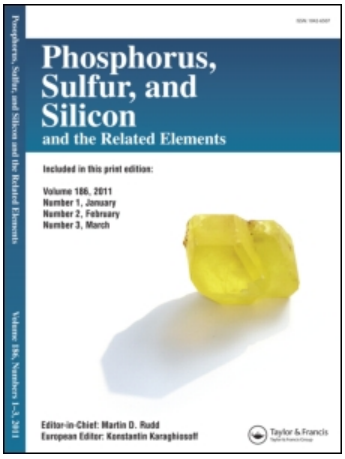


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THE PREPARATION OF DIMETHYL PHOSPHOROCHLORIDITE AND ITS HOMOLOGS FROM TRIALKYL PHOSPHITES AND DICHLOROTRIPHENYLPHOSPHORANE

Piotr Majewski[a]
[a] Institute of Organic Chemistry, Technical University (Politechnika), Łódź 40, Poland

To cite this Article Majewski, Piotr(1987) 'THE PREPARATION OF DIMETHYL PHOSPHOROCHLORIDITE AND ITS HOMOLOGS FROM TRIALKYL PHOSPHITES AND DICHLOROTRIPHENYLPHOSPHORANE', Phosphorus, Sulfur, and Silicon and the Related Elements, 33: 1, 37 — 39
To link to this Article: DOI: 10.1080/03086648708074280
URL: http://dx.doi.org/10.1080/03086648708074280

Phosphorus and Sulfur, 1987, Vol. 33, pp. 37–39
Photocopying permitted by license only

THE PREPARATION OF DIMETHYL PHOSPHOROCHLORIDITE AND ITS HOMOLOGS FROM TRIALKYL PHOSPHITES AND DICHLOROTRIPHENYLPHOSPHORANE

PIOTR MAJEWSKI

Institute of Organic Chemistry, Technical University (Politechnika), Żwirki 36, 90-924 Łódź 40, Poland

(Received October 29, 1986; in final form January 15, 1987)

A novel convenient synthesis of dialkyl phosphorochloridites based on the reaction of trialkyl phosphites with dichlorotriphenylphosphorane has been described. In this way the commonly used dialkyl phosphorochloridites (**3a–e**) were prepared in satisfactory yields. Their identity was confirmed by ^{31}P-NMR spectroscopy as well as by their refractive index.

Although a variety of synthetic approaches to dialkyl phosphorochloridites **3** have been reported[1,3] only a few of them can be used for the preparation of dimethyl phosphorochloridite (**3a**)[1g–j]. The most efficient of these methods utilize not easily available dimethyl *N,N*-dimethylphosphoroamidite which is treated with anhydrous hydrogen chloride.[1h] Another operationally simple synthesis based on the reaction of trimethyl phosphite (**1a**) with phosphorus trichloride promoted by HMPT[2] affords **3a** contaminated with considerable amounts (7–8%) of the starting material, **1a**.[2b] This paper reports a convenient synthesis of **3a** by treatment of trimethyl phosphite (**1a**) with an equimolar amount of dichlorotriphenylphosphorane (**2**). The phosphorane **2** is readily prepared by chlorination of triphenylphosphine[4] and is utilized *in situ* for further transformation.

$$(RO)_3P + Ph_3PCl_2 \xrightarrow[-RCl]{} (RO)_2PCl + Ph_3P{=}O$$

1a-e **2** **3a-e** **4**

The reaction is carried out by refluxing the starting materials in dichloromethane. Triphenylphosphine oxide (**4**) formed as a byproduct is easily removed from the reaction mixture by precipitation with ether. Evaporation of the solvent followed by distillation of the residue affords **3a** in 57% yield. The product obtained in this way is 96–98% pure according to the ^{31}P-NMR spectrum and contains ~2% of trimethyl phosphite ($\delta = 141$ ppm) and/or ~2% of methyl phosphorodichloridite ($\delta = 178.5$ ppm). It has been also found that chlorination of other trialkyl phosphites **1b–e** with **2** in benzene at higher temperature (see Table I) affords the corresponding dialkyl phosphorochloridites, **3b–e** in good yield and excellent purity (97–99% according to the ^{31}P-NMR spectrum). Presumably, the driving force of this reaction is an intermolecular ligand exchange between **1** and chlorotriphenylphosohonium chloride, which represents

