

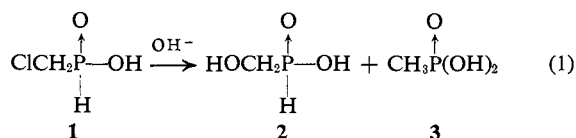
## Chemistry of Chloromethylphosphinic Acid. II.<sup>1</sup> Evidence for a 1,2-Shift of Hydride from Phosphorus to Carbon in the Hydrolytic Conversion of Chloromethylphosphinic Acid to Methylphosphonic Acid

C. E. Griffin, E. H. Uhing, and A. D. F. Toy

Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, and Research Laboratories, Stauffer Chemical Company, Chicago Heights, Illinois. Received May 21, 1965

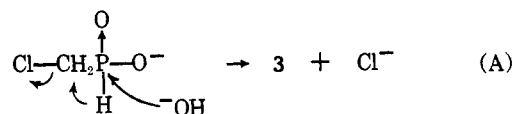
The hydrolytic conversion of chloromethylphosphinic acid (1) to methylphosphonic acid (3) by the action of aqueous sodium hydroxide has been studied by p.m.r. techniques. The insignificant incorporation of deuterium into 3 during hydrolysis in deuterium oxide established the conversion to be predominantly (95%) intramolecular. These results support a mechanistic pathway involving attack of hydroxide ion on phosphorus in 1 with a concomitant 1,2-shift of hydride ion from phosphorus to carbon displacing chloride ion to yield 3. An alternative mechanism involving a phosphorane intermediate is inconsistent with the experimental observations. Similar results are obtained from a study of the aqueous hydrolysis of the P-deuterio analog of 1.

Uhing, Rattenbury, and Toy<sup>1</sup> have shown that chloromethylphosphinic acid (1) undergoes a rapid, near quantitative, liberation of chloride ion in refluxing excess (4 moles of OH<sup>-</sup>/mole of 1) aqueous alkali. A minor yield (ca. 12%) of the anticipated displacement product, hydroxymethylphosphinic acid (2), was obtained; the major product of the hydrolysis was shown to be methylphosphonic acid (3). It was further shown that 2 was not a precursor of 3 under these



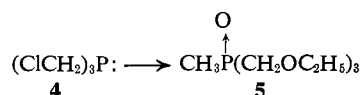
conditions. The formation of 3 from 1 was shown to be facilitated by high concentrations of hydroxide ion; the use of calcium and magnesium hydroxides and stoichiometric amounts of sodium hydroxide led to higher yields of 2 and its transformation products. On the basis of these and other reactivity studies, it was postulated that the formation of 3 proceeded by attack of hydroxide ion on the phosphorus atom of 1 with a subsequent or synchronous 1,2-shift of hydride ion from phosphorus to carbon leading to an internal displacement of chloride ion and formation of 3 (eq. A). Sommer and co-workers have postulated a similar

(1) Part I: E. Uhing, K. Rattenbury, and A. D. F. Toy, *J. Am. Chem. Soc.*, **83**, 2299 (1961).

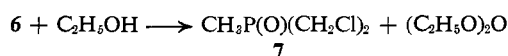
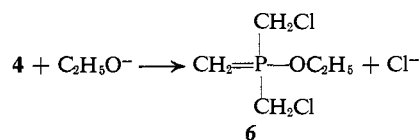


1,2-hydride shift leading to halide displacement for the rearrangement of halomethyldimethylsilanes to trimethylsilanol in alkaline solution.<sup>2</sup>

A somewhat related rearrangement process has been reported by Kabachnik and Tsvetkov<sup>3</sup> who showed that tris(chloromethyl)phosphine (4) is converted to methylbis(ethoxymethyl)phosphine oxide (5) by reaction with refluxing ethanolic sodium ethoxide. Based upon the concept of "pseudo-allylic" reactivity (ClCH<sub>2</sub>P:



← Cl-CH<sub>2</sub>=P+) developed by Nesmeyanov and Kabachnik<sup>4</sup> to account for the reactivity of similar systems, it was proposed that the conversion of 4 to 5 proceeded by attack of ethoxide ion on the phosphorus atom of 4 with displacement of chloride ion to yield an alkylidene phosphorane (6); protonation and cleavage of 6 would yield 7 and diethyl ether. Subsequent displacements of the chlorines of 7 by ethoxide ion would yield 5.

