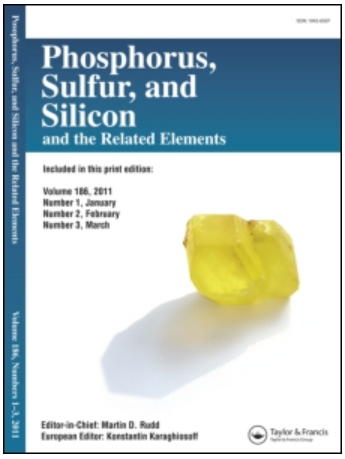


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

REACTION OF PHOSPHORUS PENTACHLORIDE WITH QUINONES

A. A. Kutyrew[a]; S. G. Gomin[a]; V. V. Moskva[a]
[a] Department of Organic Chemistry, Kazan Chemical Technological Institute, Kazan, USSR

To cite this Article Kutyrew, A. A. , Gomin, S. G. and Moskva, V. V.(1988) 'REACTION OF PHOSPHORUS PENTACHLORIDE WITH QUINONES', Phosphorus, Sulfur, and Silicon and the Related Elements, 39: 1, 19 — 25
To link to this Article: DOI: 10.1080/03086648808072850
URL: http://dx.doi.org/10.1080/03086648808072850

Phosphorus and Sulfur, 1988, Vol. 39, pp. 19–25
Reprints available directly from the publisher
Photocopying permitted by license only

REACTION OF PHOSPHORUS PENTACHLORIDE WITH QUINONES

A. A. KUTYREW, S. G. FOMIN and V. V. MOSKVA
Department of Organic Chemistry, Kazan Chemical Technological Institute, Kazan 420015, USSR

(Received August 19, 1987; in final form January 19, 1988)

Phosphorus pentachloride reacts with 1,4-benzoquinone and 2-chloro-1,4-benzoquinone at room temperature. The basic products are dichlorophosphoranes (**1a, b**). Intermediates have been ascertained. The scheme of the process has been confirmed by model reactions.

Key words: Quinones; Phosphorus pentachloride; Mechanism; Infrared; Dimethylaniline; Mass spectra.

Reactions of quinones with compounds of three- and four-coordinated phosphorus atoms are common means for obtaining phosphorus aromatic ethers. Although these reactions have been well studied,[1–4] little knowledge is available on interactions of penta-coordinated phosphorus with quinones.[5,6] Reagents presenting some interest and which are available such as halogenophosphoranes and phosphorus pentachloride in particular have not been fully investigated.

RESULTS AND DISCUSSION

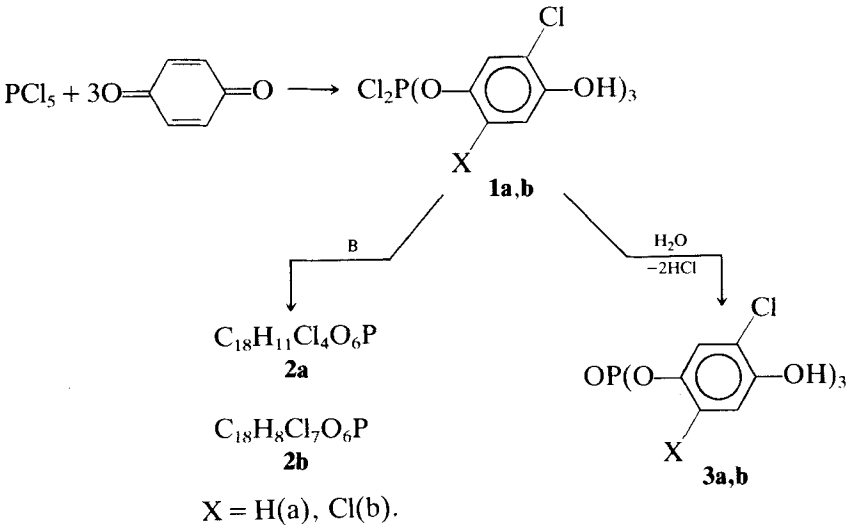
Phosphorus pentachloride reacts with 1,4-benzoquinone at room temperature. Reaction starts after mixing the reagents and is accompanied by an exothermic effect and by formation of the dichlorophosphorane (**1a**). Dichlorophosphorane (**1a**) is rather stable when kept in an atmosphere of argon. In the presence of basic reagents, amine for instance, it forms a compound (**2a**) whose structure was not identified.

