

in Nujol solution, for the β -substituted naphthalenes than for the α' substituted. It was found¹³ that the α value at 40° for α -methylnaphthalene is 0.08 and for β -methylnaphthalene, 0.16. The relaxation times of β -methylnaphthalene in Nujol are larger than those of the α -halonaphthalenes in Nujol because, due to the more elongated structure of β -methylnaphthalene, it will experience more resistance to rotation and thus have a higher relaxation time.

The free energies ΔF^* , heats ΔH^* and entropies ΔS^* of activation for dielectric relaxation, calculated in the usual manner,¹¹ are given in Table V.

It is evident that the ΔF^* values in Table V increase with increasing viscosity and molecular size, as has been observed for a number of other liquids.^{8,11,12} β -Methylnaphthalene is effectively larger than the two α -halonaphthalenes, because the direction of the dipole moment in the molecule causes the molecular rotation to sweep out a greater volume than that swept by the other two molecules in rotating around their long axes. The ΔH^* values obtained for α -bromonaphthalene in several solvents decrease as the solvent complexity and viscosity decrease. A large decrease in entropy of activation occurs when measurements are carried out in decalin or *n*-heptane as compared to Nujol.

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Synthesis of Arylphosphonous Dichlorides by Reduction of Diazonium Fluoroborate-Phosphorus Trichloride Reaction Products^{1,2}

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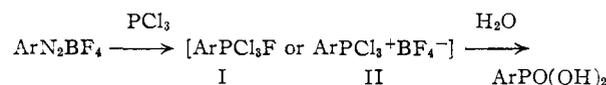
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Products of the reaction of diazonium fluoroborates with phosphorus trichloride have been reduced with magnesium to form phosphonous dichlorides. Although the yields are in the 20–35% range, the reaction serves as a source of phosphonous dichlorides unobtainable by other methods. Several new structures have been made. The reaction also has given access to new phosphinic acids, since these compounds are prepared readily by hydrolysis of the dichlorides.

Arylphosphonous dichlorides have been known almost since the beginnings of organophosphorus chemistry, but remain relatively rare compounds. The majority of the presently known phosphonous dichlorides were prepared by two methods developed by early workers.³ One method involves the aluminum chloride-catalyzed reaction between phosphorus trichloride and certain aromatic compounds. Early difficulties with product isolation have been largely overcome,⁴ but this method remains limited in scope. Thus, *meta*-directing groups present in the aromatic compound prevent substitution; ring-activating substituents lead to a mixture of *ortho* and *para* isomers, predominantly the latter. The other method involves the arylation of phosphorus trichloride with aryl mercury compounds. Two recent publications have reported the use of other organometallic compounds in this reaction. Yakubovich and Motsarev⁵ used aryl aluminum chlorides, while Weil, Prijs and Erlennmeyer⁶ have used aryl zinc chlorides. The versatility of these arylations, however, is impaired by limitations on the nature of substituents permissible on the aromatic nucleus.

For many years, most syntheses of arylphosphonic acids started with phosphonous dichlorides

or derivatives, and thus these compounds also remained relatively rare. In 1951, Doak and Freedman⁷ opened up this field with a synthesis based on the cuprous halide-catalyzed reaction of phosphorus trihalides with dry diazonium fluoroborates in organic solvents. The reaction products are not isolated but are hydrolyzed to give phosphonic acids. Yields of 30–50% or more are common, and very few failures have been recorded. In the years since 1951, a large number of new structures have been made by this general reaction, which may be expressed as



The intermediate has never been subjected to study, although structures I or II⁸ seem reasonable. Whatever its precise structure, the intermediate appeared to us to be chemically similar to the tetrahalophosphoranes (ArPX_4), also readily hydrolyzed to phosphonic acids.⁹ This suggested the possibility that the intermediate might be reduced to the phosphonous dichloride, a reaction well-known for the tetrahalophosphoranes.¹⁰ Such a reaction would then make available many new structures presently unobtainable. In a somewhat similar manner, Komkov, Karavanov and Even¹¹ and Parshall¹² have reduced structures of

(1) Some of this work was the subject of a preliminary communication; L. D. Quin and J. S. Humphrey, Jr., *J. Am. Chem. Soc.*, **82**, 3795 (1960).

