α-Chlorination and Carbonyl Olefination; Arylchloromethanephosphonic Acid Esters; Preparation, Alkylation, and Wittig-Horner Reactions

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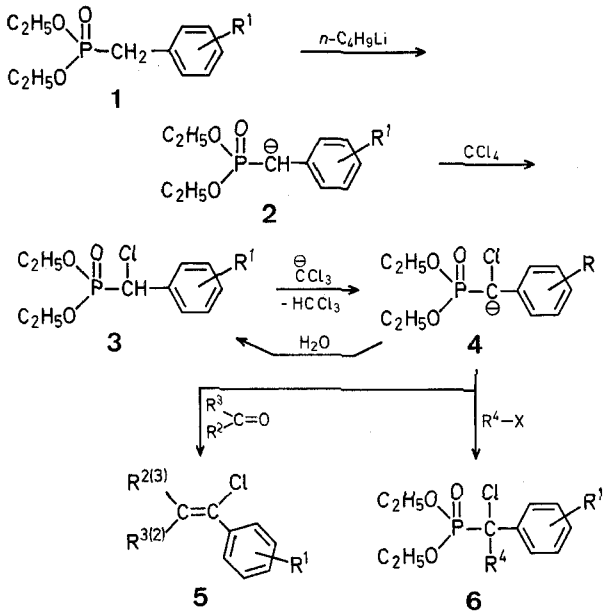
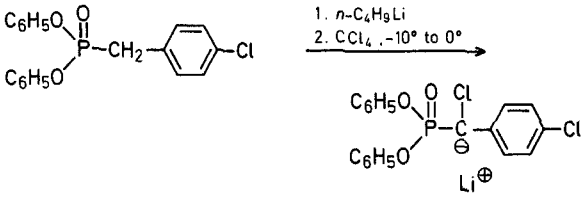
Arylchloromethanephosphonic acid esters (**3**, aryl esters) have been prepared from arylhydroxymethanephosphonic acid esters by OH/Cl exchange with phosphoryl chloride or

thionyl chloride[1]. We report here a method for the direct α-chlorination of arylmethanephosphonic acid esters (**1**) using butyllithium and carbon tetrachloride. The carbanion **2**, generated from the diethyl phenylmethanephosphonate **1** and butyllithium, reacts with carbon tetrachloride to give the diethyl α-chlorophenylmethanephosphonate **3** and trichloromethyl anion[2]; the latter deprotonates **3** to give the carbanion **4** which, upon addition of water, is reconverted into the desired chlorination product **3**. Reaction of the carbanion **4** with aldehydes or ketones leads to the formation of 1-chloro-1-phenyl-1-alkenes (**5**). With alkyl halides, alkylation (**6**) takes place.



When diphenyl phenylmethanephosphonates are used as starting materials the formation of anions of the type **4** proceeds significantly slower. This is particularly the case with diphenyl 4-chlorophenylmethanephosphonate; here, the carbanion corresponding to **2** is too much stabilized for chlorination to proceed readily. Moreover, the carbanion corresponding to **4** is not reactive.



Stabilization of the intermediate carbanions is even more pronounced in the case of alkanephosphonic acid esters having a phenylsulfonyl, cyano, or alkoxycarbonyl group at C-1; here, chlorination does not proceed at all.

Another restriction of the reactivity has been found[2] in the case of alkanephosphonic acid esters having substituents (H, CH_3) at C-1 which are not electron-withdrawing.

With diethyl 2-chlorophenylmethanephosphonate (**1**, R^1 = 2-Cl), steric hindrance is observed. The attempted chlorination-alkylation sequence **1**→**2**→**4**→**6** leads to a product mixture containing

(~30%).

The structure of all compounds prepared was determined by chemical and physical methods. The stereochemistry of the 1-chloro-1-phenyl-1-alkenes **5** was not investigated.

