of acetone containing 10 g. of *p*-toluenesulfonic acid. Following 3 hr. of reflux the solution was neutralized with methanolic sodium hydroxide solution and, after filtering out sodium *p*-toluenesulfonate, concentrated to 800 ml. On chilling 220 g. of product, m.p. 117–119°, crystallized.

The ethanolic mother liquor from the ketal preparation was evaporated, and the residual oil treated with acetone and *p*-toluenesulfonic acid as described above to give an additional 35 g. of ketone. By concentration of the combined acetone mother liquors 48 g. of impure ketone was obtained, making the overall yield of ketone (XI) 58%, based upon the original diphenylchlorophosphine.

p-(1'-Hydroxyethyl)phenyldiphenylphosphine (XII). To a suspension of 254 g. (0.84 mole) of *p*-acetylphenyldiphenylphosphine (XI) in 1.2 l. of methanol was slowly added a solution of 32 g. (0.84 mole) of sodium borohydride in 0.5 l. of methanol. Mild cooling was needed to keep the temperature below 30°. After standing overnight 150 ml. of glacial acetic acid and 200 ml. of water were added. Four hours later 1.5 l. of water was added and the product was taken up in benzene and washed with dilute hydrochloric acid, dilute base, and water. Removal *in vacuo* of the benzene left 254 g. (99%) of a very viscous oil which resisted crystallization. The infrared spectrum (Table II) confirmed its structure.

p-Styryldiphenylphosphine (XIII). Over a 4-hr. period a solution of 253 g. (0.83 mole) of the carbinol (XII) in 250 ml. of toluene was dropped into a 40 cm. × 25 mm. column filled with 7–10 mesh activated alumina. The column was heated to 400°, with an exit pressure of 2–5 mm. and an inlet pressure of 15–20 mm. The tendency of the product to crystallize in the condenser below the column caused some difficulty.

From the Dry Ice trap protecting the vacuum pump approximately one-third of the toluene and 8 ml. (53%) of water were isolated. Addition of 500 ml. of methanol to the toluene solution of the product caused 46.2 gm. of white crystals, m.p. 74–76°, to form. By removing all the solvent *in vacuo* from the mother liquor, and treating the oily residue with methanol, an additional 34.1 g. of product was obtained, giving a total yield of 38%.

Acknowledgment. We wish to thank Dr. Murray Taylor of this laboratory for the microanalyses reported, and Mr. Harry Goldberg and Miss Carolyn Aldrich for measurements of infrared spectra.

SEATTLE, WASH.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

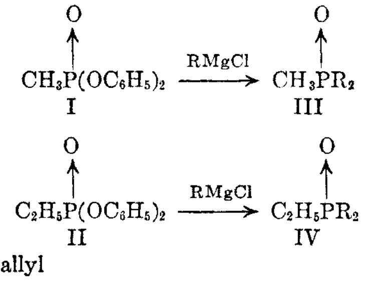
The Formation of Linear Polymers from Diene Monomers by a Cyclic Polymerization Mechanism. VII. Phosphorus-Containing Dienes[1]

K. DARRELL BERLIN[2] AND GEORGE B. BUTLER

Received May 9, 1960

Two unsymmetrical trialkylphosphine oxides, dimethallylmethylphosphine oxide and dimethallylethylphosphine oxide, have been synthesized. Polymerization of these monomers was initiated with α,α'-azobisisobutyronitrile and afforded soluble polymers. An intrinsic viscosity determination on a sample of poly(dimethallylmethylphosphine oxide) indicates it is of low molecular weight. Conversions to polymer are low for both oxides, and it is suggested that the presence of a large number of active hydrogen substituents may cause excessive degradative chain transfer.

The formation of linear polymers, *via* cyclic polymerization, from certain unsaturated, tertiary phosphine oxides has been reported from two independent studies.[3,4] Extension of this idea to include unsymmetrical trialkylphosphine oxides prompted this investigation. Dimethallylmethylphosphine oxide(III) and dimethallylethylphosphine oxide(II) were synthesized by treatment of the appropriate phosphonate with an excess of the methallyl Grignard reagent under forcing conditions. The yields approximated 50% in both cases. Preparation of diphenylmethylphosphonate (I)



$$\underset{\text{I}}{CH_3\overset{\overset{O}{\uparrow}}{P}(OC_6H_5)_2} \xrightarrow{RMgCl} \underset{\text{III}}{CH_3\overset{\overset{O}{\uparrow}}{P}R_2}$$

$$\underset{\text{II}}{C_2H_5\overset{\overset{O}{\uparrow}}{P}(OC_6H_5)_2} \xrightarrow{RMgCl} \underset{\text{IV}}{C_2H_5\overset{\overset{O}{\uparrow}}{P}R_2}$$

R = Methallyl

was by the method recorded in the literature.[5] The scheme below afforded diphenyl ethylphosphonate (II)[6,7] in an overall yield of 36%.