(2) Supported by the Duke University Research Council and in part by Research Grant No. E-3624 of the National Institute of Allergy and Infectious Diseases, U. S. Public Health Service.

(3) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, Chap. 3.

(4) W. T. Dye, *J. Am. Chem. Soc.*, **70**, 2595 (1948).

(5) A. Y. Yakubovich and G. V. Motsarev, *Zhur. Obshch. Khim.*, **23**, 1543 (1953).

(6) T. Weil, B. Prijs and H. Erlennmeyer, *Helv. Chim. Acta*, **35**, 1412 (1952); **36**, 1314 (1953).

(7) G. O. Doak and L. D. Freedman, *J. Am. Chem. Soc.*, **73**, 5658 (1951).

(8) P. C. Crofts, *Quart. Revs.*, **12**, 341 (1958).

(9) Reference 3, Chapter 4.

(10) L. D. Quin and C. H. Rolston, *J. Org. Chem.*, **23**, 1693 (1958), and other references cited therein.

(11) E. P. Komkov, K. U. Karavanov and S. Z. Even, *Zhur. Obshch. Khim.*, **28**, 2963 (1958).

(12) G. W. Parshall, *J. Inorg. Nucl. Chem.*, **12**, 372 (1960).

TABLE I

PROPERTIES OF NEW ARYLPHOSPHONOUS DICHLORIDES

R =	Yield, % ^a	B.p. ^b		Formula	Carbon, %		Hydrogen, %		Phosphorus, %	
		°C.	Mm.		Calcd.	Found	Calcd.	Found	Calcd.	Found
<i>m</i> -Cl	33 ^c	124-125	18	C ₆ H ₄ Cl ₃ P	33.76	34.04	1.89	2.06	14.51	14.65
<i>o</i> -Cl	29	76-77	0.53	C ₆ H ₄ Cl ₃ P	33.76	34.07	1.89	2.11	14.51	14.11
<i>m</i> -Br	22 ^d	119-122	6	C ₆ H ₄ BrCl ₂ P	27.97	28.11	1.56	1.76	12.02	11.71
<i>o</i> -CH ₃ O	10 ^e	88.5-89	0.52	C ₇ H ₇ Cl ₂ OP	40.42	40.76	3.39	3.32	14.89	14.62
<i>p</i> -CN	25 ^f	127-128	4.5	C ₇ H ₄ Cl ₂ NP	41.21	41.42	1.98	2.03	15.19	15.17
3-Cl-4-CH ₃	21	117-118	2.0	C ₇ H ₆ Cl ₃ P	36.96	38.04 ^g	2.66	2.87	13.62	12.82 ^g

^a Crude product by isolation procedure B, unless noted. ^b Analytical sample. ^c Isolation procedure A, including treatment with POCl₃; tri-*p*-cresyl phosphate was added as chaser in the distillation. ^d After fractionation. ^e After fractionation. Also recovered 4 g. of an unidentified liquid, b. 50-52° at 0.35 mm. *Anal.* C, 55.74; H, 4.86; P, 10.11. ^f POCl₃ was omitted in isolation. ^g Although these data are unsatisfactory, there is no doubt that the indicated compound was formed; hydrolysis gave the phosphinic acid, with correct analysis (see Table II).

the type RPhCl₂⁺ AlCl₄⁻¹³ to produce alkylphosphonous dichlorides.

The proposed reduction has been accomplished by the slow addition of magnesium turnings to the solution of the diazonium fluoroborate-phosphorus trichloride reaction product. A mildly to vigorously exothermic reaction occurs. No solid is precipitated; the magnesium presumably is converted to a halide soluble in the solvent ethyl acetate. Generally, one mole of magnesium has been used for each mole of diazonium fluoroborate charged, assuming the equation below to be correct



The magnesium usually was consumed completely. Since it is unlikely that the intermediate is formed quantitatively, the complete consumption of magnesium suggests its involvement in other reactions, such as with any hydrogen chloride present, or that its reducing action is more complicated than the equation indicates. The former suggestion receives support from the observation that when one-half of a molar equivalent of magnesium was used in one experiment, the same yield of the phosphonous dichloride as with a full equivalent was obtained.

