence for C=B double bond character in the phenyldichloroborane has been obtained from the electron diffraction studies of Coffin and Bauer.[4] The C–B bond distance in this compound is 1.52 Å. compared to a value of 1.56 Å. for trimethylborane.[5]

Previous work in this Laboratory[6] has revealed a moment of 4.90 for normally non-polar boron trichloride when it is solvated in dioxane. Moments of the organodihalogenoboranes have been obtained in dioxane to study the extent of coördination between oxygen and boron in these solutions and to determine the effect of this coördination on the polarity of the C–B and B–X bonds.

Experimental

Preparation of Solutions.—The preparation and purification of the compounds measured have been reported in preceding papers.[3,7,8] Solutions for measurement were prepared, in the weight fraction range 0.01 to 0.05, by pipetting portions of freshly distilled compounds in a nitrogen-filled dry-box into weighed glass-stoppered 60-ml. weighing bottles. The weighed samples were diluted with solvent in a similar manner.

Measurements and Calculations.—Dielectric constants were measured by the heterodyne beat method, using a one megacycle crystal controlled oscillator. The glass dielectric cell, constructed by J. C. Balsbaugh, Marshfield Hills, Mass., has five concentric nickel plates supported by wires imbedded in glass. The center, inner and outer plates are connected to the ground lead. The cell has an air capacity of 100 $\mu\mu$f, and was modified by the addition of inlet and outlet glass tubes. Solutions were introduced into the cell through glass tubing under a pressure of dry nitrogen. The cell was calibrated with benzene, ϵ 2.2730. Densities were determined with a Lipkin pycnometer having a volume of 5 ml. The average density of the benzene used was 0.8732 and that of the dioxane 1.0284.

Polarizations at infinite dilution were calculated by the Hedestrand method, using extrapolated values of $\Delta\epsilon/wf_2$ for the solutions listed in Table I and average values for the other solutions, which did not show a regular variation of the $\Delta\epsilon/wf_2$ ratio with concentration. The moments in De-

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[1] Presented at the 128th Meeting of the American Chemical Society, Minneapolis, Minn., September, 1955; see Abstracts, p. 2R.

[2] From the dissertation submitted by Henry S. Makowski in partial fulfillment of the requirements for the degree of Doctor of Philosophy, University of Notre Dame, 1957.

[3] Paper IV, P. A. McCusker and H. S. Makowski, THIS JOURNAL, **79**, 5185 (1957).

[4] K. P. Coffin and H. S. Bauer, *J. Phys. Chem.*, **59**, 193 (1955).

[5] H. A. Levy and L. O. Brockway, THIS JOURNAL, **59**, 2085 (1937).

[6] T. J. Lane, P. A. McCusker and C. Curran, *ibid.*, **64**, 2076 (1942).

[7] P. A. McCusker and L. J. Glunz, *ibid.*, **77**, 4253 (1955).

[8] P. A. McCusker, E. C. Ashby and H. S. Makowski, *ibid.*, **79**, 5182 (1957).