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(1) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract Number AF 33(616)-5616, Part I. Reproduction in whole or in part is permitted for any purpose of the United States government.

(2) Post-doctoral Fellow, 1958–1960; present address: Department of Chemistry, Oklahoma State University, Stillwater, Okla.

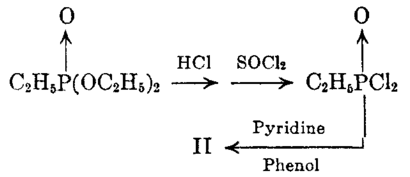
(3) K. D. Berlin and G. B. Butler, *J. Am. Chem. Soc.,* **82,** 2712 (1960).

(4) C. G. Gebelein and E. Howard, Jr., Abstracts of Papers, Third Delaware Regional Valley Regional Meeting, Philadelphia, February 25, 1960, p. 79.

(5) P. W. Morgan and B. C. Herr, *J. Am. Chem. Soc.,* **74,** 4526 (1952).

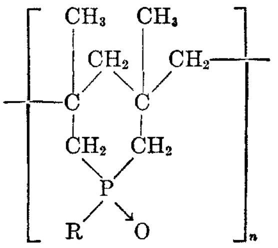
(6) A. E. Arbuzov and L. V. Nesterov, *Doklady Akad. Nauk S.S.S.R.* **92,** 57 (1953); *C.A.* **48,** 10538 (1954).

(7) A. E. Arbuzov and L. V. Nesterov, *Izvest Akad. Nauk S.S.S.R. Otdel Khim Nauk* 427 (1954); *Chem. Abstr.,* **49,** 9541 (1955).



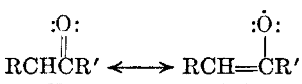
$$C_2H_5\overset{O\uparrow}{P}(OC_2H_5)_2 \xrightarrow{HCl} \xrightarrow{SOCl_2} C_2H_5\overset{O\uparrow}{P}Cl_2 \qquad C_2H_5\overset{O\uparrow}{P}Cl_2 \xrightarrow[Phenol]{Pyridine} II$$

Treatment of dimethallylmethylphosphine oxide (III) in bulk with catalytic amounts (up to 5%) of benzoyl peroxide apparently initiated little or no polymerization as unreacted monomer could be recovered in high yield. This is in contrast to the behavior of diallyphenylphosphine oxide and dimethallylphenylphosphine oxide.[3] The highest conversions of the trialkylphosphine oxides III and IV to soluble polymers were obtained by using azobisisobutyronitrile (5%) at a temperature of 110°. That poly(dimethallylmethylphosphine oxide) was not of high molecular weight was inferred by a low value (0.042) for its intrinsic viscosity. Infrared data demonstrate the existence of a small amount of residual unsaturation. Intramolecular cyclization during propagation would give polymers of the following structure.



R = CH_3, C_2H_5

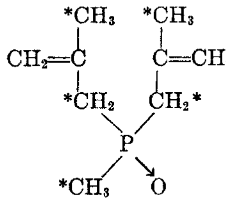
The small conversions of monomers with azobisisobutyronitrile as well as the negative results with benzoyl peroxide can probably be explained *in part* as another example of degradative chain transfer. In addition to the increased reactivity of hydrogen atoms on a carbon atom adjacent to a carbonyl function,[8,9,10] the stability of the radical resulting from hydrogen abstraction is well known.[11,12] Stabilization *via* the following contributing forms V and VI was postulated.[12] Alkylation of certain phosphonates, such as tetraethyl methanediphosphonate, attests to the activating influence of a phosphoryl group on flanking methylene hydrogen atoms.[13,14]