That the products were in fact phosphonous dichlorides was established by preparing two known structures, *p*-chlorophenyl- and *p*-tolylphosphonous dichlorides. Boiling points agreed with published values, and correct analytical data were obtained. The phosphinic acids produced on hydrolysis also had the expected melting points and analyses. All new compounds isolated have been shown to be phosphonous dichlorides.

In isolating products of the new synthesis, two procedures have been used. Procedure A employed direct distillation of the reaction mixture. Procedure B involved distillation of solvent, addition of phosphorus oxychloride to the residue, extraction several times with an alkane-benzene mixture, and finally distillation of the extract. In the early work, procedure A was used. However, the product distillation is made difficult by the large solid residue. Procedure B largely eliminated this problem, as the solvent extraction step freed the phosphonous dichloride of inorganic matter prior to distillation. Benzene alone was, sur-

prisingly, a good solvent for the residual reaction product, but either hexane or heptane added in a ratio of about 2:1 to benzene led to two readily separated layers or caused formation of a tractable residue. The alkane alone generally was not suited for the extraction, as it mixed poorly with the viscous residue. Phosphorus oxychloride, effective in decomposing AlCl₃-ArPCl₂ complexes,⁴ was added with the hope of releasing any phosphonous dichloride complexed by magnesium salts, but little improvement in yield was realized by this treatment. Procedure B was mechanically superior, but did not always lead to as high a yield as procedure A. Thus a 37% crude yield of *p*-chlorophenylphosphonous dichloride was obtained by A, but only 20% by B. This might suggest that some of the product is present in a non-extractable but thermally released form. The course of the distillation in procedure A supports this; a bath temperature about 200° above head temperature was often required to obtain even a slow rate of distillation, and this at a time when the pot contents appeared quite dry. The yields in Table I probably can be bettered with improved isolation procedures. They are, nevertheless, in many cases close to the yields of the corresponding phosphinic acids produced in the Doak-Freedman reaction. The use of reducing agents other than magnesium also may prove to be beneficial. Methyl phosphorodichloridite (CH₃OPCl₂)¹⁰ was in fact tried in a preparation of *p*-chlorophenylphosphonous dichloride, but an inferior yield of a crude product resulted. Red phosphorus gave no recognizable reduction product. Further work along these lines seems indicated, however.

The scope of the new synthesis may in part be appreciated by examination of the compounds prepared so far (Table I).

An effort was made to produce simple structures, yet ones unobtainable by other methods. For example, *o*- and *m*-chlorophenylphosphonous dichlorides have now been made to accompany the known *p*-chloro compound. Similarly, *p*-cyanophenylphosphonous dichloride, which could not be made by reaction of phosphorus trichloride with benzonitrile,¹⁴ has been made and is the only known phosphonous dichloride with a strongly electronegative group.

A small but significant quantity of diarylphos-

(13) J. P. Clay, *J. Org. Chem.*, **16**, 892 (1951); A. M. Kinnear and E. A. Perren, *J. Chem. Soc.*, 3437 (1952).

(14) A. Michaelis, *Ann.*, **293**, 193 (1896); **294**, 1 (1897).

TABLE II

 PROPERTIES OF NEW ARYLPHOSPHINIC ACIDS R--PO₂H₂

R =	Recrystn. solv.	M.p., °C.	Formula	Carbon, %		Hydrogen, %		Phosphorus, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
<i>m</i> -Cl	CCl ₄	90.5-91.5	C ₆ H ₅ ClO ₂ P	40.87	41.17	3.43	3.65	17.31	17.11
<i>o</i> -Cl	CHCl ₃	128.5-129	C ₆ H ₅ ClO ₂ P	40.87	40.62	3.43	3.31	17.31	17.16
<i>m</i> -Br	CCl ₄	97-98	C ₆ H ₅ BrO ₂ P	32.61	32.84	2.74	2.81	14.02	14.21
<i>o</i> -CH ₃ O	CCl ₄ -C ₂ H ₅ OH	100-102	C ₇ H ₉ O ₃ P	49.13	48.97	4.12	4.44	18.01	18.10
<i>p</i> -CN	CCl ₄ -C ₂ H ₅ OH	166-167	C ₇ H ₇ NO ₂ P	50.31	50.61	3.62	3.87	18.54	18.20
3-Cl-4-CH ₃	CCl ₄	97.5-98.5	C ₇ H ₇ ClO ₂ P	45.15	44.96	4.33	4.42	16.63	16.82

