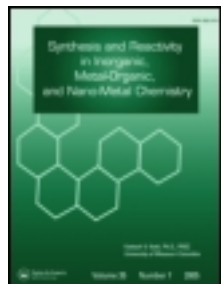


This article was downloaded by: [Pennsylvania State University]

On: 27 April 2013, At: 06:01

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office:  
Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/lsrt19>

### A Convenient One-Step, High-Yield Preparation of Methylphosphonyl Dichloride from Dimethyl Methylphosphonate

Kurt Moedritzer<sup>a</sup> & R. E. Miller<sup>a</sup>

<sup>a</sup> Corporate Research Department, Monsanto Company, St. Louis, Missouri, 63166, U.S.A.

Version of record first published: 13 Dec 2006.

To cite this article: Kurt Moedritzer & R. E. Miller (1974): A Convenient One-Step, High-Yield Preparation of Methylphosphonyl Dichloride from Dimethyl Methylphosphonate, *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry*, 4:5, 417-427

To link to this article: <http://dx.doi.org/10.1080/00945717408069671>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

A CONVENIENT ONE-STEP, HIGH-YIELD PREPARATION OF METHYLPHOSPHONYL  
DICHLORIDE FROM DIMETHYL METHYLPHOSPHONATE

Kurt Moedritzer and R. E. Miller

Corporate Research Department, Monsanto Company,  
St. Louis, Missouri 63166 U.S.A.

ABSTRACT

Based on a  $^1\text{H}$  and  $^{31}\text{P}$  nmr study of the interactions of alkylphosphonyl dichlorides,  $\text{RP}(\text{O})\text{Cl}_2$ , with dialkyl alkylphosphonates,  $\text{RP}(\text{O})(\text{OR})_2$ , a method was developed for the preparation of  $\text{CH}_3\text{P}(\text{O})\text{Cl}_2$  ( $\text{R} = \text{CH}_3$ ) in 98% yield. This method consists of the slow addition of the phosphonate to an excess of refluxing  $\text{SOCl}_2$ , thus suppressing irreversible side reactions. For  $\text{R} = \text{C}_2\text{H}_5$ , a yield of 72% was achieved; for  $\text{R} = \text{C}_4\text{H}_9$  and  $\text{ClCH}_2\text{CH}_2$  pure product could not be isolated.

INTRODUCTION

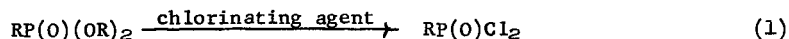
In the course of studies in organophosphorus chemistry, large amounts of methylphosphonyl dichloride of high purity were required. Since this material, to our knowledge, presently is not commercially available, we surveyed existing laboratory methods<sup>1</sup> for preparing methylphosphonyl dichloride conveniently, in high purity and high yield, possibly in a single-step reaction from low cost, readily available starting materials.

Among the methods described, the most widely used procedure is the reaction<sup>1,2</sup> of a dialkyl alkylphosphonate,  $\text{RPO}(\text{OR})_2$ , with  $\text{PCl}_5$ . However, this reaction does not proceed as cleanly as is generally assumed and a variety of side products are generated which for  $\text{R} = \text{CH}_3$  are of the type  $\text{CH}_3\text{P}(\text{O})\text{Cl}(\text{OCH}_3)$ ,  $(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{Cl}$  and  $(\text{CH}_3\text{O})\text{P}(\text{O})\text{Cl}_2$ . The latter species in particular is difficult to separate from the desired reaction product which is isolated in only about 50% yield.<sup>3,4</sup> Another method consists of the "rather lengthy and troublesome hydrolysis<sup>3</sup>" of dialkyl alkylphosphonates to the corresponding acid and subsequent conversion of the latter to the phosphoryl dichloride with  $\text{PCl}_5$  or  $\text{SOCl}_2$  in yields ranging from 50-75%. Recently, a sealed tube reaction has been reported<sup>3</sup> in which presently still rather high-priced alkylphosphonothioic dichlorides (Ethyl Corporation, Baton Rouge, La. USA) are converted to the corresponding phosphoryl dichlorides.

Since none of the above methods met our requirements, we explored in detail an approach mentioned previously in a patent<sup>5</sup> which uses  $\text{SOCl}_2$  as the chlorinating agent for the conversion of a dialkyl alkylphosphonate to the corresponding dichloride.