When treated with water or alcohol, dichlorophosphorane (**1a**) transforms into the phosphate (**3a**), which structure is proved by physicohemical means and by synthesis according to the reaction of PCL_5 with chlorohydroquinone in the presence of water (in the absence of water, the mixture of dichlorophosphorane (**1a**) and phosphate (**3a**) is formed) or by the reaction of phosphorus oxychloride with chlorohydroquinone in the presence of *N,N*-dimethylaniline (DMA). In the absence of DMA the reaction mixture becomes resinous.

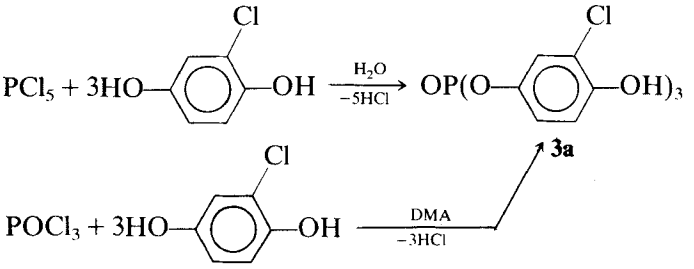
PCl_5 interacts with 2-chloro-1,4-benzoquinone similarly. The resulting product is dichlorophosphorane (**1b**) which, depending upon the other conditions, transforms into compound (**2b**) or phosphate (**3b**).

PCl_5 does not react with 1,4-naphthaquinone, tetrasubstituted quinones: 2,3,5,6-tetra-chloro-(bromo, methyl)-1,4-benzoquinones, or 9,10-anthraquinone.

Investigation of the mechanism of this new reaction was of interest. However



B = amines, acetone.



DMA = *N,N*-dimethylaniline

some difficulties arise owing to the prolonged induction period but the main one is the insolubilities of the products obtained (**1–3**) in organic solvents. Thus, usual physical and chemical methods of investigation prove to be impossible; that is kinetics, intermediate spectroscopy in solution, etc. Nevertheless we were able to construct the general scheme of interaction.

It appeared that an exothermic reaction takes place at once when a minimum quantity of gaseous HCl is passed into the reaction solution of PCl_5 and 1,4-benzoquinone. The fact that the reaction takes place can be proved by the immediate formation of crystalline dichlorophosphorane (**1a**).

In a parallel control experiment (in the absence of HCl) reaction proceeds during an eight hour period.

In the presence of base (for example *N,N*-dimethylaniline), the reaction fails to take place. The process stops if dimethylaniline is added to the reaction mixture at the moment of formation of the precipitate, dichlorophosphorane (**1a**). It is likely that dimethylaniline binds HCl present in the reaction mixture and thus inhibits the process.

It has been established that the reaction of PCl_5 with 1,4-benzoquinone can be

"switched on" or "switched off' with successive additions of HCl and dimethylaniline, resepectively.

In a special experiment we have succeeded in fixing HCl in the reaction mixture in the absence of mixing, using a minimum quantity of solvent. The other test has shown that chlorohydroquinone is present in the reaction mixture (see experimental part). It has been noticed that the more HCl or chlorohydroquinone that is isolated from the reaction mixture, the less is the yield of dichlorophosphorane (**1a**).

Assuming that HCl and chlorohydroquinone are intermediates, we carried out two model reactions in which they participated.

The First Model Reaction. Gaseous HCl is added to a benzene solution of 1,4-benzoquinone at 20°–25°C. After some seconds, the yellow colour of the 1,4-benzoquinone solution faded away. After removing the solvent, chlorohydroquinone is present in 99% yield in the residue.

This experiment shows that in the case of the PCl_5 reaction with 1,4-benzoquinone, rapid and selective formation of chlorohydroquinone from HCl and 1,4-benzoquinone is quite possible.

The Second Model Reaction: *PCl_5 with Chlorohydroquinone.* A complex mixture of unidentified compounds is formed as a result of this interaction, but in the presence of dimethylaniline the reaction takes place selectively with the formation of dichlorophosphorane (**1a**) and the chlorohydrate of dimethylaniline.

Thus, in the tested and model reactions, the same product (**1a**) is formed. In case of the PCl_5 reaction with chlorohydroquinone, to bind the HCl that is released, additions of the base (dimethylaniline) are required. In the case of 1,4-benzoquinone, these additions are not necessary. The first model reaction shows that the role of the HCl acceptor is played by 1,4-benzoquinone itself.