phinic acid (Ar₂PO(OH)) accompanies the phosphonic acid in the Doak-Freedman reaction, and it might be expected that its precursor would lead in the present work to diarylphosphinous chlorides. No search was conducted for these high-boiling side-products, and in only one case was any evidence for a diaryl compound obtained. In the preparation of *o*-methoxyphenylphosphonous dichloride, a distinct fraction preceded this compound on distillation. Its analysis (Table I, footnote *e*) clearly suggested a ratio of two phenyls per phosphorus, but the data were in poor agreement with bis-(*o*-methoxyphenyl)-phosphinous chloride and actually were somewhat better for bis-(*o*-methoxyphenyl)-phosphinyl chloride, both presently unknown. Neither of these structures would be expected to have a boiling point lower than that of the phosphonous dichloride, however. Hydrolysis of the compound failed to give a crystalline product, and its structure remains unknown.

The phosphonous dichlorides are reactive compounds serving as precursors for several other classes of organophosphorus compounds.⁸ In this study, all new dichlorides were hydrolyzed, in 60-80% yield, to phosphinic acids (Table II). Of these acids, only one, the 3-chloro-4-methyl derivative, has been claimed previously; Melchiker¹⁵ reported its m.p. as 70°. However, a value of 97.5-98.5° was found in this work. It appears that Melchiker actually had an isomer, probably 4-chloro-3-methyl. Freedman¹⁶ also has found that the 3-chloro-4-methylphenylphosphonic acid of Melchiker¹⁵ probably is the 4-chloro-3-methyl isomer. Melchiker used the reaction of phosphorus trichloride with *o*-chlorotoluene; the formation of the 4-chloro-3-methyl isomer is, of course, not unexpected in such a Friedel-Crafts reaction.

The present work may be of some significance in elucidating the nature of the intermediate of the Doak-Freedman reaction. Although boron trifluoride certainly is evolved in this reaction, Crofts⁸ nevertheless expressed the intermediate as a phosphonium fluoroborate, ArPCL₃⁺BF₄⁻. The present work has shown that some boron trifluoride is in fact retained; the boron trifluoride-ethyl acetate complex was isolated consistently in varying but significant amounts, particularly when isolation procedure A was used. A further point of interest is that no compounds containing a phosphorus-fluorine bond have been isolated after the reduction reaction. No information has been found on the relative ease of breaking P-F or

P-Cl bonds on reduction of mixed pentavalent phosphorus halides, but it seems reasonable to expect the latter to be broken more readily. This might suggest an absence of a P-F bond in the intermediate, in accord with Crofts' ionic structure. Experimental evidence on this point, however, is needed.

Experimental¹⁷

Preparation of Aryldiazonium Fluoroborates.—Procedure II described by Roe¹⁸ was used throughout this work. All salts were dried overnight *in vacuo* over phosphorus pentoxide.

General Procedure for Synthesis of Arylphosphonous Dichlorides.—Reactions generally were performed on a 0.2-0.3-mole scale. Quantities specified hereafter are based on a 0.2-mole charge. The dry diazonium fluoroborate was suspended under nitrogen in 250 ml. of ethyl acetate (dried over phosphorus pentoxide and distilled). Cuprous bromide (2.0 g.) was added, and then 27.5 g. (0.2 mole) of phosphorus trichloride was dropped in. The reaction generally started after 15-30 min.; occasionally heating was required. After gas and heat evolution were complete, the mixture was stirred 1 hour. Magnesium turnings (4.9 g., 0.2 mole) were added in small portions. The reaction required cooling and generally was held at 30-50°. Addition was complete within 1 hr. The final product was a highly colored solution with a trace of solid usually present.

Isolation of Phosphonous Dichlorides.—The reaction mixture was flash distilled *in vacuo* to remove solvent and low-boiling compounds.

Procedure A.—The viscous residue was distilled directly *in vacuo*. The boron trifluoride-ethyl acetate complex was collected at 60-64° at 35 mm.¹⁹ The bath temperature was raised to about 300-400° while the pressure was lowered to 10-20 mm. The phosphonous dichloride distilled slowly and, in some cases, unevenly, leaving a large solid residue. Fuming occasionally accompanied the distillation. Generally only a main product fraction was collected.

