[CONTRIBUTION FROM FOOD MACHINERY AND CHEMICAL CORP., SOUTH CHARLESTON, W. VA., AND DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY, DURHAM, N. C.]

Formation of Phosphonous Dichlorides by Alkylation of Phosphorus Trichloride with Methane or Ethane[1]

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The alkylation of phosphorus trichloride by alkanes in the gas phase has not been previously observed. It has now been found that at high temperatures (575–600°) and short residence times methane or ethane will react with phosphorus trichloride to form the alkylphosphonous dichloride. Conversions per pass are only moderate, but the yield on consumed phosphorus trichloride is high. The reaction is markedly catalyzed by oxygen and strongly inhibited by propylene. The attempted alkylation of phosphorus oxychloride was unsuccessful.

The occurrence of a reaction between alkanes and phosphorus trichloride was first reported by Clayton and Jensen in 1948.[3] Oxygen is also an essential reactant. The reaction is carried out by passing oxygen through a mixture of a liquid alkane and phosphorus trichloride at or near room temperature; the product is the alkylphosphonic dichloride. A large amount of phosphorus oxychloride is formed as a by-product. The reaction has been applied to several alkanes, but not to gaseous ones such as methane or ethane.

Brooks[4] states that, in the absence of oxygen, phosphorus trichloride is without reaction on the alkanes at temperatures as high as 350° or with irradiation by a mercury lamp. Phosphorus oxychloride was also stated to be without reaction on alkanes. On the other hand, benzene will react with phosphorus trichloride in a tube at red heat to form phenylphosphonous dichloride and hydrogen chloride.[5]

We thought it possible that the alkanes might undergo a reaction similar to that of benzene, if conditions more strenuous than those used unsuccessfully by others were employed. This suggestion has been explored, and we have indeed found that methane and ethane will react with phosphorus trichloride to give the corresponding alkylphosphonous dichloride. Ethylphosphonous dichloride has been known for many years,[6] but a preparation of the methyl compound was reported only recently.[7]

Experimental[8]

Materials.—Phosphorus trichloride and oxychloride were technical grade from Chemicals and Plastics Division, Food Machinery and Chemical Corp., Nitro, W. Va., and were used without purification. Methane was either pure grade (99% min.) from Phillips Petroleum Co. or technical grade (97.5%) from Carbide and Carbon Chemicals Corp. Ethane (95%) was obtained from Matheson Co. Oxygen was U.S.P. grade from Ohio Chemical Co.

Apparatus and Procedure.—The reactor was a quartz tube 24 mm. o.d. by 40 cm., 33 cm. of which was enclosed vertically in an electric furnace. Concentric through the entire reactor was a 7 mm. o.d. quartz tube holding a sliding thermocouple. Generally the reactor was packed with 4–8 mesh quartz chips. The alkane was passed through a calibrated rotameter and then bubbled through a flask of phosphorus trichloride held at a temperature predetermined to vaporize the proper amount for a definite molar ratio of the reactants. The weight loss of the flask at the conclusion of the experiment gave the exact amount of phosphorus trichloride used. The gas mixture was passed directly to the top of the reactor. A "T" in this inlet tube permitted entry of gaseous additives when desired. The additive was passed through a calibrated rotameter. The gaseous mixture emerging from the reactor was conducted to a flask chilled in a Dry Ice-bath, where the bulk of the liquid product and some yellow, gummy solids were collected. The gas passed through two more Dry Ice traps and finally through a series of three water scrubbers to absorb hydrogen chloride and any uncondensed phosphorus chlorides.

At the conclusion of the experiment, usually lasting several hours, the trap contents were combined and analyzed by one or more of the procedures described below. The scrubber contents were combined, and aliquots were titrated to the modified methyl orange end-point and to the phenolphthalein end-point. The difference between the acidity values was attributed to secondary ionization of phosphorous acid, and served as a measure of the amount of phosphorus trichloride hydrolyzed in the scrubbers. The vapor pressure of methylphosphonous dichloride is close to that of phosphorus trichloride, and it was assumed that the same ratio of these compounds was present in the hydrolysate as in the condensed liquid product. The amount of methylphosphonous dichloride collected in the scrubbers and the amount of hydrogen chloride formed in the reactor were determined from these data.