The following results are summarized:

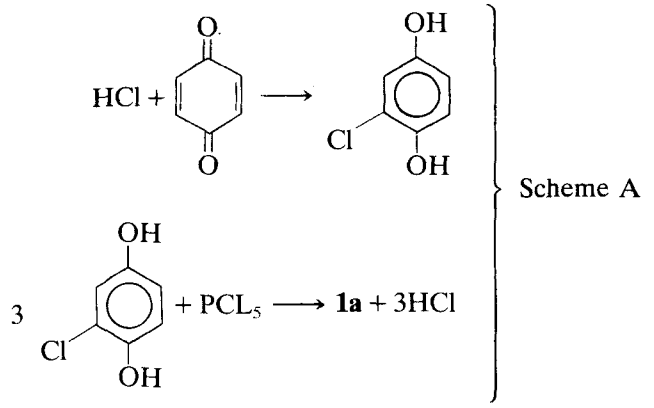
1) HCl initiates and dimethylaniline inhibits the reaction.

2) HCl and chlorohydroquinone are fixed in the reaction mixture.

3) Two stages of the process are simulated: (a) the HCl reaction with 1,4-benzoquinone yielding chlorohydroquinone, and (b) the PCl_5 reaction with chlorohydroquinone yielding dichlorophosphorane (**1a**).

According to the present data, it can be assumed that the PCl_5 reaction with 1,4-benzoquinone proceeds in two stages (Scheme A). During the first stage, HCl attachs to 1,4-benzoquinone forming chlorohydroquinone. During the second stage, chlorohydroquinone interacts with PCl_5 forming dichlorophosphorane (**1a**) and HCl. The latter participates in the first stage of the process once more, attaching itself to unreacted 1,4-benzoquinone thus allowing the reaction to continue until the reagents are spent.

Scheme A is consistent with the experimental data obtained but is not able to explain the reaction completely. For example, there is the problem as to where the HCl initiator comes from and why, after a long pause, rapid reaction starts. One can assume that HCl appears at the beginning of the reaction either as a result of PCl_5 hydrolysis or as a result of some slow process taking place before the main reaction occurs in accordance with Scheme A. To solve this problem,



two additional model reactions were carried out with 2-chloro-1,4-benzoquinone reacts with the formation of 2,5-dichlorohydroquinone and PCl_5 with 2,5-dichlorohydroquinone in the presence of dimethylaniline reacts with the formation of dichlorophosphorane (**1b**).

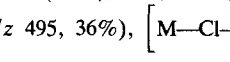
These data confirm that PCl_5 reacts with 2-chloro-1,4-benzoquinone in a manner analogous to that in Scheme A.

In the case of other quinones investigated, we did not carry out the model reactions. HCl is not known to add to tetrachloro(bromine, methyl)quinones and it has been established that HCl fails to add to 1,4-naphthaquinone. It can be assumed that the latter quinones (especially 1,4-naphthaquinone which is the nearest structural analogue to 1,4-benzoquinone) fail to react with PCl_5 because they are unable to react with HCl.

EXPERIMENTAL

All procedures were carried out in an atmosphere of argon. Absolute solvents were used. Phosphorus pentachloride and the quinones were sublimated twice. IR spectra were recorded on a UR-20 spectrometer (vaseline oil pulp), ^{31}P NMR on a WP-80 Brucker spectrometer (solution DMFA, NS 60,000), and mass spectra on a MAT-212 (Finigan) instrument.

Tris-(3-chloro-4-hydroxyphenoxy)dichlorophosphorane (**1a**).

A) A solution of a mixture of 1.2 g (0.006 m) PCl_5 and 1.9 g (0.018 m) of 1,4-benzoquinone in 150 ml of benzene was left at 20°–25°C. After 8 hours, the residue was filtered off, washed with 150 ml of benzene and dried in vacuum. Obtained: 2.9 g of dichlorophosphorane (**1a**) in 95% yield. IR spectrum, cm^{-1}: 3290 (OH), 1600 (Ph), 990 (POC), 550, 450 (PCl). ^{31}P NMR spectrum: δ_P −17.5 m.p. (Mass spectrum: $[M-Cl]^+$ (*m/z* 495, 36%),  (*m/z* 352, 20%), $[M-2Cl]^+$ (*m/z* 460, 45%). Anal. for $C_{18}H_{12}Cl_5O_6P$. Calc. %: C 40.56; H 2.25; Cl 33.33; P 5.82. Found %: C 40.39; H 2.41; Cl 32.16; P 5.30.