Procedure B.—The residue was treated with 60 g. of phosphorus oxychloride and dissolved in 100 ml. of benzene. The solution was poured into 200 ml. of hexane or heptane. After a solid or liquid lower layer settled, the supernatant liquid was decanted and saved. The extraction was repeated twice with 100 ml. of 2:1 (v./v.) alkane-benzene. Extracts were combined, flash distilled, and the residual liquid distilled at 10-20 mm. Only a small amount of boron trifluoride-ethyl acetate complex was obtained. The pot residue was quite small compared to that of procedure A and the distillation was much smoother. The crude distillate from either procedure was redistilled through a 20-cm. column of Heli-pak (Hastelloy B). Generally only a small forerun was collected and little or no high boiling residue remained. All products, except 3-chloro-4-methylphenylphosphonous dichloride, were analytically pure after this

(17) Melting and boiling points are uncorrected. Analyses are by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y., and Galbraith Microanalytical Laboratories, Knoxville, Tenn.

(18) A. Roe in "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 193.

(19) G. T. Morgan and R. Taylor, *J. Soc. Chem. Ind.*, **50**, 869 (1931), reported b.p. 123° at 772 mm. The present compound was not obtained analytically pure; however, values for C and F were near the expected range and no P was present.

(15) P. Melchiker, *Ber.*, **31**, 2915 (1898).

(16) L. D. Freedman, private communication, Aug., 1960.

rectification. For the new compounds, yields, boiling points and analytical results are recorded in Table I, along with notes on minor variations in the general isolation procedures. Previously reported *p*-chlorophenyl- and *p*-tolylphosphonous dichlorides were also prepared; their b.p. of 132–133° at 20 mm. and 109–110° at 11 mm., respectively, agreed with literature values^{20,21} and they gave correct analyses. The best yields for these two compounds in several

(20) D. R. Nijk, *Rec. trav. chim.*, **41**, 461 (1922).

(21) B. Buchner and L. B. Lockhart, Jr., *J. Am. Chem. Soc.*, **73**, 755 (1951).

experiments were 37 and 20%, respectively, employing isolation procedure A.

Preparation of Phosphinic Acids.—A 5–10-g. sample of the phosphonous dichloride was dropped into an ice-water mixture with stirring. The acid precipitated and after filtration was recrystallized from appropriate solvents (Table II). Properties of new compounds appear in Table II. *p*-Chlorophenyl- and *p*-tolylphosphinic acids also were prepared; their m.p.'s were 131–132° and 104–105°, respectively, in agreement with literature values.^{13,22}

(22) A. Michaelis and C. Panek, *Ann.*, **212**, 203 (1882).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH, PITTSBURGH, PENNSYLVANIA, AND DOW CORNING CORPORATION, MIDLAND, MICHIGAN]

Electric Moments and Structures of Organosilicon Compounds. IV. The Silicon-Hydrogen Bond^{1,2}

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Dielectric constants and densities at 25° have been determined for benzene solutions of *meta*- and *para*-chlorophenyltrimethylsilanes, -dimethylsilanes, -methylsilanes and -silanes; these are quadratic functions of the concentrations. The dipole moments of the compounds have been calculated by means of the Hedestrand and Debye equations. The dipole moments in benzene solution have been found to be: *meta*-chlorophenyltrimethylsilane, 1.83 *D*; *para*-chlorophenyltrimethylsilane, 1.84 *D*; *meta*-chlorophenyldimethylsilane, 1.74 *D*; *para*-chlorophenyldimethylsilane, 1.69 *D*; *meta*-chlorophenylmethylsilane, 1.61 *D*; *para*-chlorophenylmethylsilane, 1.45 *D*; *meta*-chlorophenylsilane, 1.42 *D*; *para*-chlorophenylsilane, 0.99 *D*. From the moment of *meta*-chlorophenylsilane a value of 0.41 *D*, with hydrogen negative, has been calculated for the C_{ar}SiH group moment. Inconsistency between the *meta* and *para* series has been attributed to the greater importance in the latter of (dπ-π) bonding of the phenyl ring into silicon, and within the former to hindered rotation about the SiC_{ar} bond, resulting from intramolecular dipole-dipole interaction.