#### RESULTS AND DISCUSSION

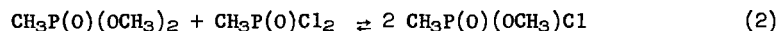
The conversion of a dialkyl alkylphosphonate to the corresponding alkylphosphonyl dichloride,



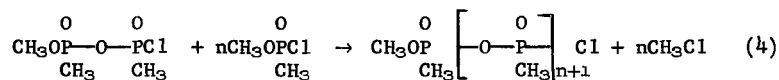
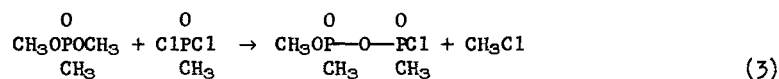
employing chlorinating agents on first sight appears to be fairly straightforward. However, the relatively low yields of product observed with e.g.  $\text{PCl}_5$  as the chlorinating agent<sup>3,4</sup> suggest ex-

tensive, yield-reducing side reactions. One has to take into consideration that under ordinary experimental conditions, molecules of the reactants as well as the product will be present simultaneously in the reaction mixture during a finite period of the reaction time. Regarding, at this time, only the potential interactions of these two species, a number of side reactions may be discussed. These may take place concurrently with the actual chlorination steps and may lead to side products or merely provide a detour of the reaction path to the final product.

As has been shown earlier,<sup>6</sup> mixtures of  $\text{CH}_3\text{P}(\text{O})\text{Cl}_2$  and  $\text{CH}_3\text{P}(\text{O})(\text{OCH}_3)_2$  undergo facile, reversible scrambling reactions in accord with the reaction of eq. (2), which proceed quite rapidly even at room temperature.



Concurrently with the above reaction, nonreversible condensation reactions were observed to take place, such as the sequence of reactions in eqs. (3) and (4)

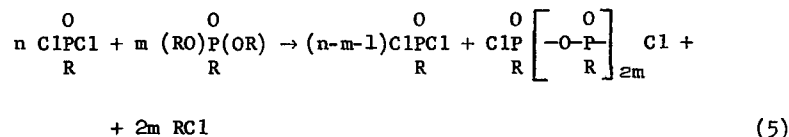


The above condensation reactions also are fairly rapid at room temperature.<sup>6</sup> We were able to show by proton nmr measurements in neat mixtures of  $\text{CH}_3\text{P}(\text{O})\text{Cl}_2$  and  $\text{CH}_3\text{P}(\text{O})(\text{OCH}_3)_2$  in the mole ratio 2.5:1 that in 1 hour at room temperature, 42 mol % of the orig-

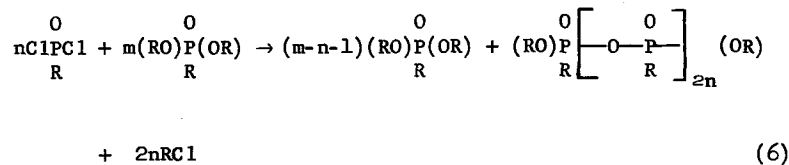
nally present  $\text{OCH}_3$  groups had undergone condensation to form P-O-P bonds and  $\text{CH}_3\text{Cl}$ . Concurrently with the appearance of  $\text{CH}_3\text{Cl}$ , additional peaks show up in the nmr spectra of such mixtures (doublets in the  $^1\text{H}$  and singlets with  $^{31}\text{P}$  nmr spectra). These, as suggested by the reactions of eqs. (3) and (4) indicate the formation in the reaction mixture of "end" groups,  $\text{CH}_3\text{OP}(\text{CH}_3)(\text{O})\text{O}-$  or  $\text{ClP}(\text{CH}_3)(\text{O})\text{O}-$  and "middle" groups,  $-\text{OP}(\text{CH}_3)(\text{O})\text{O}-$ . These are parts of oligomeric and polymeric poly(methylphosphonates) and their relative concentration is equilibrium controlled.<sup>6</sup>

In our studies, we were able to show, based on proton and  $^{31}\text{P}$  nmr spectra of mixtures of  $\text{RP}(\text{O})\text{Cl}_2$  and  $\text{RP}(\text{O})(\text{OR})_2$  ( $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$ ), in the mole ratios 1:3 and 3:1 in sealed tubes, that upon heating at  $100^\circ$  for several hours, the following general over-all reactions take place.

