

Formation of Aryl Dialkylphosphinates from Dialkylphosphinous Chlorides and Arylmagnesium Bromides under Oxidative Conditions

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ABSTRACT: *The reaction of dialkylphosphinous chlorides (1) with arylmagnesium bromides carried out in the air atmosphere was found to afford aryl-dialkylphosphine oxides (2) and aryl dialkylphosphinates (3) in a comparable quantity. Formation of the latter product (3) is the first example that an aryl-dialkylphosphine, formed as an intermediate, is autooxidized to the corresponding phosphinate. © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:38–41, 2001*

INTRODUCTION

The P-oxides of phosphorus heterocycles with a trialkylphenyl substituent on the heteroatom have proved to possess unique properties [1] and have been useful intermediates in a novel [2 + 2] cycloaddition reaction [2]. For comparative purposes, we desired to elaborate the synthesis of the alicyclic an-

alogues, dialkyl-arylphosphine oxides. In this article, we give an account of our results on the preparation of the phosphine oxides with an aryl- (e.g., 2,4,6-triisopropylphenyl) substituent on the phosphorus atom.

RESULTS AND DISCUSSION

The aryl-dialkylphosphines, starting materials for the corresponding phosphine oxides, are known to have been synthesized by the reaction of arylphosphonous dichlorides (aryl-dichlorophosphines) with two equivalents of an alkylmagnesium bromide [3,4]. We wished to utilize another approach for the preparation of our target molecules, the reaction of dialkylphosphinous chlorides with arylmagnesium bromides. The phosphinous chlorides **1a–c** were reacted with one equivalent of triisopropylphenylmagnesium bromide in THF solution at 26–67°C. In order to obtain the desired phosphine oxides (**2a–c**) directly, the Grignard reaction was performed in the air atmosphere. This is quite unusual, as the Grignard reactions are normally carried out in an inert

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atmosphere. We found that the formation of the expected phosphine oxides (2a–c) was accompanied by that of the corresponding phosphinates (3a–c) (Scheme 1). The reaction of chloride 1c with phenylmagnesium bromide under the aforementioned conditions also led to a mixture of the same type of products (2d and 3d) (Scheme 1). The conditions of the substitution reactions together with the product compositions obtained after flash column chromatography are listed in Table 1. The ^{31}P NMR chemical shifts and the molecular weights obtained by electron impact–mass spectrometry (EI-MS) are also included. The compounds prepared (2a–d and 3a–d) are all new species; the analogous $\text{Et}_2\text{P}(\text{O})\text{Ph}$ and $\text{Et}_2\text{P}(\text{O})\text{OPh}$ derivatives were, however, described earlier [5,6]. For the former compound, a δ_{p} of 48.8 [5], and for the latter, a δ_{p} of 61.0 were reported [6], which seem to match our values (Table 1). The mass spectrum of the individual components were determined by gas chromatography–mass spectrometry (GC-MS) (Table 2). Utilizing repeated column chromatography, we could separate phosphine oxide 2b and phosphinate 3b that were characterized by MS (Table 2) and ^{13}C NMR (Table 3). It can be seen from the data that for 2b and 3b, a $^1J_{\text{PC}}$ of 67 Hz and a $^1J_{\text{PC}}$ of 89 Hz were detected, respectively, for C_1 of the alkyl substituent. These data are also consistent with the different substitution patterns of the phosphorus atom in the two types of compounds (2 and 3).

It was found that, in an inert atmosphere, the reaction of phosphinous chloride 1a with phenylmagnesium bromide furnished diethylphenylphosphine (4e) in an almost quantitative yield (δ_{p} –16.9; δ_{p} lit [7] –16.0). Oxidation of 4e by bubbling air through its THF solution at 26°C resulted in a mixture of phosphine oxide 2e (39%) and phosphinate 3e (61%) with δ_{p} 49.3 (δ_{p} lit. [5] 48.8) and δ_{p} 61.6 (δ_{p} lit. [6] 61.0), respectively (Scheme 2).

Surveying the literature, we found that some examples for the autooxidation of trialkylphosphines into the mixture of the corresponding phosphine ox-

ides and phosphinates have been described [8,9]. It was observed, however, that the arylphosphines are more resistant to oxidation, than the trialkyl derivatives. A radical mechanism involving $\text{R}\cdot$, $\text{RO}_2\cdot$, and $\text{RO}\cdot$ as the radicals was suggested [8,9]. It is worthy of mention that in our cases only the aryl dialkylphosphinates (3) were formed, but not the alkyl alkyl-arylphosphinates. According to GC-MS analysis, phosphonates from double O-insertion were present in only traces in the crude reaction mixtures.