Despite the importance of the Si-H bond in synthetic and theoretical organosilicon chemistry, its moment has received relatively little attention. The dipole moments of a number of Si-H containing compounds have been measured, but in interpreting the results the effect of the Si-H bond moment has in general been neglected. Brockway and Coop⁴ compared the moments of the series H_{*n*}-SiCl_{4-*n*}, and Reilly, Curran and McCusker⁵ those of H₃SiCl and Et₃SiCl, with the moments of the carbon analogs, but directed their attention entirely to the SiCl and SiC bonds, assuming the equivalence of the Si-H and C-H bond moments. The latter⁵ also measured the dipole moments of the series bromotriphenylsilane, dibromophenylsilane and bromophenylsilane and considered the decrease of the moments with increasing hydrogen substitution in terms only of steric inhibition of resonance.

Spauschus and his co-workers⁶ used the electronegativity difference⁷ for Si-H, 0.3 *D* with hydrogen negative, in estimating a value for comparison with their measured moment for triethylsilane. This assignment of direction to the Si-H moment is supported by direct chemical evidence. The direction of addition of SiH compounds to olefinic

double bonds,⁸ the fact that on hydrolysis of Si-H containing compounds the hydrogen leaves the silicon as the hydride anion,⁹ the reaction of triorgano-substituted silanes with alkyllithium compounds¹⁰ and the failure of experiments aimed at effecting the interchange of silane hydrogen for deuterium in EtOD, D₂O, and Et₂ND¹¹ have all been interpreted as evidence for Si⁺H⁻ polarization of the bond. The success of Sommer and Frye¹² in effecting isotope interchange between a deuterio-silane and lithium aluminum hydride is in accordance with this interpretation.

One calculation of the Si-H bond moment has been reported: Altshuller and Rosenblum¹³ obtained for it a value of 1.0 *D*, with hydrogen negative. This value was based on that of 2.3 *D* for the moment of the Si-F bond obtained from infrared intensity measurements on silicon tetrafluoride¹⁴ and on those of 1.26 and 1.268 *D* for the dipole moments of trifluorosilane¹⁵ and fluorosilane¹⁶ obtained from measurements on the Stark

(8) L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, *J. Am. Chem. Soc.*, **69**, 188 (1947); A. J. Barry, L. DePree, J. W. Gilkey and D. E. Hook, *ibid.*, **69**, 2916 (1947); G. H. Wagner and C. O. Strother, U. S. 2,632,013 (March 17, 1953).

(9) F. P. Price, *J. Am. Chem. Soc.*, **69**, 2600 (1947).

(10) H. Gilman and S. P. Massie, Jr., *ibid.*, **68**, 1128 (1946).

(11) A. I. Brodskii and I. G. Khaskin, *Doklady Akad. Nauk S.S.S.R.*, **74**, 299 (1950) [*C. A.*, **45**, 423 (1951)]; I. G. Khaskin, *ibid.*, **85**, 129 (1952) [*C. A.*, **46**, 10999 (1952)].

(12) L. H. Sommer and C. L. Frye, *J. Am. Chem. Soc.*, **81**, 1013 (1959).

(13) A. P. Altshuller and L. Rosenblum, *ibid.*, **77**, 272 (1955).

(14) P. N. Schatz and D. F. Hornig, *J. Chem. Phys.*, **21**, 1516 (1953).

(15) S. N. Ghosh, R. Trambarulo and W. Gordy, *ibid.*, **21**, 308 (1953).

(16) A. H. Sharbaugh, V. C. Thomas and B. S. Pritchard, *Phys. Rev.*, **78**, 64 (1950).

(1) Paper III, *J. Am. Chem. Soc.*, **75**, 2824 (1953).

(2) Taken from the Ph.D. thesis of A.M.C., August, 1958.

(3) Department of Chemistry, University of Arizona, Tucson, Ariz. Reprints from A.M.C., Dow Corning Corporation, Midland, Michigan.

(4) L. O. Brockway and I. E. Coop, *Trans. Faraday Soc.*, **34**, 1429 (1938).

(5) E. L. Reilly, C. Curran and P. A. McCusker, *J. Am. Chem. Soc.*, **76**, 3311 (1954).

(6) H. O. Spauschus, A. P. Mills, J. M. Scott and C. A. MacKenzie, *ibid.*, **72**, 1377 (1950).

(7) L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, New York, 1939, p. 64.