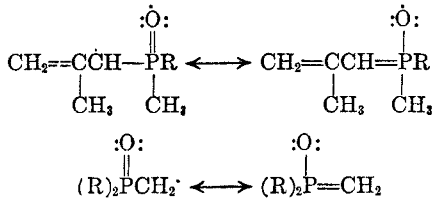
$$RCH\overset{:O:}{\overset{\|}{C}}R' \longleftrightarrow RCH{=}\overset{:\dot{O}:}{\overset{|}{C}}R'$$

V VI

The trialkylphosphine oxides encountered in this study possess hydrogen activated by unsaturated functions. For example, any of the carbon atoms marked by an asterisk in dimethallylmethylphosphine oxide (IIIa) might lose a hydrogen atom[15] to produce a radical which could be stabilized through interaction with a carbon-carbon double bond and/or through an enolic structure involving the phosphoryl group. Delocalization of the former type is well known in the polymerization of allyl compounds.[16] The enolic forms would include species which may also contribute to the overall phenomena of autoinhibition:



IIIa

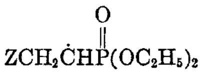


$$CH_2{=}\underset{CH_3}{C}CH{-}\overset{:\dot{O}:}{\overset{\|}{\underset{CH_3}{P}}}R \longleftrightarrow CH_2{=}\underset{CH_3}{C}CH{=}\overset{:\dot{O}:}{\overset{|}{\underset{CH_3}{P}}}R$$

$$(R)_2\overset{:O:}{\overset{\|}{P}}CH_2\cdot \longleftrightarrow (R)_2\overset{:O:}{\overset{|}{P}}{=}CH_2$$

R = Methallyl

Objections to this kind of delocalization have been expressed.[17] Attempts to copolymerize diethyl vinylphosphonate with styrene resulted in the incorporation of only a small amount of the phosphonate in the polymer. As a partial explanation it was suggested that the radical VII may not receive additional stabilization through enolic structures due to difficulty in creating carbon-phosphorus double bonds. A previous report indicated that the phosphonate did polymerize, however, but no conditions were presented.[18] Recent developments have established that carbon-phosphorus double bonds do exist and that the phosphorus-oxygen linkage does have some double-bond character



$$ZCH_2\dot{C}H\overset{O}{\overset{\|}{P}}(OC_2H_5)_2$$

VII

Z = Initiating radical

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[8] N. G. Gaylord and F. R. Eirich, *J. Am. Chem. Soc.*, **74**, 337 (1952).

[9] M. S. Kharasch, J. Kuderna, and W. Nudenberg, *J. Org. Chem.*, **18**, 1225 (1953).

[10] P. Gray and A. Williams, *Chem. Revs.*, **59**, 267 (1959).

[11] C. Walling, *Free Radicals in Solution*, John Wiley and Sons, Inc., New York, 1957, p. 276.

[12] T. M. Patrick, Jr., *J. Org. Chem.*, **17**, 1269 (1952).

[13] G. M. Kosolapoff and J. S. Powell, *J. Am. Chem. Soc.*, **72**, 4198 (1950).

[14] G. M. Kosolapoff, *J. Am. Chem. Soc.*, **75**, 1500 (1953).

[15] This could result from abstraction of hydrogen by the radical produced by decomposition of the initiator or by the radical generated during propagation.

[16] R. C. Labile, *Chem. Revs.* **58**, 807 (1958).

[17] C. L. Arcus and R. J. S. Matthews, *J. Chem. Soc.*, 4607 (1956).

[18] G. M. Kosolapoff, *J. Am. Chem. Soc.*, **70**, 1971 (1948).

reminiscent of a carbonyl function.[19] More recently it was found that di-*n*-propenylphenylphosphine oxide and diisopropenylphenylphosphine oxide could not be obtained by a Grignard reaction as the oxides polymerized *in situ* to give both soluble and insoluble polymers.[4]

EXPERIMENTAL[20]

Diethyl ethylphosphonate. This chemical was obtained from the Victor Chemical Company.

Diphenyl methylphosphonate. Diphenyl methylphosphonate was prepared in a manner similar to that described in the literature[5] with a few modifications which improved the yield slightly.

