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A New Synthesis of Unsymmetrically Substituted Halophosphines

Jan Omelańczuk

Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Department of Organic Sulfur Compounds, 90-363 Łódź, Sienkiewicza 112, Poland

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ABSTRACT

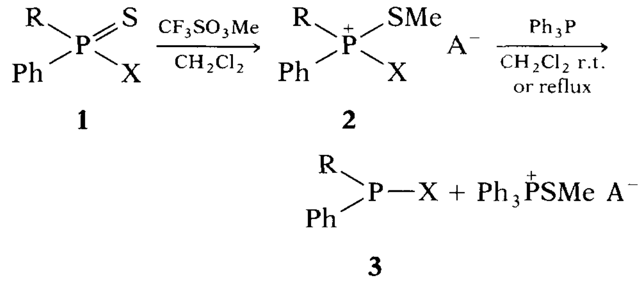
Chiral, racemic alkylaryl-, or diarylhalophosphines have been obtained in 50–70% yields by treatment of alkylaryl- or diaryl-methylthiohalophosphonium triflates with triphenylphosphine in methylene chloride solution at room temperature or under reflux.

Chlorophosphines are key substrates in the synthesis of a variety of organophosphorus compounds. Although many methods of synthesis of halophosphines are known, those dealing with the synthesis of unsymmetrically substituted ones, are rather limited in number [1]. Most of them consist of the reaction of organometallic reagents such as tetraalkyllead [2], dialkyl(aryl)mercury [3], or organocadmium compounds [4] with aryldihalophosphines. Direct arylation of dihalophosphines in the Friedel-Crafts type reaction gives satisfactory yields of products, although their isolation creates some inconveniences connected with complexation of the catalyst (aluminium trichloride) with the chlorophosphines [5].

The most commonly used synthesis of unsymmetrically substituted halophosphines is the two step procedure which involves the reaction of Grignard or organolithium reagents with alkyl- or arylaminochlorophosphines, with the subsequent reaction of the alkylarylaminophosphines formed with hydrogen chloride or phosphorus trichloride [6]. Another group of methods leading to the unsymmetrically substituted halophosphines involves the reduction of the easily available dialkyl(aryl)phosphinothioic chlorides with metals [7], phosphines [8] or triphenyl phosphite [9]. All these reducing procedures require, however, the use of the sealed tube technique or a very high temperature.

Some years ago we described [10, 11] a new two-step method for the reduction of thiophosphinic esters: alkylation of thionophosphinic derivatives by means of methyl trifluoromethanesulfonate (methyl triflate), followed by the reaction of the methylthiophosphonium salts formed with thiophilic reagents, such as mercaptide anions or tris(dimethylamino)phosphine. This method has been successfully applied for the stereoselective synthesis of optically active phosphines, phosphinite, and thiophosphinite esters.

In the course of our studies, we have now found that the action of triphenylphosphine on the alkylarylmethylthiophosphonium salts of type 2 in a dichloromethane solution at room temperature or under reflux results in the formation of the corresponding alkylarylhalophosphines **3** in 50–70% yields.



X = Cl, Br; $A^- = CF_3SO_3^-$; R = alkyl, aryl

The required starting salts **2** were obtained by the addition of alkylarylphosphinothioic halides **1** to a boiling solution of methyl triflate [12]. Such a procedure was found to lead selectively to the alkylation products **2**. The formation of the salts **2** is

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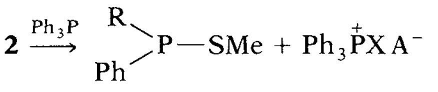
completed (80–100% yield) within 30 minutes to 2 hours as evidenced by ^{31}P NMR spectra. In the subsequent step, a dichloromethane solution of the latter was treated with a solution of an equimolar amount of triphenylphosphine in the same solvent at room temperature or under reflux. Both steps of the **1** → **3** conversion can be more conveniently performed as a one-pot procedure without isolation of the salts **2**. The trace of impurities (mainly starting phosphinothioic chloride **1**) do not usually exceed 2–5% (^{31}P NMR assay) and may be removed by a careful redistillation.

We did not observe under these conditions the alternative products of the reaction, that is, the phosphinothioites **4**, which might arise as the result of a dehalogenation process [13].



$$2 \xrightarrow{Ph_3P} \mathrm{R(Ph)P{-}SMe} + Ph_3\overset{+}{P}X\,A^-$$

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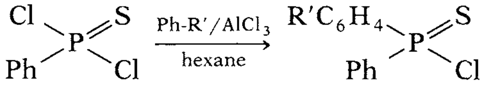
In extension of this work, we have found that desulfurisation of diphenylmethylthiochlorophosphonium triflate **2e** (R = Ph) can also be achieved by using triphenylphosphine. This fact allowed us to obtain a number of chiral, racemic diarylchlorophosphines whose synthesis by other methods is less effective.