When  $[\text{RP}(\text{O})\text{Cl}_2] > [\text{RP}(\text{O})(\text{OR})_2]$ , ( $n > m$ ):



When  $[\text{RP}(\text{O})\text{Cl}_2] < [\text{RP}(\text{O})(\text{OR})_2]$ , ( $n < m$ ):



For the first case where  $[\text{RP}(\text{O})\text{Cl}_2] > [\text{RP}(\text{O})(\text{OR})_2]$ , the reaction of eq. (5) proceeds quantitatively resulting in mixtures show-

ing three  $^{31}\text{P}$  nmr signals having the following shifts (in ppm) for  $\text{R} = \text{CH}_3$  (for  $\text{R} = \text{C}_2\text{H}_5$  in parentheses):  $\text{RP}(\text{O})\text{Cl}_2$ :  $-44.2$  ( $-53.8$ ); end groups,  $\text{ClP}(\text{R})(\text{O})\text{O}-$ :  $-31.5$  ( $-37.8$ ); middle groups,  $-\text{OP}(\text{R})(\text{O})\text{O}-$ :  $-14.4$  ( $-17.7$ ).

Similarly, in the second case where  $[\text{RP}(\text{O})\text{Cl}_2] < [\text{RP}(\text{O})(\text{OR})_2]$ , the reaction of eq. (6) was seen to proceed quantitatively resulting in mixtures also exhibiting three  $^{31}\text{P}$  nmr signals, the shifts of which (in ppm) being the following for  $\text{R} = \text{CH}_3$  (for  $\text{R} = \text{C}_2\text{H}_5$  in parentheses):  $\text{RP}(\text{O})(\text{OR})_2$ :  $-33.3$  ( $-31.8$ ); end groups,  $\text{ROP}(\text{R})(\text{O})\text{O}-$ :  $-24.7$  ( $-25.9$ ); middle groups,  $-\text{OP}(\text{R})(\text{O})\text{O}-$ :  $-13.7$  ( $-16.4$ ).

These findings are corroborated by the somewhat more complex  $^1\text{H}$  spectra. A characteristic feature of these is the appearance of the signals for  $\text{RCl}$  in the amount corresponding to the stoichiometry of eqs. (5) and (6).

In view of the above irreversible condensation reactions of eqs. (5) and (6), it would appear imperative in the chlorination of dialkyl alkylphosphonate by any chlorinating agent [reaction of eq. (1)], that at all times the concentration of  $\text{RP}(\text{O})(\text{OR})_2$  be kept at a minimum. This may be accomplished by adding the dialkyl alkylphosphonate slowly to an excess of the chlorinating agent. In the case of  $\text{SOCl}_2$  as the chlorinating agent and  $\text{R} = \text{CH}_3$ , this procedure indeed resulted in a 98% yield of pure  $\text{CH}_3\text{POCl}_2$ . The same procedure does not work as well for  $\text{R} = \text{C}_2\text{H}_5$  (72% yield) and does not work at all for  $\text{R} = \text{C}_4\text{H}_9$  and  $\text{ClCH}_2\text{CH}_2$ . Apparently, in the latter cases, the rate of the reaction of eq. (1) is slow relative to the condensations of the reaction of eq. (5). Once condensed species have formed, these will not be chlorinated by

$\text{SOCl}_2$ . They remain upon distillation as undistillable, oily residues which were identified by  $^{31}\text{P}$  nmr as Cl-terminated poly(alkylphosphonates), and it is these polymers which are responsible for the observed low yields of alkylphosphonyl dichloride. Even for  $\text{R} = \text{CH}_3$ , considerably lower yields of  $\text{CH}_3\text{POCl}_2$  were obtained when the two reagents, contrary to the above procedure, were combined at once and refluxed.

Attempts to apply the same reasoning to  $\text{PCl}_5$  as chlorinating agent were not successful since for  $\text{R} = \text{CH}_3$ , only a 50% yield of (impure) methylphosphonyl dichloride was obtained. It appears that in this case, the rate of chlorination is not fast enough to prevent condensations from taking place. Considerable amounts of undistillable residue [poly(methylphosphonates)] were formed.

#### EXPERIMENTAL

Materials and Instrumentation.-- $\text{CH}_3\text{P}(\text{O})(\text{OCH}_3)_2$  was obtained from Aldrich Chemical Company, Inc., and was used as received;  $\text{C}_2\text{H}_5\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2$  and  $\text{C}_4\text{H}_9\text{P}(\text{O})(\text{OC}_4\text{H}_9)_2$  were purchased from Columbia Organic Chemicals Co., Inc. and  $\text{ClCH}_2\text{CH}_2\text{P}(\text{O})(\text{OCH}_2\text{CH}_2\text{Cl})_2$  from Pfaltz and Bauer, Inc., respectively, and distilled before use. Thionyl chloride was from Fisher Scientific and was used as received. All reactions and manipulations were performed in an atmosphere of dry nitrogen.