The reactor was cleaned by rinsing with solvent after each experiment. A deposit of carbon formed on the quartz surface, but seemed to cause no deleterious effects until so extensive after many runs as to impede gas flow. The reactor was then burned out with air and was again serviceable.

The reaction temperatures recorded herein are the uncorrected maximum values observed in the thermowell of the reactor. For calculations of residence time a zone within 50° of this temperature was considered arbitrarily as the site of reaction.

Many experiments were also performed in an all-metal apparatus similar in design to the glass apparatus. Moderate pressure (50 p.s.i.g.) was employed in these experiments. Results with such apparatus were quite similar to those with the glass apparatus, and no further comment will be made on these experiments.

Reaction of Methane with Phosphorus Trichloride. Typical conditions for effecting this reaction appear in

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[1] Presented in part at the 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1961. This work was performed in the Food Machinery and Chemical Corp. Research Laboratories under a contract with the U. S. Army Chemical Corps.

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[3] J. O. Clayton and W. L. Jensen, *J. Am. Chem. Soc.*, **70**, 3880 (1948). W. H. Woodstock, U. S. Patent 2,137,792 (Nov. 22, 1938), claimed a reaction of alkanes, mostly as petroleum fractions, with phosphorus trichloride in the presence of aluminum chloride. However, the products, presumed to be phosphonous dichlorides, were not isolated, but were converted to acids or esters. No pure compounds were reported. The reaction was said not to be practical with alkanes containing fewer than five or six carbon atoms.

[4] B. T. Brooks, "Chemistry of Nonbenzenoid Hydrocarbons," 2nd ed., Reinhold Publishing Corp., New York, N. Y., 1950, p. 192.

[5] A. Michaelis, *Ber.*, **6**, 601 (1873), and several later references.

[6] A. Michaelis, *ibid.*, **13**, 2174 (1880).

Khim., **28**, 2963 (1958). This compound was first mentioned in the literature several years earlier: L. Z. Soborovskii and V. M. Zinov'ev, *ibid.*, **24**, 516 (1954).

[8] Elemental analyses were performed by G. S. Haines and associates. Infrared analyses were performed by D. K. Chapman and associates.

TABLE I

REACTION OF METHANE WITH PHOSPHORUS TRICHLORIDE[a]

Expt. no.	B-17	B-18	B-19	B-22
Temp., °C.	630	595	570	550
Moles CH_4 per hr.	3.0	3.0	3.0	3.0
CH_4:PCl_3, moles	5.9	5.5	6.0	5.7
CH_3PCl_2 in prod., wt. %[b]	15.5	14.5	12.0	3.5
Convn. to CH_3PCl_2, mole %	14.5	13.9	10.9	3.3
HCl:CH_3PCl_2, moles	1.9	1.8	1.9	1.8

[a] Residence time, 0.3 sec. [b] By sp. gr. analysis.

Table I. Methylphosphonous dichloride was the only identifiable organic product. This was established by rectification of the reaction mixture with a 1.8 cm. o.d. by 37 cm. column of Helipak (Hastelloy C). The fraction boiling at 81–82°[6] was taken as product.

Anal. Calcd. for CH_3Cl_2P: Cl, 60.65. Found: Cl, 60.4, 60.6.

This compound had a sp. gr. 35/4° of 1.280. The value is considerably below that of phosphorus trichloride (1.548); since these two compounds comprised the bulk of the reaction product, a reasonably accurate analysis of the crude product was possible by determining its sp. gr. and referral to a calibration curve prepared from known mixtures. An analysis based on an infrared absorption band for methylphosphonous dichloride at 14.51 μ was also devised. Carbon disulfide solutions in the concentration range of 0–25 g. per l. were used in salt cells of 1.0 mm. thickness. All reaction products were analyzed by one or both of these procedures, which checked quite well.

Conversions were calculated by dividing the molar sum of methylphosphonous dichloride in the condensate and in the scrubber (from titration) by the moles of phosphorus trichloride charged. Scrubber values were quite small but were included to provide a complete representation of the extent of the reaction. Yields, based on the amount of phosphorus trichloride consumed, were generally around 80–85%. Conversions were reproducible as long as a single source of methane was used, but occasionally dropped drastically when a new cylinder was used. Conversions reported are the maximum obtained.