The starting diarylphosphinothioic chlorides **1f**, **1g**, **1h** have been obtained by a slightly modified Maier's [16] procedure in about 40–50% yields from phenylphosphonothioic dichloride and the corresponding substituted benzenes in the presence of aluminium trichloride in hexane.



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R′ = Me, Et, Cl, Br

According to Maier's [16] and our results this thiophosphinylation affords as the main product the *p*-isomer in the benzene ring, contaminated with certain amounts (*ca.* 5–10%, GC and ^{31}P NMR assay) of its *o*-isomer. Greater amounts of the *o*-isomer were observed for phenylbromophenylchloridophosphinothionate **1h** (*ca.* 25%). The mixture of these isomers was used for the synthesis of diarylchloridophosphines **3**, some properties of which are listed in Table 1.

In summary, the method of synthesis of unsymmetrically substituted halogenophosphines **3** presented herein may be a useful alternative to other methods reported in the literature due to its simplicity, easily available substrates and mild reactions conditions.

EXPERIMENTAL

Alkylaryl or Diaryl Halophosphines 3

To a boiling solution of methyl triflate (0.01 mol) in methylene chloride (15 mL), a solution of alkylaryl- or diarylphosphinothioic halide **1** (0.01 mol) in methylene chloride (5 mL) was added dropwise. The mixture was refluxed for the next 0.5 to 2 hours (^{31}P NMR control) and then a solution of triphenylphosphine (0.01 m) in methylene chloride (5 mL)

TABLE 1 Preparation of chiral racemic alkyl(aryl)arylhalophosphines **3**

	R	*X*	**2** $\delta^{31}P$ (CH_2Cl_2)	**3** $\delta^{31}P$ (C_6H_6)	**3** *Yield [10]* %	**3** *bp / mmHg*	**3** n_D^{20}
a	t-Bu	Cl	127.1[d]	106.0 107.0 [15]	58	59 / 0.6; 87-9 / 3; [15]	1.5545 1.5551
b	Me	Br	64.2	76.9 77.0 [10]	67	58 / 0.2; 65 / 0.5 [17];	1.6240
c	t-Bu	Br	120.6	105.0[a]	60	71 / 0.6;	1.5760
d	Et	Cl	110.0[d]	97.5[b] 97.0 [17]	56	62 / 0.8; 73 / 5 / 2 [17];	1.5715
e	Ph	Cl	94.2[d]	81.6 81.5 [17]	68.7	114 / 0.6; 112-13 / 0.5; [18]	1.6365 1.6358 [18]
f	p-Me—C_6H_4 o—	Cl	94.7 95.0	83.3[c] 83.4	55.5	121 / 0.05	1.6251
g	P—Cl—C_6H_4 o—	Cl	94.4 95.1	80.6[c] 82.5	53.0	135-40 / 0.1-0.15;	1.6408
h	p-Br—C_6H_4 o—	Cl	94.6 95.0	80.6[c] 82.4	30.0	155-60 / 0.1;	1.6512

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[a] Without solvent.
[b] In CH_2Cl_2.
[c] In $CDCl_3$
[d] The salts **2a**, **2d**, **2e** gave correct elemental analysis; the other were not analyzed.

was added dropwise. After *ca.* 0.5 hour methylene chloride was evaporated and the residue was extracted with ether (2 × 15 mL). After the removal of ether, the crude product was distilled under vacuum giving **3** (Table 1).

Isolation of Salts 2

A solution of the salt **2** in methylene chloride prepared as described above was concentrated and the residual mixture was extracted with ether (4 × 10 mL). Then the traces of the solvent were removed and the salt was analyzed.

Preparation of Diarylphosphinothioic Chlorides 1

A mixture of phenylphosphonothioic dichloride (3.2 g, 0.015 mol), aluminium trichloride (2 g, 0.015 mol) and the proper benzene derivative (0.02 mol) in dry hexane (20 mL) was refluxed for 1.5 to 3 hr. Then, the mixture was poured on crushed ice and the cold aqueous solution thus obtained was extracted with chloroform (3 × 20 mL). The chloroform solution was dried over magnesium sulfate, concentrated and the residue fractionally distilled under vacuum to give the corresponding phenylarylphosphinothioic dichloride, some of whose properties are given below.