TABLE I

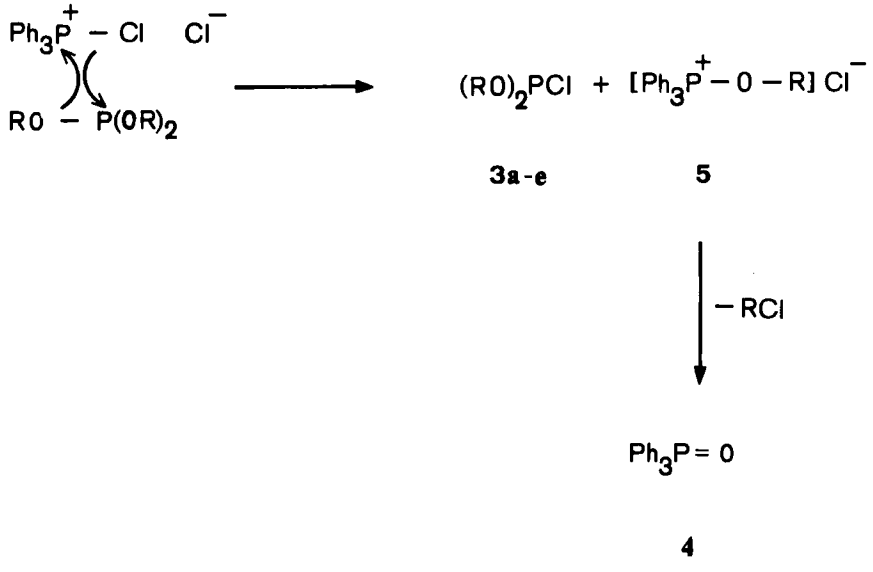
Dialkyl phosphorochloridites $(RO)_2PCl$, **3a–e**

3	R	Reaction conditions[a] Temperature [°C]	Time [h]	Yield [%]	b.p. [°C]/torr Observed	Literature	^{31}P-NMR δ [ppm] Observed[b]	Literature	n_D^{20} Observed	Literature
a	CH_3	40	3	57	45/80	30/35[1g]	167	169[1g]	1.4367	1.4356[1i]
b	C_2H_5	50	1.5	71	48/15	45-50/12[1f]	164	165[1f]	1.4372	1.4376[1f]
c	n-C_3H_7	50	1	76	78-80/17	80/17[1d]	170	164[3]	1.4430	1.4426[1d]
d	i-C_3H_7	50	1	38	60/12	62-64/12[1d]	163	165[3]	1.4335	1.4331[3]
e	n-C_4H_9	50	1	69	88-90/10	115-117/25[1d]	162	164[3]	1.4451	1.4454[1d]

[a] All reactions are carried out under dry argon. Commercially available trialkyl phosphites were purified by conventional methods.

[b] Measured at 36.43 MHz on a Bruker HFX 90 NMR Spectrometer (C_6H_6/85% H_3PO_4 ext.).

an ionic structure of **2**, leading to the products **3a–e** and the quasiphosphonium salts **5**. The salts **5** are subsequently stabilized by dealkylation to produce triphenylphosphonium oxide **4** and the corresponding alkyl chlorides.