Experiments employing oxygen as a catalyst are recorded in Table II. Rectification of typical products revealed that in addition to methylphosphonous dichloride they contained 1–2 wt. % of methyl phosphorodichloridite,[9] b.p. 93–94°, sp. gr. 35/4° 1.348, having the correct analysis.

About 1–2% each of phosphorus oxychloride and of methylphosphonic dichloride,[10] m.p. 33.0°, b.p. 165°, were also obtained. The amount of gummy solids appeared greater in these runs, but exact amounts were not readily determined.

Experiments with gaseous inhibitors are described in Table III. Experiments using natural gas as a source of methane are described in Table IV. Purification of the natural gas was accomplished by counter - current flow through an absorption oil (Esso Mentor 28) and then passage through an activated carbon tower to remove traces of oil.

Reaction of Ethane with Phosphorus Trichloride.—An ethane–phosphorus trichloride mixture (4.8 molar ratio) was prepared as described for methane reactions and passed for 3 hours through the reactor at 575° at an ethane rate of 3 moles per hr. An oxygen catalyst (1 part to 100 parts of reactants) was employed. Residence time was 0.3 sec. Rectification of the product gave 21 g. of pure ethylphosphonous dichloride,[11] b.p. 111°.

Anal. Calcd. for $C_2H_5Cl_2$ P: Cl, 54.1; P, 23.6. Found: Cl, 53.8; P, 23.9.

Additional product in intermediate fractions gave a total conversion of about 15%. Repetition of the reaction gave substantially the same results.

Attempted Reaction of Methane with Phosphorus Oxychloride.—Using the same apparatus and general procedure, several attempts were made to cause methane to react with phosphorus oxychloride. Conditions employed in three typical experiments are given in Table V. Some of the liquid products had specific gravities less than that of pure phosphorus oxychloride (1.648 at 35/4°), but on distillation no indication of high boiling compounds was obtained.

Results and Discussion

It has been demonstrated that methane will react with phosphorus trichloride to establish a carbon–phosphorus bond, giving as the product methylphosphonous dichloride. The data of Table I indicate that a high temperature is required to effect this reaction; at a temperature less than 500°, no product was found,[12] in agreement with the literature.[4] A moderate conversion, about 10–15%, but a high yield (80–85%) can be realized. The product appears to be free of other compounds, except for a small amount of gummy solids. The methylphosphonous dichloride can be recovered by rectification with an efficient column. Short exposure time of the reactants to the severe temperature conditions appears to be an important factor in this reaction. Somewhat arbitrarily, residence times of 0.2–0.3 sec. were employed in this work. The ratio of the two products, hydrogen chloride to methylphosphonous dichloride, is considerably greater than unity, and may indicate some decomposition of the latter compound, or the occurrence of other reactions involving phosphorus trichloride.

The conversions of Table I are the highest obtained for a given set of conditions. They are reproducible if the same batch of reactants is employed. However, drastic alterations of the conversions were occasionally experienced, particularly when a new cylinder or a new source of methane was used. To illustrate, in later work a conversion of only 1.3% was obtained when expt. B-19 was repeated. These results suggest that the reaction is prone to inhibition.

After establishment of some of the factors described above, it was discovered that small amounts of oxygen, introduced into the gas fed to the reactor, caused a substantial improvement in conversion, and largely eliminated the wide fluctuation in conversion occasionally experienced. The data of Table II (expt. B-2-O through B-9-O) show a gradual increase in conversion to a maximum of about 20% as the oxygen content is raised by increments. In the absence of oxygen, the highest conversion obtained under similar conditions was about 11%. The maximum effectiveness of oxygen is obtained at a concentration of about 1 mole %; further increase did not appreciably raise the conversion and caused a higher production of solids and of hydrogen chloride. In later work, conversions as high as 22% were occasionally obtained under the same conditions as expt. B-6-O. The hydrogen chloride–methylphosphonous dichloride ratio is closer to the expected value of unity in these runs than in the uncatalyzed runs.

Also in Table II appear data illustrating the direct dependence of conversion on the ratio of methane to phosphorus trichloride.

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(9) D. R. Martin and P. J. Pizzolato, *J. Am. Chem. Soc.*, **72**, 4584 (1950) reported b.p. 93.0°.