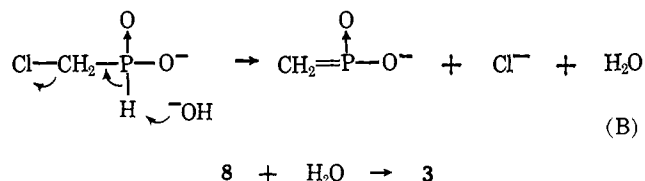


Based upon these considerations, Kabachnik and Tsvetkov suggested that the conversion of 1 to 3 could also follow a "pseudo-allylic" reaction path, i.e., abstraction of the P-proton of 1 by hydroxide ion with the concomitant elimination of chloride to yield an intermediate 8 which then undergoes hydration by solvent to yield the observed product (3).

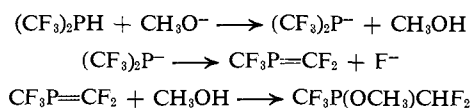
(2) L. H. Sommer, W. P. Barie, Jr., and D. R. Weyenberg, *ibid.*, **81**, 251 (1959).

(3) M. I. Kabachnik and E. N. Tsvetkov, *Proc. Acad. Sci. USSR, Chem. Sect.*, **143**, 211 (1962).

(4) A. N. Nesmeyanov and M. I. Kabachnik, *Zh. Obsch. Khim.*, **25**, 41 (1955).



Intermediates similar to **6** and **8** have also been proposed by Haszeldine and co-workers in the reactions of  $\alpha$ -fluorinated phosphines with bases.<sup>5</sup> Thus, in the conversion of bis(trifluoromethyl)phosphine to methyl difluoromethyltrifluoromethylphosphinite with methanolic sodium methoxide, the following reaction pathway is proposed.



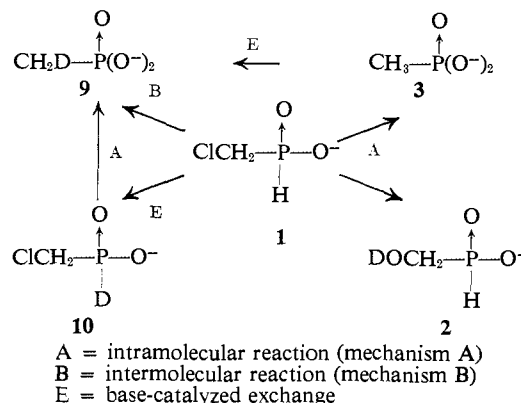
Since a number of rearrangements related to that of eq. 1 have recently been observed in these laboratories, a determination of the mechanism of this reaction became desirable. A clear choice exists between the two possible mechanisms (A and B). In mechanism A, the proton which ultimately replaces the chloride of **1** is the proton originally attached to phosphorus, while in mechanism B the solvent provides this proton. Thus, it was felt that deuteration studies should provide a clear differentiation between the essentially intramolecular (A) and intermolecular (B) mechanistic possibilities. Hydrolysis of **1** with NaOD in D<sub>2</sub>O should produce the nondeuterated product (**3**) if process A is operative and the mono- $\alpha$ -deuterated analog (**9**) of **3** if process B is operative. Thus analysis of the reaction mixture for the presence and relative amounts of products (**3** and **9**), unreacted **1**, and the normal displacement product (**2**) should provide the basis for a choice of mechanism.

The proton magnetic resonance (p.m.r.) parameters of **1**, **2**, and **3** (**9**) suggested that the course of hydrolysis could be followed conveniently by this method. The following doublets were observed: **1**,  $\tau_{\text{CH}_2}$  6.33 ( $J_{\text{PCH}} = 8.0$  c.p.s.),  $\tau_{\text{PH}}$  3.32 ( $J_{\text{PH}} = 697$  c.p.s.); **2**,  $\tau_{\text{CH}_2}$  6.03 ( $J_{\text{PCH}} = 9.1$  c.p.s.),  $\tau_{\text{PH}}$  2.75 ( $J_{\text{PH}} = 710$  c.p.s.); **3**,  $\tau_{\text{CH}_3}$  8.37 p.p.m. ( $J_{\text{PCH}} = 14.3$  c.p.s.). The chemical shifts for each of the signals were such that integrations could be carried out satisfactorily and the relative amounts of **1**, **2**, **3**, and **9** determined by conventional normalization techniques.