Proton nmr spectra at 60 MHz were recorded on a Varian A56/60 or T-60 Spectrometer, 90 MHz spectra on a Bruker HX-90E Spectrometer using tetramethylsilane as internal reference.  $^{31}\text{P}$  nmr spectra were obtained at 40.5 MHz on a Varian HR-100 using 85%  $\text{H}_3\text{PO}_4$  as external reference.

Preparation of  $\text{CH}_3\text{POCl}_2$  by the  $\text{SOCl}_2$  Method.--A quantity of 500 g (4.03 mole) of  $\text{CH}_3\text{PO}(\text{OCH}_3)_2$  was added dropwise over a period of 5 hours to 1200 g (10.1 mole) of  $\text{SOCl}_2$  being kept at reflux in a stirred 2-l flask. After the addition was completed, refluxing was continued overnight and subsequently the mixture was distilled at atmospheric pressure to remove excess  $\text{SOCl}_2$  and then at reduced pressure over a 50 cm vacuum-jacketed column packed with glass helices. After collecting a forerun of 19 g distilling mainly at  $40\text{--}50^\circ$  at 44 mm [ $^{31}\text{P}$  nmr ( $\text{CDCl}_3$ ):  $-3.5$  ppm;  $^1\text{H}$  nmr ( $\text{CDCl}_3$ ): doublet at 1.62 ppm ( $J = 6.6$ ) and several multiplets in the range 3.4 to 4.4 ppm], the main product distilled at  $98^\circ$  at 53 mm to give 525 g (3.95 mole) of methylphosphonyl dichloride corresponding to a 98% yield (based on dimethyl methylphosphonate).  $^{31}\text{P}$  nmr ( $\text{CDCl}_3$ ): single peak at  $-42.6$  (lit.<sup>7</sup>  $-44.5$  ppm);  $^1\text{H}$  nmr ( $\text{CDCl}_3$ ): doublet at  $\delta$  2.5 ppm,  $^2J = 16.9$  Hz; mp.  $33^\circ$  (lit.<sup>1</sup>:  $33^\circ$ ). The residue (about 10 g) hydrolyzed exothermically upon addition of water to give a solution of methylphosphonic acid;  $^{31}\text{P}$  nmr:  $-30.5$  ppm (lit.<sup>7</sup>  $-31.1$ ).

Preparation of  $\text{C}_2\text{H}_5\text{P}(\text{O})\text{Cl}_2$  by the  $\text{SOCl}_2$  Method.--A quantity of 83 g (0.5 mole) of  $\text{C}_2\text{H}_5\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2$  was added in the course of 6 hours to 179 g (1.5 mole) of refluxing  $\text{SOCl}_2$ , as described above for the corresponding methyl derivative. The  $^1\text{H}$  and  $^{31}\text{P}$  nmr spectra of the reaction solution taken after completed addition indicated the presence of about 75 mol %  $\text{C}_2\text{H}_5\text{P}(\text{O})(\text{OC}_2\text{H}_5)\text{Cl}$  ( $^{31}\text{P}$  nmr:  $-44.6$  ppm) and 25 mol %  $\text{OC}_2\text{H}_5$ -terminated end groups ( $^{31}\text{P}$  nmr:  $-25.2$  ppm). After refluxing for 24 hours, the nmr spectra showed the presence of ca. 75 mol %  $\text{C}_2\text{H}_5\text{POCl}_2$  ( $^{31}\text{P}$  nmr:  $-55.3$ ),



ca. 20 mol % Cl-terminated end groups ( $^{31}\text{P}$  nmr: -38.9 ppm) and 5 mol % middle groups ( $^{31}\text{P}$  nmr: -14.7 ppm). This composition did not change appreciably upon refluxing for an additional 24-hour period. Distillation of the reaction mixture, first at atmospheric pressure to remove excess  $\text{SOCl}_2$  and subsequently at reduced pressure yielded 52.8 g (0.36 mole) of pure  $\text{C}_2\text{H}_5\text{P}(\text{O})\text{Cl}_2$ , bp.  $102^\circ/43$  mm, corresponding to a 72% yield. Nmr data:  $^{31}\text{P}$ (neat): -52.8 ppm (lit.<sup>7</sup>: -52.5 ppm);  $^1\text{H}$ : at 60 MHz a higher order spectrum is seen for the protons of the ethyl group, at 90 MHz the spectrum becomes first order representing a doublet of quartets at  $\delta$  2.67 ppm ( $\text{CH}_2$ ,  $^3J_{\text{HH}} = 7.5$  Hz,  $^2J_{\text{HP}} = 14.5$  Hz) and a doublet of triplets at  $\delta$  1.42 ppm ( $\text{CH}_3$ ,  $^3J_{\text{HH}} = 7.5$  Hz,  $^3J_{\text{HP}} = 30$  Hz).