(10) A. W. Hofmann, *Ber.*, **6**, 303 (1873), reported m.p. 32°, b.p. 163°.

(11) R. B. Fox, *J. Am. Chem. Soc.*, **72**, 4147 (1950), reported b.p. 112°.

(12) In later work in larger apparatus with 0.8–1.0 sec. residence time, small conversions were obtained at temperatures below 500°. Results of these experiments will be reported in a more appropriate journal.

TABLE II

OXYGEN CATALYSIS OF THE METHANE–PHOSPHORUS TRICHLORIDE REACTION[a]

Expt. no.	B-2-O	B-3-O	B-4-O	B-5-O	B-6-O	B-7-O	B-8-O	B-9-O	B-20-A	B-21-A	B-22-A	B-23-A
Moles CH_4 per hr.	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	2.9	2.7	2.4
CH_4:PCl_3, moles	4.8	4.7	4.8	4.8	4.7	4.7	4.8	4.6	5.0	3.7	2.7	1.9
$CH_4 + PCl_3$:O_2, moles	500	250	167	125	91	71	59	50	60[b]	50[b]	50[b]	50[b]
CH_3PCl_2 in prod., wt. %	11.3	15.5	15.4	16.9	18.1	18.7	19.1	20.2	16.0	14.0	11.9	7.8
Convn. to CH_3PCl_2, mole %	12.4	16.9	16.4	17.9	18.6	19.0	19.0	19.5	16.9	15.6	13.3	8.8
HCl:CH_3PCl_2, moles	1.1	1.1	1.1	1.2	1.2	1.2	1.3	1.4	1.2	1.1	1.0	1.3

[a] At 575°, 0.3 sec. residence. [b] Introduced as air.

Even in the oxygen-catalyzed reaction, occasional unexpected reductions in conversions were experienced. The persistence of this effect promoted a consideration of possible causes. It is probable that the reaction occurs by a free radical mechanism (*vide infra*), and for this reason the well-known inhibitor propylene was purposely added to the reaction mixture to observe its effect. As seen in Table III (expts. 35 and 36), pronounced reduction in conversion occurred, even in the presence of oxygen. It does not appear, however, that propylene is present in the methane commonly used. Higher alkanes are more probable contaminants; under the severe reaction conditions, cracking to alkenes might occur and thus in effect serve as inhibitors. This possibility was demonstrated in expt. 79, where *n*-butane reduced the conversion to about 8%.

TABLE III

INHIBITION OF THE METHANE–PHOSPHORUS TRICHLORIDE REACTION[a]

Expt. no.	14	35	36	79
Moles CH_4 per hr.	5.0	4.0	3.9	4.1
CH_4:PCl_3, moles	4.6	4.4	4.5	4.2
$CH_4 + PCl_3$:O_2, moles	112	110	103	102
Inhibitor	None	C_3H_6	C_3H_6	*n*-C_4H_{10}
Inhibitor, mole %	...	0.5	0.1	2.0
CH_3PCl_2 in prod., wt. %	19.0	9.5	12.5	6.5
Convn. to CH_3PCl_2, mole %	21.2	10.6	14.1	7.6
HCl:CH_3PCl_2, moles	1.0	1.1	1.1	1.3

[a] At 575°, 0.2 sec. residence.

The adverse effect of higher alkanes was also demonstrated by attempts to employ natural gas as a source of methane. The gas used had the composition[13]: 86.8 mole % methane, 7.4% ethane, 2.3% propane, 0.3% isobutane, 0.2% *n*-butane, the remainder being nitrogen and carbon dioxide. Much hydrogen chloride but little methylphosphonous dichloride was formed (Table IV, expts. 129 and 130). The low infrared value for methylphosphonous dichloride was confirmed by rectification of the combined products; a value of 4.9 wt. % was obtained. The rectification also revealed that the liquid product contained 2.4 wt. % of ethylphosphonous dichloride. When the natural gas was passed through a system designed to remove higher alkanes, normal liquid products (19 wt. % methylphosphonous dichloride, expt. 27-A) were obtained. The purified gas had the alkane analysis[13]: 90.2 mole % methane, 2.3% ethane, 0.06% *n*-butane, no detectable propane or isobutane. It thus contained only a trace of alkane higher than ethane. These experiments also serve to implicate higher alkanes in the inhibition of the methane–phosphorus trichloride reaction.