One major competing reaction which could exert an effect on the results was anticipated. The exchange of the phosphorus-bonded proton of phenylphosphinic acid with deuterium in D<sub>2</sub>O has been shown to be catalyzed by base.<sup>6</sup> If such an exchange occurred with **1** at any rate comparable with the conversion of **1** to **3**, significant amounts of **10** would be formed. Intramolecular conversion (mechanism A) of **10** would then produce **9**, the product of intermolecular reaction of **1**. An intermolecular conversion of **10** would also produce **9**. However, the p.m.r. spectra of the reaction mixture components provide a check on the extent of such exchange. The difference between the adjusted

integrals of the 6.33- ( $\text{CH}_2$  of **1** and **10**) and 3.32- p.p.m. (P-H of **1**) signals should reflect the extent of formation of **10**. A correction could then be applied for the maximum amount of **9** arising by internal conversion of **10**. The various reactions and products envisioned in the treatment of **1** with NaOD in D<sub>2</sub>O are summarized in Chart I.

Chart I. Hydrolysis of Chloromethylphosphinic Acid with NaOD in D<sub>2</sub>O



The hydrolysis of a 15% solution of **1** in 99.8% D<sub>2</sub>O containing an eightfold excess of NaOD was carried out at 80° for 4 hr. A high concentration of base was employed to minimize the formation of **2**.<sup>1</sup> Aliquots of the reaction mixture were removed at 30-min. intervals and analyzed.<sup>7</sup> The results presented in Table I represent the average values of at least six separate determinations. Neglecting the exchange reaction (**1** → **10**) as a source of **9**, the relative yields of **3** and **9** indicate that 92–94% of the conversion proceeds by the intramolecular process (mechanism A). The detection of **10** in the reaction mixture indicates that the simple exchange reaction proceeds to a measurable extent under these conditions.

Table I. Product Yields in the Reaction of Chloromethylphosphinic Acid (**1**) with NaOD in D<sub>2</sub>O

Time, hr.	Yield, mole %				
	<b>1</b>	<b>10</b>	<b>3</b>	<b>9</b>	<b>2</b>
0.0	100.0	...	...	...	...
0.5	88.9	0.1	10.0	0.0	0.7
1.0	77.4	0.6	19.4	1.4	1.2
1.5	67.5	0.9	27.8	2.0	1.8
2.0	54.4	1.4	38.8	3.2	2.2
2.5	44.9	1.1	47.5	3.7	2.8
3.0	32.7	2.6	57.3	4.0	3.4
3.5	21.0	3.1	66.5	5.2	4.2
4.0	10.2	3.4	75.7	5.8	4.9

Another source of **9** in this system was also considered to be feasible. A number of examples of phosphono group labilization of  $\alpha$ -CH functions toward the action of base have been reported,<sup>8,9</sup> although, in general, abstraction of this proton is slow in the absence of a second activating group. In a relevant example, it has been shown that diethyl

(7) Details of the p.m.r. analytical method are presented in the Experimental Section.

(8) G. M. Kosolapoff, *J. Am. Chem. Soc.*, **75**, 1500 (1953); D. J. Cram and R. D. Partos, *ibid.*, **85**, 1093 (1963).

(9) V. F. Martynov and V. E. Timofeev, *J. Gen. Chem. USSR*, **32**, 3383 (1962); C. E. Griffin and R. H. Churi, unpublished observations.

(5) G. M. Burch, H. Goldwhite, and R. N. Haszeldine, *J. Chem. Soc.*, 572 (1964); H. Goldwhite, R. N. Haszeldine, and D. G. Roswell, *Chem. Commun.* (London), 83 (1965).

(6) J. Reuben, D. Samuel, and B. L. Silver, *J. Am. Chem. Soc.*, **85**, 3093 (1963).

chloromethylphosphonate can be converted to its anion by the attack of alkoxide.<sup>9</sup> If the  $\alpha$  protons of **3** were sufficiently acidic, OD<sup>-</sup> catalyzed deuteration would serve to convert **3** to **9**; subsequent deuteration of **9** could produce the dideuterio analog **11**, and ultimately the trideuterio compound. Since the occurrence of such deuteration would provide a higher yield of **9** than would be obtained directly from **1** by process B, the extent of deuteration of **3** under the reaction conditions cited above was determined. The decrease in the integrated intensity of the methyl signal of **3** indicated a maximum of 1.7% deuteration after 4 hr. Percentage exchange at 1, 2, and 3 hr. was 0.3, 0.7, and 1.2, respectively.