EXPERIMENTAL

Dimethyl phosphorochloridite, **3a**. A gaseous chlorine (7.09 g, 0.1 mol) in a stream of dry argon is passed slowly through a stirred solution of triphenylphosphine (26.2 g, 0.1 mol) in dichloromethane (200 ml) at +5°C and the mixture is set aside for 30 min at room temperature. To the resulting mixture trimethyl phosphite (12.4 g, 0.1 mol) is added dropwise with stirring at +5°C, the mixture is kept for 1 h at room temperature and then refluxed for 3 h. The solvent is then evaporated under reduced pressure (100 Torr) using a short Vigreux column and 70 ml of dry ether is added to the residue. The mixture is refrigerated for 3–8 h, the triphenylphosphine oxide precipitated is filtered off, and the solvent is evaporated under reduced pressure (80 Torr, using a short Vigreux column). The residue is distilled *in vacuo*. Yield: 7.3 g (57%); b.p. 45°C/80 Torr, Lit.[1g] b.p. 30°C/35 Torr.

Dialkyl phosphorochloridites, **3b–e** (general procedure). To dichlorotriphenylphosphorane prepared as described above, (**2**; 0.1 mol, dissolved in 200 ml of benzene) the trialkyl phosphite (**1b–e**; 0.1 mol) is added dropwise at +5°C and the mixture is stirred for 1 h at room temperature and then for 1 h or 1.5 h (see Table I) at 50°C. The solvent is evaporated under reduced pressure (45 Torr) and 70 ml of

dry ether is added to the residue. The triphenylphosphine oxide, **4** precipitated is filtered off. The filtrate is evaporated under reduced pressure and the residue is distilled in vacuo to give pure **3b–e** (see Table I).

ACKNOWLEDGEMENT

The author is grateful to Professor Dr hab. A. Zwierzak for many stimulating discussions. The author acknowledges support of this work by grant No. MR-I-12 from the Polish Academy of Sciences.

REFERENCES

1. (a) E. Müller, Ed., *Methoden Org. Chem.* Houben-Weyl 4th Ed., **12/2,** 45 (1964); (b) H. G. Cook, J. D. Ilett, B. C. Saunders, G. J. Stacey, H. G. Watson, I. G. E. Wilding and S. J. Woodcock, *J. Chem. Soc.*, **1949,** 2921; (c) A. I. Razumov, B. G. Kiorber, V. V. Moskva and Z. M. Khammatova, *Tr. Kazans. Khim.-Tekhnol. Inst.*, **30,** 265 (1962); C.A. **60,** 1571 g (1964); (d) J. Michalski, T. Modro and A. Zwierzak, *J. Chem. Soc.*, **1961,** 4904; (e) W. Gerrard, M. J. D. Isaacs, G. Machell, K. B. Smith and P. L. Wyvill, *J. Chem. Soc.*, **1953,** 1920; (f) J. Gloede, M. Mikolajczyk, A. Lopusiński and J. Omelańczuk, *J. Prakt. Chem.*, **316,** 703 (1974); (g) A. E. Lippman, *J. Org. Chem.*, **30,** 3217 (1965); (h) O. J. Scherer and R. Thalacker, *Z. Naturforsch.*, **27b,** 1429 (1972); (i) M. Baudler, *Z. Elektrochem.*, **59,** 173 (1955); (j) C. E. Jones and K. J. Coskran, *Inorg. Chem.*, **10,** 1536 (1971); (k) W. Gerrard and M. Lindsay, *Chem. Ind. (London)*, **1960,** 152.
2. (a) Z. Mazour, (Ciba-Geigy A.-G.), German Patent, 2643442 (07 Apr 1977); C. A., **87,** 52758u (1977); Z. Mazour, H. Brunetti, (Ciba-Geigy A.-G.), German Patent, 2643474 (07 Apr 1977); C.A. **87,** 52757t (1977); Z. Mazour, (Ciba-Geigy Corp.) U.S. Patent, 4079103 (14 March 1978); (b) N. T. Thuong, Ch. Tran, U. Asseline and P. Chabrier, *C.R. Acad. Sci., Ser. C*, **290,** 53 (1980).
3. M. M. Kabachnik, E. V. Snyatkova, Z. S. Novikova and I. F. Lutsenko, *Zh. Obshch. Khim.*, **50,** 227 (1980).
4. R. Appel and H. Schoeler, *Chem. Ber.*, **110,** 2382 (1977).