TABLE IV

REACTION OF NATURAL GAS WITH PHOSPHORUS TRICHLORIDE[a]

Expt. no.	129[c]	130[c]	27-A[d]
Moles CH_4[b] per hr.	4.03	4.03	2.88
CH_4:PCl_3, moles	4.8	5.0	4.8
$CH_4 + PCl_3$:O_2, moles	110	110	101
Res. time, sec.	0.2	0.2	0.3
CH_3PCl_2 in prod., wt. %	5.8	2.4	19.0
Convn. to CH_3PCl_2, mole %	6.7	2.9	20.6
HCl:CH_3PCl_2, moles	3.3	8.2	1.37

[a] At 575°. [b] Calculated on the assumption that the gas was 100% CH_4. [c] Dried natural gas. [d] Natural gas purified by oil absorption.

It was found that pure ethane could also be involved in reaction with phosphorus trichloride. A conversion to ethylphosphonous dichloride of about 15% was obtained with conditions found favorable for effecting the methane reaction. For propane or higher hydrocarbons, however, less strenuous conditions would have to be employed, as cracking is extensive at this temperature range.

Consideration was given to the possible importance of the surface on the reaction. The quartz reactor was generally packed with quartz chips, but the conversion to methylphosphonous dichloride in an unpacked quartz reactor was essentially the same. The reactor develops a carbonaceous coating on continued use, but no effect could be attributed to this material. The use of quartz chips pre-coated with magnesium oxide similarly had no effect. Furthermore, substitution of a metallic (Hastelloy C or Stainless Steel 316) reactor had no important effect on conversion, although a slight improvement in conversion was noted when a quartz reactor packed with turnings of Hastelloy C or Stainless Steel 316 was used. It seems likely from these observations that surface effects are not important in this reaction, although further study of this point would be desirable.

The characteristics of the alkane–phosphorus trichloride reaction suggest that a free radical mechanism is involved. The need for high temperatures, the catalysis by oxygen, and the inhibition by propylene are in accord with this postulate. It was also observed, by infrared examination of the first fractions from rectifications, that trace amounts of chloromethanes are formed in the oxygen-catalyzed reaction with methane. Such products can best be explained by radical intermediates. In the absence of a catalyst, the following reactions might be involved in the formation of methylphosphonous dichloride

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[13] Mass spectral analyses by Consolidated Electrodynamics Corp.

$$PCl_3 \longrightarrow PCl_2\cdot + Cl\cdot \qquad (1)$$

$$Cl\cdot + CH_4 \longrightarrow HCl + CH_3\cdot \qquad (2)$$

$$CH_3\cdot + PCl_2\cdot \longrightarrow CH_3PCl_2 \qquad (3)$$

$$CH_3\cdot + PCl_3 \longrightarrow CH_3PCl_2 + Cl\cdot \qquad (4)$$

The homolysis of phosphorus trichloride, eq. 1, appears to be favored over that of methane as the primary source of radicals; the bond dissociation energy of C–H in methane is 101 kcal. per mole,[14a] while the bond energy (in the absence of a value for the bond dissociation energy) for P–Cl in PCl_3 is 78 kcal. per mole.[14b] The formation of methylphosphonous dichloride can be visualized as occurring by combination of $PCl_2\cdot$ and $CH_3\cdot$ radicals, eq. 3, or by a radical displacement as in eq. 4.

The role of oxygen as a catalyst may be that of increasing the concentration of methyl radicals through processes such as

$$O_2 + CH_4 \longrightarrow CH_3\cdot + HO_2\cdot \qquad (5)$$

or

$$O_2 + PCl_3 \longrightarrow POCl_3 + \cdot O\cdot \qquad (6)$$

$$\cdot O\cdot + CH_4 \longrightarrow HO\cdot + CH_3\cdot \qquad (7)$$

Reaction 5 has been postulated[15] in the oxidation of methane. A reaction for the formation of oxygen atoms similar to that in reaction 6 was suggested for phosphorus oxidation.[16] Attack of the oxygen atoms on methane, reaction 7, has also been proposed in the oxidation of methane.[17] Small amounts of $POCl_3$, as well as CH_3POCl_2, are found in oxygen-catalyzed reaction products, in accord with eq. 6. No mechanism is obvious for oxygen promoting formation of $PCl_2\cdot$ radicals.