If 0.006 ml of *N,N*-dimethylaniline is added to the above reaction mixture, phosphorane residue is not formed.

B) Gaseous HCl at 20°C was passed slowly for 10 seconds into a soluton of 1.2 g (0.006 m) of PCl_5 and 1.9 g (0.018 m) of 1,4-benzoquinone in 150 ml of benzene. After 15 minutes, the precipitate was filtered off, washed with 150 ml of benzene, and dried in vacuum. Obtained: 3.0 g of dichlorophosphorane (**1a**) (98%).

C) A suspension of 1.2 g (0.006 m) of PCl_5 and 1.9 g (0.018 m) of 1,4-benzoquinone in 10 ml of benzene at 20°C was sealed in a (hermetic) vessel provided with a gas removing tube which was immersed into an aqueous solution of $AgNO_3$. After 7 hours, the precipitate was filtered off from the

reaction mixture, washed with 150 ml of benzene and dried in vacuum. Obtained: 2.4 g of dichlorophosphorane (**1a**) (78%).

The precipitate (0.49 g) of AgCl was filtered off from the aqueous solution of $AgNO_3$, the former corresponding to 0.125 g of HCl (20%).

At the temperature of the reaction mixture, 40°C, 1.9 g of dichlorophosphorane (**1a**) (62%) was produced from 1.2 g of PCl_5 and 1.9 g of 1,4-benzoquinone. From the aqueous solution of $AgNO_3$, 0.868 g of AgCl or 0.221 g of HCl (35%) was obtained.

If the reaction is conducted at 20°–40°C, and other conditions are the same except that greater quantity of solvent is used (>100 ml), HCl is fixed neither with $AgNO_3$ nor in the reaction mixture itself.

D) A solution of 1.2 g (0.006 m) of PCl_5 and 1.9 g (0.018 m) of 1,4-benzoquinone in 300 ml of benzene was left to stand at 8°C. After 5–6 hours, the precipitate was filtered off from reaction mixture and washed with benzene.

A 0.3 g quantity of a complex of 1,4-benzoquinone with chlorohydroquinone (20%) m.p. 145°C (lit. 145°C). was obtained.

The filtrate was left at 8°C. After 24 hours, the precipitate was filtered off, washed with benzene, and dried. Obtained: 2.1 g dichlorophosphorane (**1a**) (68%).

E) A solution of 2.5 g (0.018 m) of chlorohydroquinone and 2.0 g (0.018 m) of *N,N*-dimethylaniline was added to the solution of 1.2 g (0.006 m) of PCl_5 in 100 ml of benzene at 20°–25°C. The mixture was stirred during 0.5 hour. The precipitate was filtered off, washed with benzene, dried in vacuum and analysed. Obtained: 5.5 g of precipitate. According to mass and IR spectral data, the precipitate is a mixture of dichlorophosphorane (**1a**) and the chlorohydrate of *N,N*-dimethylanaline.

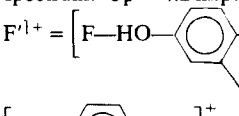
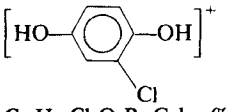
To the latter mixture, 100 ml of water was added. After 15 minutes, the precipitate was filtered off, washed with H_2O and dried. Obtained: 2.6 g of phosphate (**3a**) (95%).

Chlorohydroquinone. Into the solution of 1.9 g of 1,4-benzoquinone in 150 ml of benzene, gaseous HCl was passed slowly for 10 minutes at 20°C. After 15 minutes, the solvent was removed. Obtained: 2.5 g of chlorohydroquinone (99%).

Compound (**2a**). Triethylamine (10 ml, 0.07 m) was added to dichlorophosphorane (**1a**) (20 g, 0.004 m) at 20°C. The residue obtained was filtered off, washed with 10 ml of triethylamine and then with 10 ml of hexane. Obtained: 1.6 g of compound (**2a**). IR spectrum, cm^{-1}: 3295 (OH), 1610 (Ph), 1000 (POC), 560 (PCl). ^{31}P NMR spectrum: δ_P −9 m.p. Anal. for $C_{18}H_{11}Cl_4O_6P$. Calc. %: C 43.55; H 2.22; Cl 28.63; P 6.25. Found %: C 45.04; H 1.56; Cl 30.10; P 6.15. .