A mixture consisting of 155.0 g. (0.5 mole) of triphenyl phosphite, 71.0 g. (0.5 mole) of methyl iodide, and several boiling chips, was warmed slowly until a reaction began. After 48 hr. at reflux, the mixture was allowed to cool to room temperature whereupon it solidified. The solid was washed with dry ether and was decomposed (cautiously) in the following manner: 200 ml. of 10% aqueous sodium hydroxide was added slowly with cooling and stirring; 200 ml. of 5% aqueous sodium hydroxide was added, and the entire mixture was transferred to a separatory funnel. When excessive base was used or when the decomposition was effected without cooling, the yield of phosphonate was decreased presumably through saponification. The brown-colored mixture was extracted rapidly with four 200-ml. portions of ether. The ether solution was dried over sodium sulfate. Evaporation of the ether left an oil which was fractionated to give 86.8 g. (70%) of colorless diphenyl methylphosphonate, b.p. 145–148° (0.4 mm.); $n_{\rm D}^{21}$ 1.5519. The reported boiling point is 151° (0.8 mm.).[5]

Dimethallylmethylphosphine oxide. The general procedure was the same as that described previously in the preparation of dimethallylphenylphosphine oxide.[3]

To the methallyl Grignard reagent, prepared from 72.0 g. (3.0 g. atom) of magnesium and 181.0 g. (2.0 moles) of methallyl chloride in 1200 ml. of dry ether, was added a solution of 49.6 g. (0.2 mole) of diphenyl methylphosphonate in 400 ml. of dry benzene. The reaction mixture was decomposed and worked up in the usual manner, and the organic solvents were distilled. Careful fractionation of the residual oil gave 19.0 g. (57.5%) of dimethallylmethylphosphine oxide which distilled at 135–141° (2 mm.). The average yield in several runs was 50%. The oxide is extremely hygroscopic and was dried in a vacuum oven over phosphorus pentoxide for a month. The infrared spectrum[21] has peaks which can be ascribed to aliphatic hydrogen (2900 cm.$^{-1}$), a carbon-carbon double bond (1645 cm.$^{-1}$), a methyl-phosphorus linkage (1290 cm.$^{-1}$), a phosphoryl group (1185 cm.$^{-1}$), and a terminal methylene function (890 cm.$^{-1}$). There is also absorption of medium intensity at 1450 (broad), 1370, and 715 cm.$^{-1}$ (broad) as well as a small peak for water.

Anal.[22] Calcd. for $C_9H_{17}OP$: C, 62.79; H, 9.88; P, 18.02. Found: C, 62.56; H, 9.82; P, 17.40, 17.98.

Diphenyl ethylphosphonate. Although this compound has been reported previously, the procedures have involved the preparation of several uncommon intermediates at high temperatures.[6,7] The following procedure does not give superior yields but it can be carried out with general laboratory equipment and readily available starting materials.

Diethyl ethylphosphonate (166.0 g., 1.0 mole) was hydrolyzed with boiling, concd. hydrochloric acid (150 ml.) over a 16-hr. period. To the mixture was added a solution of benzene-toluene (100 ml.–50 ml.), and the water was azeotroped from the reaction flask. A white solid separated from the mixture upon cooling. An excess of thionyl chloride (216 ml.) was added to the solid and, as a reaction appeared to occur immediately, the solution was allowed to stand at room temperature for 12 hr. and was then refluxed for 4 hr. Excess thionyl chloride was removed under aspirator pressure, and the residual oil was fractionated. The acid chloride, which was faint-yellow in color, distilled at 56–60° (2.5 mm.); yield, 92.0 g. (62.5%). Bands for aliphatic hydrogen (2950 cm.$^{-1}$) and a phosphoryl group (1275 cm.$^{-1}$ are present in the infrared spectrum. Absorption is also evident at 1460, 1245, 750, and 715 cm.$^{-1}$