Obviously, the strong affinity of phosphorus to oxygen may be the driving force for the formation of the phosphinates (3).

EXPERIMENTAL

The ^{31}P - and ^{13}C NMR spectra were taken on a Bruker DRX-500 spectrometer operating at 202.4 and 125.7 MHz, respectively. GC-MS was performed at 70 eV on a MAT 312 apparatus equipped with a MASPEC II³² data system and a Varian 3700 gas chromatograph.

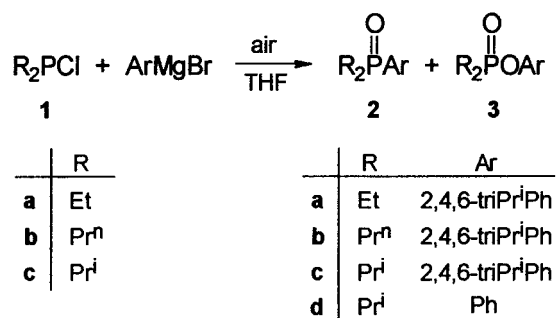
Phosphinous chlorides 1a and 1b were purchased from Aldrich, while 1c was synthesized by us.

Di-*n*-propylphosphinic acid (7.50 g, 50 mmol) [10] in chloroform (40 mL) was treated with thionyl chloride (4.4 mL, 60.0 mmol), and the solution was stirred at room temperature for 19 hours. The volatile components were evaporated, and the residue so obtained fractionated in vacuo to give 2.85 g (34%) of di-*n*-propylphosphinyl chloride (b.p. 138–141°C/18 mmHg; ^{31}P NMR (CDCl_3) δ 72.3).

The phosphinyl chloride (2.80 g, 16.6 mmol) from the previous reaction was dissolved in dichloromethane (25 mL). After removal of the air by bubbling nitrogen through the solution, trichlorosilane (2.50 mL, 24.8 mmol) was added, and the contents of the flask were stirred at 0°C in an inert atmosphere. After a 4 hour reaction time, the volatile components were removed and the crude product so obtained was distilled in vacuo (140°C oil bath/18 mmHg) to afford 0.76 g (30%) of di-*n*-propylphosphinous chloride. MS, m/z (rel. int.) 152 (M^+ (1Cl), 12), 110 (22), 43 (100).

General Procedure for the Preparation of the Aryl-dialkylphosphine Oxide (2a–d)–Aryl Dialkylphosphinate (3a–d) Mixtures

To 4.0 mmol of the dialkylphosphinous chloride (1) in 15 mL of tetrahydrofuran (THF) was added dropwise the Grignard reagent [prepared from 0.10 g (4.0 mmol) of magnesium and 1.25 g (4.42 mmol) of 1-bromo-2,4,6-triisopropylbenzene, or 0.69 g (4.40



SCHEME 1

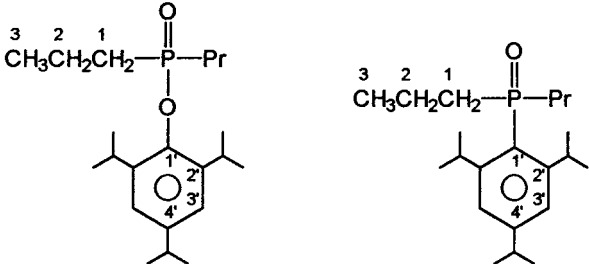
TABLE 1 The Results of the $R_2PCl + ArMgBr$ Reaction Carried Out in an Air Atmosphere

Entry	Starting Material	Conditions		Products ([%cb, ^a δ_p (CDCl ₃), M ⁺)	Total Yield ^b [%]	
		(°C)	(h)			
(1)	1a	triPrC ₆ H ₂ MgBr	26	4	2a (32, 50.2, 308), 3a (68, 58.1, 324)	71
(2)	1b	triPrC ₆ H ₂ MgBr	26	4	2b (20, 45.8, 336), 3b (80, 54.8, 352)	62 ^c
(3)	1c	triPrC ₆ H ₂ MgBr	67	5	2c (58, 56.3, 336), 3c (42, 63.9, 352)	44
(4)	1c	PhMgBr	26	4	2d (37, 51.4, 210), 3d (63, 64.3, 226)	81

^aOn the basis of relative ³¹P NMR intensities after flash column chromatography.^bAfter column chromatography.^cAfter repeated chromatography, **2b** and **3b** were obtained in 8% and 33% yields, respectively.**TABLE 2** Mass Spectroscopic Fragmentation of Products **2a–d** and **3a–d** m/z (fragment, rel. int. in %)