N,N-dimethylanaline and acetone can be used instead of triethylamine.

Tris-(3-chloro-4-hydroxyphenyl)phosphate (**3a**).

A) Water (100 ml, 5.5 m) was added to dichlorophosphorane (**1a**) (2.1 g, 0.004 m) at 20°C, the residue was filtered off, dried in vacuum at 150°C. Phosphate (**3a**) (1.7 g) was obtained in 90% yield. M.p. 314°C. IR spectrum, cm^{-1}: 3320 (OH), 1600 (Ph), 1290 (P=O), 980 (POC). ^{31}P NMR spectrum: δ_P −4.2 m.p. Mass spectrum: M^+ (*m/z* 476, 61%), $F^+ = [M - Cl]^+$ (*m/z* 441, 31%), $F'^{1+} =$  (*m/z* 279, 23%), $[F'—C_6H_3]^+$ (*m/z* 202, 31%), $F''^{1+} =$  (*m/z* 144, 69%), $[F''—Cl]^+$ (*m/z* 107, 31%). M^+ 476. Anal. for $C_{18}H_{12}Cl_3O_7P$. Calc. %: C 45.23; H 2.51; Cl 22.30; P 6.49. Found %: C 45.15; H 2.46; Cl 22.91; P 6.37. M 477.62.

B) Water (0.098 g, 5.4 mm) and benzene (100 ml) were added to dichlorophosphorane (**1a**) (2.900 g, 5.4 mm) at 20°C. After 2 hours, the residue was filtered off and dried. Obtained: 2.6 g (5.4 mm) of phosphate (**3a**) in 100% yield; m.p. 314°C. A solution of $AgNO_3$ in water was added to the filtrate (solution of HCl in benzene). The mixture was stirred for a few hours. Obtained: 1.435 g of $AgNO_4$ or 0.3652 g (0.010 mm) of HCl.

C) A solution of PCl_5 (1.2 g, 0.006 m) and of chlorohydroquinone (2.6 g, 0.018 m) was boiled in 200 ml of damp benzene for 30 min. The residue formed was filtered off, and dried in vacuum at 150°C. Obtained: phosphate (**3a**) (2.2 g) in 80% yield. m.p. 314°C.

D) A solution of 2.6 g (0.018 m) of chlorohydroquinone in 100 ml of benzene was added to a solution of 1.2 g (0.006 m) of PCl_5 in 100 ml of benzene at 20°–25°C. The mixture was stirred for 1.5 hour. The precipitate was filtered off, washed with 150 ml of benzene and dried in vacuum. Obtained: 2.0 g of

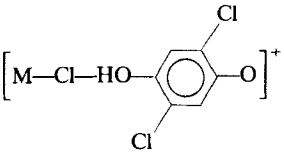
mixture of dichlorophosphorane (**1a**) and phosphate (**3a**) (correlation 1:3). ^{31}P NMR spectrum: δ_P −17.5 m.p. (**1**) and −4.2 m.p. (**3**).

E) A solution of 5.0 g (0.024 m) of chlorohydroquinone and 4.0 g (0.024 m) of *N,N*-dimethylaniline was added to a solution of 1.8 g (0.012 m) of $POCl_3$ in 100 ml of benzene at 20°–25°C. The mixture was stirred for 0.5 hour. The precipitate was filtered off, washed with 100 ml of benzene and 100 ml of H_2O and dried in vacuum. Obtained: 2.5 g of phosphate (**3a**) (45%). m.p. 314°C.

F) A solution of 5.0 g (0.024 m) of chlorohydroquinone in 100 ml of benzene was added to a solution of 1.8 g (0.012 m) of $POCl_3$ in 100 ml of benzene at 10°C. The mixture was stirred for 0.5 hour. The benzene was poured off. The residue obtained is an insoluble viscous resin.

Tris-(2,5-dichloro-4-hydroxyphenoxy)dichlorophosphorane (**1b**).