The distillation residue represented 12.4 g of a dark, viscous liquid, the  $^{31}\text{P}$  nmr spectrum of which (in  $\text{CDCl}_3$ ) consisted of a major peak at -18.5 ppm ("middle groups") and a minor peak at -38.3 ppm (Cl containing "end groups"). The proton nmr spectrum of this material (in  $\text{CDCl}_3$ ) gave a broad peak at  $\delta$  1.44 ppm ( $\text{CH}_2$  protons) and a broad doublet ( $J \sim 20$  Hz) at  $\delta$  1.39 ppm ( $\text{CH}_3$  protons).

When the rate of addition of  $\text{C}_2\text{H}_5\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2$  was faster (2 h/0.5 mole)  $\text{C}_2\text{H}_5\text{P}(\text{O})\text{Cl}_2$  was obtained in 62% yield.

Attempt to Prepare  $\text{C}_4\text{H}_9\text{P}(\text{O})\text{Cl}_2$  by the  $\text{SOCl}_2$  Method.--Addition of 82 g (0.33 mole) of  $\text{C}_4\text{H}_9\text{P}(\text{O})(\text{OC}_4\text{H}_9)_2$  to 131 g (1.1 mole) of  $\text{SOCl}_2$  in the course of 4 hours using the procedure described above, after 24 h of refluxing, resulted in a quantitative conversion of the diester to the ester chloride,  $\text{C}_4\text{H}_9\text{P}(\text{O})(\text{OC}_4\text{H}_9)\text{Cl}$ ;  $^{31}\text{P}$  nmr: single peak at -43.2 ppm;  $^1\text{H}$  nmr: multiplet at  $\delta$  4.20 ppm ( $\text{CH}_2\text{-O}$

protons) and two multiplets at  $\delta$  1.85 and 0.98 ppm ( $\text{CH}_2\text{-P}$  and  $\text{CH}_3$  protons) in the area ratio 2:17 (calc. 2:16).

Distillation yielded 17 g of a fraction with bp  $92\text{-}120^\circ/5$  mm consisting of a mixture of  $\text{C}_4\text{H}_9\text{P(0)Cl}_2$  ( $^{31}\text{P}$ : -49.5 ppm) and  $\text{C}_4\text{H}_9\text{P(0)(OC}_4\text{H}_9\text{)Cl}$  ( $^{31}\text{P}$ : -43 ppm), 27.4 g of pure  $\text{C}_4\text{H}_9\text{(0)P(OC}_4\text{H}_9\text{)Cl}$ , bp  $89^\circ/0.5$  mm,  $^{31}\text{P}$ : -42.8 ppm;  $^1\text{H}$ : multiplet at  $\delta$  4.23 ppm ( $\text{CH}_2\text{-O}$ ) and multiplets at  $\delta$  1.87 and 1.00 ppm ( $\text{CH}_2\text{-P}$  and  $\text{CH}_3$ ). Anal. calcd. for  $\text{C}_8\text{H}_{18}\text{ClO}_2\text{P}$ : C, 45.18; H, 8.53; P, 14.57. Found: C, 44.51; H, 8.06; P, 14.60.

Attempted Preparation of  $\text{ClCH}_2\text{CH}_2\text{P(0)Cl}_2$  by the  $\text{SOCl}_2$  Method.--