2a	308 (M^+ , 100), 293 ($M - 15$, 57), 280 ($M - 29 + H$, 99), 279 ($M - 29$, 39), 265 ($M - 43$, 88), 252 ($280 - 29 + H$, 51), 251 ($280 - 29$, 40), 203 (Ar, 8)
2b	336 (M^+ , 30), 321 ($M - 15$, 16), 294 ($M - 43 + H$, 88), 293 ($M - 43$, 39), 252 ($294 - 43 + H$, 100), 251 ($294 - 43$, 41), 203 (Ar, 36)
2c	336 (M^+ , 37), 321 ($M - 15$, 7), 294 ($M - 43 + H$, 93), 293 ($M - 43$, 76), 252 ($294 - 43 + H$, 92), 251 ($294 - 43$, 100), 203 (Ar, 16)
2d	210 (M^+ , 2), 168 ($M - 43 + H$, 82), 167 ($M - 43$, 72), 125 ($168 - 43$, 100)
3a	324 (M^+ , 48), 309 ($M - 15$, 5), 295 ($M - 29$, 2), 281 ($M - 43$, 54), 219 (ArO, 10), 203 (Ar, 19), 202 ($203 - H$, 63), 187 ($203 - 15 - H$, 100)
3b	352 (M^+ , 36), 309 ($M - 43$, 40), 219 (ArO, 21), 203 (Ar, 36), 202 (Ar - H, 90), 187 ($203 - 15 - H$, 100)
3c	352 (M^+ , 35), 309 ($M - 43$, 37), 219 (ArO, 16), 203 (Ar, 38), 202 (Ar - H, 76), 187 ($203 - 15 - H$, 100)
3d	226 (M^+ , 17), 184 ($M - 43 + H$, 11), 142 ($184 - 43 + H$, 51), 141 ($184 - 43$, 100)

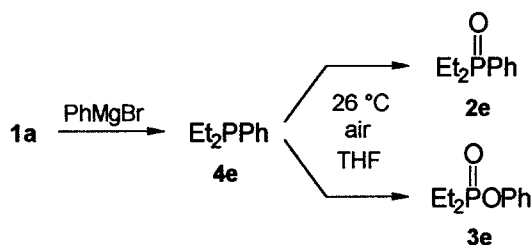
TABLE 3 ¹³C NMR Spectral Parameters for Compounds **3b** and **2b** in $CDCl_3$ Solution

									
	$\delta_C(J_{PC} \text{ in Hz})$								
	C_1	C_2	C_3	$C_{1'}$	$C_{2'}$	$C_{3'}$	$C_{4'}$	$o\text{-CH}(\underline{CH_3})_2$	$p\text{-CH}(\underline{CH_3})_2$
3b^a	30.4 (89.3)	15.8 (3.3)	15.4 (15.9)	143.5 (11.0)	139.7	121.7	145.0	23.4	23.9
2b	35.6 (66.8)	15.7 (3.4)	15.4 (15.9)	^b	^b	122.6 (10.2)	^b	24.8	23.9

^a $o\text{-CHMe}_2$: 27.1, $p\text{-CHMe}_2$: 33.7.^bNot resolved.

mmol)] of bromobenzene in 6 mL of THF] at 0°C. After complete addition, the cooling bath was removed, and the contents of the flask were stirred at 26–67°C for 4–5 hours, as shown in Table 1. The volatile components were removed in vacuo, and the residue was taken up in a mixture of 16 mL of

chloroform and 3 mL of water. The organic phase was dried (Na_2SO_4), and the crude mixture obtained after evaporation was purified by column chromatography (silica gel, 3% methanol in chloroform) to furnish the mixtures of products **2** and **3** in a purity of at least 95% as shown in Table 1. Components **2b**



SCHEME 2

and **3b** were separated by repeated column chromatography.

The ^{31}P NMR and the mass spectroscopic data of products **2a–d** and **3a–d** are listed in Tables 1 and 2, respectively. Compounds **2b** and **3b** were also characterized by ^{13}C NMR spectral parameters (Table 3).

By the reaction of chloride **1a** with phenylmagnesium bromide as described previously, but strictly under a nitrogen atmosphere, after evaporation, 0.69 g (98%) of phosphine **4e** was obtained in a purity of

ca. 94%. ^{31}P NMR (CDCl_3) δ –16.9 (δ_{P} lit. [7] –16.0); MS, m/z 166 (M^+).

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- [10] ^{31}P NMR (CDCl_3) δ 61.8; MS, m/z 150 (M^+).