The demonstration of the exchange processes leading to the formation of **10** and **9** from **1** and **3** indicates that a portion of the monodeuterio compound (**9**) observed in the reaction (Table I) could arise by direct exchange (**3**  $\rightarrow$  **9**) or by a process A reaction of **10**. Using the data regarding exchange with **3**, exchange of **1** to form **10** and the extent of conversion of **1** to **3** from Table I, it is possible to correct the data of Table I to reflect the relative amounts of rearrangement occurring by intra- and intermolecular routes. Thus, for the 4-hr. reaction data, a total of 76% of the observed **9** can be attributed to either direct exchange with **3** or intramolecular conversion of **10**. The corrected percentages of product formed by mechanisms A and B are 80.1 and 1.4, respectively, indicating that the reaction proceeds to the extent of 97–98  $\pm$  2.5% by the intramolecular pathway. Because of the errors in the analytical method and the inability to detect trace amounts of di- and trideuterated products, the occurrence of conversion by the intermolecular process postulated by Kabachnik and Tsvetkov<sup>3</sup> for this reaction cannot be ruled out; however, contributions from this reaction pathway probably represent no more than a maximum of 5%.

The results cited above were confirmed by a parallel study of the hydrolysis of **10** in H<sub>2</sub>O with NaOH. The preparation of **10** was achieved by the hydrolysis of chloromethylphosphonous chloride with a concentrated solution of DCl in D<sub>2</sub>O. Within experimental error, figures comparable to those of Table I were obtained for the yields of the analogous products. Thus, after a 4-hr. reaction period, the following products were observed: **10**, 10.2%; **1**, 2.8%; **9**, 76.2%; **3**, 5.9%; and **2**, 4.9%. Similar data were obtained on shorter reaction times and, again, it is indicated that the rearrangement proceeds by process A to the extent of 97–98%.

In order to demonstrate the lack of unanticipated reactions and side products which would render the analytical method invalid, the mass spectra of a number of reaction mixtures were examined. No peaks which could not be attributed to the products already cited were observed; good qualitative agreement with the p.m.r. analytical results was obtained. Parent peaks corresponding to the di- (**11**) and trideuterated methylphosphonic acids were observed, but their intensities indicated them to be present in only trace quantities.

To provide a further check on the analytical method and confirmation of the extent of deuteration, the product of a large-scale hydrolysis of **1** with NaOD in D<sub>2</sub>O was treated with excess thionyl chloride to

convert the acids to the corresponding chlorides. The methylphosphonic dichloride was isolated and esterified with methanol to yield dimethyl methylphosphonate (**12**) in 66.4% yield; p.m.r. analysis of the hydrolysis mixture had indicated **3** and **9** to be formed in 81.9% yield (93% **3**; 7% **9**). The ratio of the integrated intensities of the O- and P-methyl signals of **12** isolated by this procedure indicates 92.5% P-methyl and 7.5% P-CH<sub>2</sub>D products to be present, confirming the results of p.m.r. analysis.

The studies cited above establish the hydrolytic conversion of **1** to **3** to be an example of a 1,2-shift of hydride ion from phosphorus to carbon, confirming the originally postulated mechanism.<sup>1</sup> Further studies of this general type of reaction proceeding with both phosphorus-hydrogen and phosphorus-carbon bond cleavages are in progress.

### Experimental Section<sup>10</sup>

**Materials and Hydrolytic Procedure.** Chloromethylphosphonic acid (**1**) and hydroxymethylphosphonic acid (**2**) were prepared by established procedures<sup>1</sup>; P-deuterio **1** (**10**) was prepared by the hydrolysis of chloromethylphosphonous chloride<sup>1</sup> with a concentrated solution of DCl in D<sub>2</sub>O. Methylphosphonic acid (**3**) was prepared by hydrolysis of dimethyl methylphosphonate with constant boiling hydrochloric acid. Deuterium oxide (99.8%) was obtained from BioRad Laboratories.