To the acid chloride in 250 ml. of dry ether was added, with cooling and stirring, a solution of 116.5 g. (1.24 moles) of phenol in 97.9 g. (1.24 moles) of pyridine. A cloudiness appeared in the mixture, and a precipitate began to settle almost immediately. The addition required 1 hr. and stirring was continued for another 4 hr. at room temperature. The pyridine hydrochloride was filtered, and the ether was evaporated. Diphenyl ethylphosphonate distilled at 159–161° (1–2 mm.), $n_{\rm D}^{21}$ 1.5453; yield 94.2 g. (57% based on the acid chloride or 36% based on the diethyl ethylphosphonate converted). The reported boiling point is 202° (13 mm.), $n_{\rm D}^{20}$ 1.5451.[6] The results were obtained from only one run, and undoubtedly they could be improved by meticulous purification at each stage. The infrared spectrum of this phosphonate is similar to the spectrum of diphenyl methylphosphonate. The ethyl compound has bands which can be assigned to aromatic hydrogen (3050 cm.$^{-1}$), aliphatic hydrogen (2950 cm.$^{-1}$) and a phosphoryl function (1200 cm.$^{-1}$, broad). Bands of strong intensity are also present at 1290, 1270, 1160, 930, 770, and 690 cm.$^{-1}$ (probably monosubstituted phenyl).

Dimethallylethylphosphine oxide. The methallyl Grignard reagent was prepared[3] from 72.0 g. (3.0 g.-atoms) of magnesium and 181.0 g. (2.0 moles) of methallyl chloride in 1500 ml. of dry ether. To the Grignard mixture was added a solution of 52.0 g. (0.2 mole) of diphenyl ethylphosphonate in 175 ml. of dry benzene. The procedure from this point was identical with that described in the preparation of dimethallylphenylphosphine oxide.[3] Fractionation of the crude oil gave 16.0 g. (43%) of a colorless oil which distilled at 115–118° (0.3 mm.). In several runs the yields ranged from 40 to 50%. This oxide is also very hygroscopic, and the compound partially solidified after being placed in a vacuum oven with phosphorus pentoxide for one month. An infrared analysis revealed absorption for aliphatic hydrogen (2900 cm.$^{-1}$), a carbon-carbon double bond (1640 cm.$^{-1}$), a phosphoryl group (1180 cm.$^{-1}$), and a terminal methylene function (890 cm.$^{-1}$). There are bands at 1550, 1375, 1040, and 875 cm.$^{-1}$ of medium to strong intensity. The presence of water was indicated by a small peak near 3300 cm^{-1}.

Anal. Calcd. for $C_{10}H_{19}OP$: C, 64.51; H, 10.21; P, 16.66. Found: C, 64.49; H, 10.32; P, 16.46.

Polymerizations. Attempts to polymerize dimethallylmethylphosphine oxide in bulk failed with benzoyl peroxide at 75° at concentrations up to 5% catalyst and for as long as 30 days. Oils resulted from which a large amount of unchanged oxide could be recovered. This behavior was unlike that of diallylphenylphosphine oxide and dimethallylphenylphosphine oxide both of which polymerized under the above conditions.[3] It was possible to obtain soluble polymers from both of the trialkylphosphine oxides, however, and the data can be found in Table I.

Poly(dimethallylmethylphosphine oxide). A general procedure for the preparation of the polymers was as follows: A sample of monomer and catalyst were placed in a glass tube, one end of which was sealed. To the other end of the

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(19) P. C. Crofts, *Quart. Revs.*, **12**, 341 (1958), see pages 45–347.

(20) All melting points are corrected. All boiling points are uncorrected.

(21) The infrared spectra were recorded by Mr. Leo Pijanowski, Jr., and Miss Anna M. Yoakum on a Perkin-Elmer Model 21.

(22) The microanalyses were preformed by Galbraith Laboratories, Knoxville, Tenn.

TABLE I

POLYMERIZATION DATA

Monomer	Initiator	Wt. g. Monomer	Wt. g. Initiator	Temp.	Time	Intrinsic[b] Viscosity	Yield, %	M.P. of Polymer
I	[a]	6.5871	0.2632	110°	10 days	0.042	15.0	150–160°
I	[a]	9.8249	0.4910	110°	15 days	[c]	15.2	162–170°
II	[a]	12.1216	0.4848	110°	10 days	[c]	4.0	141–152°
II	[a]	12.3215	0.6160	110°	15 days	[c]	4.7	130–140°
II	[a]	6.3001	0.3150	110°	30 days	[c]	5.5	165–185°

[a] α,α'-Azodiisobutyronitrile. [b] In alcohol at 30°; concentrations of solutions were less than 1%, and the flow times were obtained in a modified Ubbelohde viscometer. [c] Not determined.

tube was attached a condenser and nitrogen inlet. The polymerization mixture was maintained at 110°. Partial purification of the polymers was achieved by dissolving the crude solid in a minimum of absolute alcohol and reprecipitating with dry ether. Poly(dimethallylmethylphosphine oxide) is soluble in alcohol and acetic acid. The infrared spectrum indicates the presence of some residual unsaturation by a small peak at 1640 cm.$^{-1}$ Additional data can be found in Table I. Although the polymer did not appear to be hygroscopic, the analytical results checked well for a monohydrate.