Preparation of Diethyl Arylchloromethanephosphonates (3); General Procedure:

To a stirred solution of the diethyl arylchloromethanephosphonate **1** (5.2 g, 0.02 mol) in tetrahydrofuran (100 ml) a solution of butyllithium (0.02 mol + 10%) in ether is added dropwise at −75°. The mixture is stirred for 15 min at −70°. Then, carbon tetrachloride (3.2 g, 0.02 mol) in tetrahydrofuran (20 ml) is added at −75° to −70° and stirring is continued for 15 min at 70°. To the resultant dark-red solution containing the carbanion **4**, water (40 ml) is added. The mixture is extracted with dichloromethane (2 × 50 ml), the combined organic layers are dried with magnesium sulfate, the solvent is removed under reduced pressure, and the residue distilled in vacuo (Table 1).

Table 1. Diethyl Chlorophenylmethanephosphonates (**3**) and Diethyl 1-Chloro-1-phenylethanephosphonates (**6**)

	R^1	R^4	Yield [%]	b.p./0.1 torr	Brutto formula[a]
3	H	H	90	120–125°	$C_{11}H_{16}ClO_3P$ (262.5)
3	4-Cl	H	85	130–135°	$C_{11}H_{15}Cl_2O_3P$ (297)
3	4-Br	H	82	130–135°	$C_{11}H_{15}BrClO_3P$ (341.5)
6	4-Cl	CH_3	90	135–140°	$C_{12}H_{17}Cl_2O_3P$ (311)
6	4-Br	CH_3	83	138–142°	$C_{12}H_{17}BrClO_3P$ (355.5)

[a] The elemental analyses were in good accordance with the calculated values

Table 2. 1-Chloro-1-phenyl-1-alkenes (**5**)

R^1	R^2	R^3	Yield [%]	b.p./ 0.1 torr	Brutto formula[a]
H	i-C_3H_7	H	69	49–53°	$C_{11}H_{13}Cl$ (180.5)
4-Cl	i-C_3H_7	H	80	68–70°	$C_{11}H_{12}Cl_2$ (215)
2-Cl	i-C_3H_7	H	20	70–71°	$C_{11}H_{12}Cl_2$ (215)
4-Cl	i-C_4H_9	H	87	90–94°	$C_{12}H_{14}Cl_2$ (229)
4-Cl	3,4-O–CH_2–O–C_6H_3–	H	69	m.p. 84°	$C_{15}H_{10}O_2Cl_2$ (293)
4-Cl		H	85	—	$C_{12}H_8Cl_2S$ (255)
4-Cl	—$(CH_2)_4$—		73	95–100°	$C_{13}H_{14}Cl_2$ (241)

[a] The elemental analyses were in good accordance with the calculated values.

Preparation of Diethyl 1-Chloro-1-phenylethanephosphonates (6, R^4 = CH_3); General Procedure:

The generation of the carbanion **4** is carried out as described above. To the dark-red solution of **4**, methyl iodide (3.1 g, 0.02 mol + 10%) is added with stirring at −75° to −70°. The mixture is allowed to warm to room temperature and then hydrolyzed with water (40 ml). The product is extracted with dichloromethane (2 × 50 ml), the combined organic layers are dried with magnesium sulfate, the solvent is removed under reduced pressure, and the residue distilled in vacuo (Table 1).

Preparation of 1-Chloro-1-phenyl-1-alkenes (5) by Carbonyl Olefination; General Procedure:

The generation of the carbanion **4** is carried out as described above. To the dark-red solution of **4**, the aldehyde or ketone (0.02 mol) is added with stirring at −75° to −70°. Stirring is continued for 30 min at −70°. The red-brown reaction mixture is then allowed to warm to room temperature over a period of 60 min, and hydrolyzed by the addition of water (40 ml). The product is extracted with ether (3 × 50 ml). The combined organic layers are dried with magnesium sulfate, the solvent is removed under reduced pressure, and the residue purified by column chromatography on alumina (40 g) using petroleum ether as eluent (Table 2).

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