A) It was prepared similarly to dichlorophosphorane (**1a**) (Method A) in 90% yield. IR spectrum, cm^{-1}: 3350 (OH), 1580 (Ph), 985 (POC), 550, 440 (PCl). Mass spectrum: $[M—Cl]^+$ (*m/z* 597, 30%),



(*m/z* 420, 23%), $[M—2Cl]^+$ (*m/z* 562, 56%). Anal. for $C_{18}H_9Cl_8O_6P$.

Calc. %: C 33.96; H 1.41; Cl 44.65; P 4.87. Found: C 35.70; H 1.93; Cl 43.14; P 5.08.

B) A solution of 3.7 g (0.018 m) of dichlorohydroquinone and 2.0 g (0.018 m) of *N,N*-dimethylaniline was added to a solution of 1.2 g (0.006 m) of PCl_5 in 100 ml of benzene at 20°–25°C. The precipitate was filtered off, washed with benzene, dried in vacuum and analysed. Obtained: 6.2 g of precipitate. According to mass and IR spectral data, the precipitate is a mixture of dichlorophosphorane (**1b**) and the chlorohydrate of *N,N*-dimethylaniline.

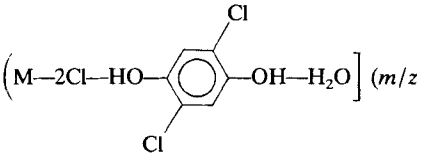
To a mixture of 6.2 g dichlorophosphorane (**1b**) and the chlorohydrate of *N,N*-dimethylaniline, 100 ml of H_2O was added. After 15 minutes, the precipitate was filtered off, washed with H_2O and dried. Obtained: 3.2 g of phosphate (**3b**) (95%).

2,5-Dichlorohydroquinone. Into a solution of 2.0 g of 2-chloro-1,4-benzoquinone in 200 ml benzene, gaseous HCl was passed slowly for 30 minutes at 20°C. After 40 minutes, the solvent was removed. Obtained: 2.2 g of 2,5-dichlorohydroquinone (91%).

Compound (**2b**). The same procedure was applied as for compound (**2a**). IR spectrum, cm^{-1}: 3360 (OH), 1600 (Ph), 985 (POC), 580 (PCl). Anal. for $C_{18}H_8Cl_7O_6P$. Calc. %: C 36.03; H 1.33; Cl 41.45; P 5.17. Found: C 38.11; H 2.16; Cl 44.00; P 5.98.

Tris-(2,5-dichloro-4-hydroxyphenyl)phosphate (**3b**). This compound was obtained similarly to that used for phosphate (**3a**) (Method A, 89% yield), (Method B, 100% yield). M.p. 130°C. IR spectrum, cm^{-1}: 3380 (OH), 1580 (Ph), 1295 (P═O), 1000 (POC). Mass spectrum: M^+ (*m/z* 578, 43%),

$[M—Cl]^+$ (*m/z* 543, 25%), $[M—2Cl]^+$ (*m/z* 508, 39%),



(*m/z* 312, 17%). M^+ 578. Anal. for $C_{18}H_9Cl_6O_7P$. Calc. %: C 37.18; H 1.55; Cl 36.66; P 5.33. Found %: C 36.82; H 1.53; Cl 37.03; P 5.40.

Reaction of 1,4-naphthaquinone with HCL. Into a solution of 2.0 g of 1,4–naphthaquinone in 100 ml of benzene, gaseous HCl was passed slowly for 24 hours at 20°–25°C. The solvent was removed. Obtained: 1.8 g of 1,4-naphthaquinone.

REFERENCES

1. F. Ramirez and N. B. Desai, *J. Am. Chem. Soc.*, **85,** 3252 (1963).
2. Ch. Grudmann, Methoden der Organischen Chemie (Houben-Weyl) B. 7/3A. S. 496, 643. Stuttgart: Georg Thieme (1977).

3. R. O. Duthaler, P. A. Lyle and Ch. Heuberger, *Helv. Chim. Acta,* **67,** 1406 (1982).
4. G. A. Kutyrew, A. A. Kutyrew, R. A. Cherkasow and A. N. Pudovik, *Phosphorus and Sulfur,* **13,** 135 (1982).
5. F. Ramirez, *Bull. Soc. Chim. France,* 2443 (1966).
6. F. Ramirez, H. J. Kugler and C. P. Smith, *Tetrahedron,* **24,** 1931 (1968).
7. Beilsteins Handbuch, (H.) B. 7, S. 617. Berlin: J. Liebig (1925).