Anal. Calcd. for $(C_9H_{17}OP)_n$: C, 62.79; H, 9.88; Calcd. for $(C_9H_{17}OP{\cdot}H_2O)_n$: C, 59.99; H, 10.55; Found: C, 59.34, 59.95, H. 10.01, 9.89.

Poly(dimethallylethylphosphine oxide). The polymer was prepared and purified as described above; it is also soluble in alcohol and acetic acid. A small peak for the carbon-carbon double bond (1640 cm.$^{-1}$) can be found in the infrared spectrum, but no band is evident for a terminal methylene function (890 cm.$^{-1}$). Table I contains further experimental details. This polymer also had an analysis consistent with a monohydrate but it was not hygroscopic.

Anal. Calcd. for $(C_{10}H_{19}OP)_n$: C, 64.51; H, 10.21; P, 16.66. Calcd. for $(C_{10}H_{19}OP{\cdot}H_2O)_n$: C, 58.82; H, 9.31; P, 14.21. Found: C, 59.18, 59.17; H, 10.26, 9.99; P, 13.18.

GAINESVILLE, FLA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, LAFAYETTE COLLEGE]

The Preparation of Aryl Difluoromethyl Ethers[1]

THOMAS G. MILLER AND JOHN W. THANASSI

Received March 2, 1960

Aryl difluoromethyl ethers may be prepared in acceptable yields by the reaction of chlorodifluoromethane with phenols in an aqueous dioxane solvent and in the presence of an excess of sodium hydroxide. Aryl orthoformates are formed as by-products. Difluoromethylene, the reactive intermediate in the synthesis, affords only *O*-alkylation of the aryloxide ion in contrast to dichloromethylene which, in the Reimer-Tiemann synthesis, causes considerable C-alkylation.

Previous methods for the preparation of α-fluoroethers have involved replacement of chlorine and bromine in ethers by fluorine, addition of metal alcoholates to fluorine-containing olefins, electrochemical fluorination of ethers, and the reaction of metal alcoholates with saturated, fluorine-containing carbon compounds.[2] The latter method when used with halogenated ethanes and propanes often proceeds through a dehydrohalogenation step, and thus resembles the method of addition of metal alcoholates to fluoroolefins.[3] Alkyl difluoromethyl ethers have been prepared by the reaction of metal alcoholates with difluoromethylene generated by treatment of bromo- or chlorodifluoromethane with a strong base.[4] One aryl difluoromethyl ether, α,α-difluoroanisole, was reported to have been prepared in 28% yield from dibromodifluoromethane and potassium phenoxide.[5] The stoichiometry of this reaction is not obvious, and no equation was given in the brief note.

It has now been found that the reaction of phenols with chlorodifluoromethane, under conditions favorable for the Reimer-Tiemann reaction between phenols and chloroform, gives acceptable yields of aryl difluoromethyl ethers (Table I). Appreciable quantities of the corresponding orthoformate esters were also formed in the reaction and were isolated and characterized in several cases. In no instance could any carbonyl compounds be detected by testing the neutral products or the aqueous mother liquor with 2,4-dinitrophenylhydrazine reagent.[8]

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(1) This work was supported by a grant, NSF-G6578, from the National Science Foundation.

(2) W. H. Pearlson in J. H. Simons (ed.), *Fluorine Chemistry*, Academic Press, Inc., New York, 1950, Vol. I, p. 486.

(3) (a) P. Tarrant and J. A. Young, *J. Am. Chem. Soc.*, **75**, 932 (1953); (b) E. T. McBee and R. O. Bolt, *Ind. Eng. Chem.*, **39**, 412 (1947).

(4) (a) A. L. Henne and M. A. Smook, *J. Am. Chem. Soc.*, **72**, 4378 (1950); (b) J. Hine and J. J. Porter, *J. Am. Chem. Soc.*, **79**, 5493 (1957).

(5) R. F. Clark and J. H. Simons, *J. Am. Chem. Soc.*, **77**, 6618 (1955).