R = Me—C_6H_4: 58.2% yield; bp 132°C/0.05 mmHg; n_D^{20} 1.6470; ^{31}P NMR $\delta = 81.28$ (*p*-isomer); 6% *o*-isomer (GC), not distinguished in ^{31}P NMR. Anal. for $C_{13}H_{12}ClPS$: Calcd. C, 58.54; H, 4.53; P, 11.61. Found: C, 57.85; H, 4.65; P, 11.69.

R = Et—C_6H_4: 47.6% yield; bp 125–7°C/0.02 mmHg; n_0^{20} 1.6400; ^{31}P NMR $\delta = 81.16$ (*p*-isomer); 10% *o*-isomer (GC), ^{31}P NMR $\delta = 80.56$. Anal. for $C_{14}H_{14}ClPS$: Calcd. C, 59.89; H, 5.03; P, 11.03. Found: C, 59.87; H, 5.18; P, 10.90.

R = Cl—C_6H_4: 38.8% yield; bp 165–70°C/0 mmHg; n_D^{20} 1.6633; ^{31}P NMR $\delta = 78.79$ (*p*-isomer); 4.3% *o*-isomer (GC), not distinguished in ^{31}P NMR. elem. analysis for $C_{12}H_9Cl_2PS$: Anal. Calcd. for $C_{12}H_9ClPS$ C, 50.20; H, 3.16; P, 10.79. Found: C, 50.24; H, 3.25; P, 10.61.

R = Br—C_6H_4: 32.7% yield; bp 160–70°C/0.3–0.3 mmHg; n_D^{20} 1.6762 ^{31}P NMR $\delta = 78.97$ (*p*-isomer); 25% *o*-isomer (GC), ^{31}P NMR $\delta = 80.79$. Anal. for $C_{12}H_9ClBrPS$: Calcd. C, 43.96; H, 2.74; P, 9.34. Found: C, 44.11; H, 3.20; P, 9.65.

REFERENCES

[1] M. Field and R. Schmutzler in, *Organic Phosphorus Compounds*, ed., G. M. Kosolapoff and L. Maier, Wiley Interscience, a Division of John Wiley and Sons Inc., New York, London, Sydney, Toronto, Vol. 4, p. 75.

[2] B. Bartocha, C. M. Douglas, N. Y. Gray, *Z. Naturf. 14b*, 1959, 809.

[3] W. J. Pope, B. C. S. Gibson, *J. Chem. Soc. 101*, 1911, 735.

[4] W. Jare, G. Guillerm, W. Chodkiewicz, *J. Organomet. Chem. 149*, 1978, C7–C9.

[5] G. Nagy, D. Balde, France Patent 1950691/*Chem. Abstr. 67*, 1967, p. 3142.

[6] L. Horner, F. Schedlbauer, P. Beck, *Tetrahedron. Lett. 22*, 1964, 1421.

[7] L. C. D. Groenweghe, US Patent 3024278 (1962)/ *Chem. Abstr. 57*, 1962, 7311c.

[8] M. E. Ulmer, L. C. D. Groenwenghe, L. Maier, *J. Inorg. Nucl. Chem. 20*, 1961, 82.

[9] L. Maier, R. Gredig, *Helv. Chim. Acta, 52*, 1969, 827.

[10] J. Omelańczuk, M. Mikołajczyk, *J. Am. Chem. Soc. 101*, 1979, 7292.

[11] J. Omelańczuk, M. Mikołajczyk, *Tetrahedron Lett. 25*, 1984, 2493.

[12] When the reversed procedure is applied, that is, the aklylating agent is added to substrates, the formation of substantial amounts of by-products is observed. Moreover, in spite of the "normal" procedure used, such by-products were always present in the case of the salts **2a**, **2g**, **2h**. On the basis of similar results of Crich and Dyker [14], a structure of diphosphonium salts, may be ascribed to these compounds. However, this point is under current studies. We also suppose that lowered yields of **3** in some cases may be due to the presence of these unidentified compounds.

[13] In the case of the salt **2a**, phenyl *t*-butylphosphinothioite was observed at low temperature (−70°) as a result of the alternative dehalogenation process.

[14] D. Crich, H. Dyker, *Tetrahedron Lett. 30*, 1989, 475.

[15] V. L. Voss, V. A. Soldatenko, Ju. A. Veits, and L. F. Lutsenko, *Zh.-Obshei Khim., 49*, 1979, 1724.

[16] L. Maier, *Helv. Chim. Acta, 47*, 1964, 120.

[17] L. Maier, *J. Inorg. Nucl. Chem. 24*, 1962, 1073.

[18] J. Goubeau, R. Baumgärtner, W. Koch, U. Müller, *Z. Anorg. Allg. Chem., 537*, 1965, 174.