Formation of chloromethanes may follow an established path such as

$$Cl\cdot + CH_3\cdot \longrightarrow CH_3Cl$$

$$CH_3Cl + Cl\cdot \longrightarrow HCl + ClCH_2\cdot$$

$$ClCH_2\cdot + Cl\cdot \longrightarrow Cl_2CH_2, \text{ etc.}$$

Methyl phosphorodichloridite may be accounted for by

$$CH_3\cdot + \cdot O\cdot \text{ (or } O_2) \longrightarrow CH_3O\cdot$$

$$CH_3O\cdot + PCl_2\cdot \longrightarrow CH_3OPCl_2$$

or similar processes.

The conditions effective in the phosphorus trichloride reaction might be expected to lead to a similar reaction between methane and phosphorus oxychloride, particularly with oxygen catalysis. However, the expected product from such a reaction, methylphosphonic dichloride, was never obtained under a variety of experimental conditions (Table V), although substantial amounts of hydrogen chloride were formed. The possibility that methylphosphonic dichloride was indeed formed but was decomposed under the severe reaction conditions cannot, however, be excluded on the basis of this work.

TABLE V

ATTEMPTED REACTION OF METHANE WITH PHOSPHORUS OXYCHLORIDE

Expt. no.	8	11	12
Temp., °C.	780	620	750
Moles CH_4 per hr.	0.25	3.0	3.0
CH_4:$POCl_3$, moles	2.0	7.3	5.1
CH_4 + $POCl_3$:O_2, moles	...	20	100
HCl formed, mole	0.35	0.15	0.18
Sp. gr. 35/4°, product	1.588	1.648	1.647
Distillation dry-point, °C.	110	109	109

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(14) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd ed., Butterworths Scientific Publications, London, 1958; (a) p. 176, (b) p. 255.

(15) G. H. N. Chamberlain and A. D. Walsh, *Rev. Inst. fran Petrole*, **4**, 301 (1948).

(16) F. S. Dainton and H. M. Kimberley, *Trans. Faraday Soc.*, **46**, 629 (1950).

(17) R. G. W. Norrish, *Disc. Faraday Soc.*, **10**, 269 (1951).

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Reactions of Phosphorus Compounds. III. Synthesis of Phosphinedihalomethylenes via Dihalocarbenes. A Novel Synthesis of 1,1-Dihaloölefins[1]

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A new method of synthesis of previously unknown trialkyl- or triarylphosphinedihalomethylenes by reaction of dihalocarbenes with tertiary phosphines is described. The phosphinemethylenes react with ketones or aldehydes to give good yields of 1,1-dihaloölefins. The reactivity of the dihalo ylids with *t*-butyl alcohol and carbonyl compounds can be related to the relative stabilization of the localized anionic charge of the dipolar resonance form.

Dihalocarbenes, the subject of intensive research in recent years, have been shown to possess electrophilic character.[2-4] Their reaction with tertiary phosphines would lead to formation of a new class of phosphinemethylenes, the dihalo derivatives (I, X = halogen). The Wittig reaction of such phosphinedihalomethylenes could provide a novel synthesis of 1,1-dihaloölefins.

Phosphorus ylids have been prepared by several methods,[5-7] the most useful being treatment of

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(1) A preliminary communication concerning this work has appeared; A. J. Speziale, G. J. Marco and K. W. Ratts, *J. Am. Chem. Soc.*, **82**, 1260 (1960); for part II in this series, see A. J. Speziale and R. C. Freeman, *ibid.*, **82**, 903 (1960).

(2) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956).

(3) J. Hine and A. M. Dowell, *ibid.*, **76**, 2688 (1954).

(4) W. von E. Doering and W. A. Henderson, Jr., *ibid.*, **80**, 5274 (1958).

(5) L. Horner and H. Oediger, *Chem. Ber.*, **91**, 437 (1958).

(6) H. Staudinger and J. Meyer, *Helv. Chem. Acta*, **2**, 619, 635 (1919); H. Staudinger and G. Luscher, *ibid.*, **5**, 75 (1922).