For hydrolysis studies, a stock solution containing 1.5 g. of **1** in 10 ml. of D<sub>2</sub>O containing an eightfold excess of NaOD was prepared. Aliquots (1 ml.) of this stock solution were sealed in glass ampoules and held at 80  $\pm$  1° with ampoules being removed from the bath at 30-min. intervals for analysis. The hydrolysis of **10** with NaOH in H<sub>2</sub>O was carried out in the same manner.

**Reference Spectra and Analytical Method.** The p.m.r. spectra of compounds **1**, **2**, and **3** were determined in D<sub>2</sub>O containing a two-molar excess of NaOD. The following parameters were observed: **1**,  $\tau_{\text{CH}_2}$  6.33 (216 and 224 c.p.s. downfield from DSS, A),  $\tau_{\text{PH}}$  3.32 (52 and 749 c.p.s., B); **2**,  $\tau_{\text{CH}_2}$  6.03 (234 and 243 c.p.s., C),  $\tau_{\text{PH}}$  2.75 (80 and 790 c.p.s.); **3**,  $\tau_{\text{CH}_3}$  8.37 (91 and 105 c.p.s., D). The analysis of reaction mixtures from the hydrolysis of **1** (NaOD in D<sub>2</sub>O) for the components **1**, **2**, **3**, **9**, and **10** was carried out in the following manner. Aliquots (1 ml.) of the reaction mixture were taken at the times indicated in Table I, cooled rapidly, and stored at 5°; in blank studies, it was shown that no detectable hydrolysis of **1** occurred at 5° for periods of less than 8 hr. The p.m.r. spectra of all of the aliquots from a given 4-hr. run were recorded at one time, and at least six separate integrations of all of the observed peaks were recorded for each separate aliquot. Spectrometer operating and integration parameters were chosen to give a near full scale deflection for the highest intensity peak of each spectrum. The integrated intensity of the methylene peak (A) of **1** at zero time was used as a reference (area = 1.0), and all peak areas in subsequent aliquots were normalized on this basis. Concentrations of

(10) All p.m.r. spectra were determined with a Varian Associates A-60 spectrometer (probe temperature 32°). All chemical shifts are given on the  $\tau$  scale with DSS (sodium 3-trimethylsilylpropanesulfonate) as an internal standard ( $\tau$  10.00).

each of the species in the reaction mixture were determined by solution of the following equations.

$$\text{mole \% } 2 = \text{area C}$$

$$\text{mole \% } (1 + 10) = \text{area A}$$

$$\text{mole \% } 10 = \text{area A} - 2(\text{area B})$$

$$\text{mole \% } [\frac{2}{3}(3 + 9)] = \frac{2}{3}(\text{area D})$$

$$\text{mole \% deuterium incorporated} = \frac{\text{mole \% } (9 + 10)}{\text{area } (A + B + C + D)} = 1.0 -$$

Known mixtures of **1**, **2**, **3**, **9**, and **10** were analyzed by this procedure and good agreement was obtained among separate determinations; the probable error was  $\pm 1.5\%$ . Analyses of reaction mixtures were also carried out by the use of weighed amounts of both DSS and maleic acid as internal standards. Use of either the Si-CH<sub>3</sub> or vinylic proton signals of these materials as references gave results which agreed with those of the normalization technique within experimental error. The same techniques were also used for the study of the hydrolysis of **10** in H<sub>2</sub>O with NaOH.

*Large-Scale Hydrolysis.* A solution of 15.0 g. (0.13 mole) of **1** in 100 ml. of D<sub>2</sub>O containing 1.00 mole of NaOD was held at 80° for 4 hr. The reaction mixture was acidified with excess concentrated hydrochloric