A quantity of 82.5 g (0.31 mole) of  $\text{ClCH}_2\text{CH}_2\text{P(0)(OCH}_2\text{CH}_2\text{Cl)}_2$  was added to 119 g (1 mole) of  $\text{SOCl}_2$  in the course of 5 hours following the procedure described above. After completed addition, the  $^{31}\text{P}$  and  $^1\text{H}$  nmr spectra of the reaction solution showed that no reaction had occurred;  $^{31}\text{P}$  nmr: one signal at -26.1 ppm (authentic  $\text{ClCH}_2\text{CH}_2\text{P(0)(OCH}_2\text{CH}_2\text{Cl)}_2$ ,  $^{31}\text{P}$ : -26.4 ppm). Upon refluxing overnight and in the course of additional refluxing over a period of 65 hours, the starting material was gradually converted to the ester chloride ( $^{31}\text{P}$  -36.8 ppm) as the major product (minor  $^{31}\text{P}$  peaks at -26 and -19.2 ppm);  $^1\text{H}$  nmr: multiplets at  $\delta$  4.54 ( $\text{CH}_2\text{-O}$ ),  $\delta$  3.88 ( $\text{CH}_2\text{-Cl}$ ) and  $\delta$  3.03 ( $\text{CH}_2\text{-P}$ ). Upon distillation, 21.2 g of a fraction with bp in the range  $78\text{-}98^\circ/1$  mm was observed which consisted of about 75 mol % ester chloride ( $^{31}\text{P}$ : -38 ppm), about 15 mol % of the desired  $\text{ClCH}_2\text{CH}_2\text{POCl}_2$  ( $^{31}\text{P}$ : -43.8 ppm; lit.<sup>7</sup>: -43.6, -41.9) and an additional product in an amount of 15 mol % having a broad  $^{31}\text{P}$  nmr peak at -26.4 ppm.

The distillation residue consisted of 34.9 g of a dark viscous liquid which gave three  $^{31}\text{P}$  nmr peaks (approximate peak areas in parentheses): -38.7 ppm (10%), -28.4 ppm (80%) and -10 ppm (10%).

Preparation of  $\text{CH}_3\text{POCl}_2$  ( $\text{PCl}_5$  Method).--To a slurry of 1700 g (8.06 mole)  $\text{PCl}_5$  in 2 l benzene heated at 60-70° with stirring, 500 g (4.03 mole) of  $\text{CH}_3\text{PO}(\text{OCH}_3)_2$  was added dropwise over a period of 8 hours. Subsequently the reaction mixture was refluxed for 4 hours and distilled, first at atmospheric pressure to a bp of 115° and subsequently at reduced pressure using a 50 cm vacuum-jacketed column filled with glass helices. After collecting 22 g of a forerun, bp 50-100° at 80 mm ( $^{31}\text{P}$  nmr: -146.5 ppm (50%), -42 ppm (30%) and -3 ppm (30%), the main fraction distilled at 100-105° at 80 mm giving 282 g (2.12 mole) of product which solidified to the greatest part upon standing.  $^{31}\text{P}$  nmr of this product confirmed that it is  $\text{CH}_3\text{POCl}_2$  (-44.0 ppm) in a purity of 95% with the  $^{31}\text{P}$  chemical shifts of impurities at -147 and -3 ppm. This corresponds to a yield of  $\text{CH}_3\text{POCl}_2$  of about 50%. A large amount (122 g) of dark, viscous, water-soluble residue remained in the distillation flask which, after hydrolysis, gave one peak in the  $^{31}\text{P}$  nmr spectrum at -32.4 ppm and, in the  $^1\text{H}$  nmr spectrum, a doublet at  $\delta$  1.9 ( $J = 16$  Hz), indicating  $\text{CH}_3\text{P}(\text{O})(\text{OH})_2$ .

#### REFERENCES

1. M. Fild, R. Schmutzler and S. C. Peake, "Organic Phosphorus Compounds," G. M. Kosolapoff and L. Maier, eds., John Wiley and Sons, New York, N. Y., 1972, Vol. 4, p. 155.

PREPARATION OF METHYLPHOSPHONYL

2. K. Sasse, "Houben-Weyl; Organische Phosphorverbindungen," Georg Thieme Verlag, Stuttgart, 1963, Vol. XII/1, p. 388.
3. L. Maier, *Helv. Chim. Acta*, 56, 492 (1973).
4. See Experimental part of this paper.
5. T. P. Dawson and J. W. Armstrong, U. S. Patent 2,847,469, issued August 12, 1958; *Chem. Abstr.*, 53, 3058 (1959).
6. D. Grant, J. R. Van Wazer, and C. D. Dungan, *J. Polym. Sci. A.1*, 5, 57 (1967).
7. V. Mark, C. H. Dungan, M. M. Crutchfield, and J. R. Van Wazer, "Topics in Phosphorus Chemistry," 5, 227 (1967).

Received: May 23, 1974  
Accepted: June 14, 1974

Referee I: D.E. Arrington  
Referee II: V. Gutmann