acid, evaporated to dryness, and extracted with ethyl alcohol following the established isolation procedure.<sup>1</sup> The alcoholic extract was concentrated at 70° (0.1 mm.) to a viscous liquid residue. Thionyl chloride (29.0 g., 0.25 mole) was added with stirring to the liquid residue; a large amount of hydrogen chloride was evolved and the reaction temperature rose to 55°. The reaction mixture was distilled to yield methylphosphonic dichloride, b.p. 105–110° (100 mm.), m.p. 30–31° (lit.<sup>1</sup> m.p. 30–32°). A solution of the dichloride in 100 ml. of methanol containing 0.5 mole of pyridine was refluxed for 8 hr. The solution was concentrated under reduced pressure, diluted with water, and extracted with ether. After drying over sodium sulfate, the ethereal solution was concentrated and distilled to give 10.7 g. (66.4%) of dimethyl methylphosphonate (**12**) which was identified by infrared, p.m.r., and gas-liquid chromatographic comparisons with an authentic sample. The ratio of the integrated intensities of the O-CH<sub>3</sub> ( $\tau$  6.33,  $J_{\text{PH}} = 10.8$  c.p.s.) and P-CH<sub>3</sub> ( $\tau$  8.59,  $J_{\text{PH}} = 17.4$  c.p.s.) signals in CCl<sub>4</sub> indicated the presence of 7.5% of the monodeuterated compound. The mass spectrum of this material showed parent peaks at  $m/e$  124 (major), 125 (minor), 126 (trace), and 127 (trace) attributable to **12**, **12-d<sub>1</sub>**, **12-d<sub>2</sub>**, and **12-d<sub>3</sub>**, respectively.

## Electrophilic Catalysis in Nucleophilic Substitution and Elimination. III. Conductances of Some Silver and Tetraethylammonium Salts in Acetonitrile and the Kinetics of Reaction of 2-Octyl Bromide with Tetraethylammonium and Silver Nitrates in That Solvent<sup>1,2</sup>

Y. Pocker<sup>3</sup> and D. N. Kevill

*Contribution from the William Ramsay and Ralph Forster Laboratories, University College, London, England. Received January 30, 1965*

*In preparation for a kinetic study in acetonitrile in which tetraethylammonium and silver salts were used as reagents, a study was made of the conductance, at kinetically useful concentrations, of AgClO<sub>4</sub>, AgNO<sub>3</sub>, AgNO<sub>2</sub>, Et<sub>4</sub>NClO<sub>4</sub>, Et<sub>4</sub>NNO<sub>3</sub>, and Et<sub>4</sub>NNO<sub>2</sub> and of the equimolar mixtures AgNO<sub>3</sub>-Et<sub>4</sub>NNO<sub>3</sub> and AgNO<sub>2</sub>-Et<sub>4</sub>NNO<sub>2</sub>. The respective dissociation constants  $M^+X^- \rightleftharpoons M^+ + X^-$  were obtained by a Fuoss-Shedlovsky treatment. Of the six salts mentioned above only silver nitrite behaves abnormally in that for concentrations above  $2 \times 10^{-3}$  M there is little variation in the equivalent conductance as concentration is varied. The dominant dissociation of silver nitrite in the range 0.002–0.16 M is explained in terms of the following equilibrium:  $2\text{Ag}^+\text{NO}_2^- \rightleftharpoons \text{Ag}^+ + \text{Ag}(\text{NO}_2)_2^-$ . The*

*kinetics of the reaction of 2-octyl bromide with nitrate ions supplied (a) as Et<sub>4</sub>NNO<sub>3</sub>, (b) as AgNO<sub>3</sub>, and (c) as mixtures of Et<sub>4</sub>NNO<sub>3</sub>-AgNO<sub>3</sub> have been investigated, and the olefin proportion of the products has been determined. The extent of heterogeneous catalysis by silver bromide produced during the reaction with AgNO<sub>3</sub> is relatively unimportant. The reaction kinetics and the olefin proportion of the products have also been determined for the reaction of 2-octyl chloride and 1-octyl bromide with silver nitrate in acetonitrile. The reaction of 2-octyl bromide with Et<sub>4</sub>NNO<sub>3</sub> is a reversible bimolecular nucleophilic substitution with practically no elimination accompanying it. The proposed mechanistic scheme for silver nitrate catalysis involves the formation of an alkyl halide-silver ion complex. The subsequent reaction of this complex is rate determining. Anionic assistance (i.e., intervention by NO<sub>3</sub><sup>-</sup>) is shown to occur within this rate-determining step. The more detailed nature of this nucleophilic assistance requires that rates and products are determined by two different steps.*

(1) Part II: Y. Pocker, *J. Chem. Soc.*, 1972 (1960).

(2) Taken from part of the thesis presented by Dennis N. Kevill in partial fulfillment of the requirements for the Ph.D. Degree, University of London, Jan. 1960.

(3) To whom inquiries should be directed. Department of Chemistry, University of Washington, Seattle, Wash. 98105.