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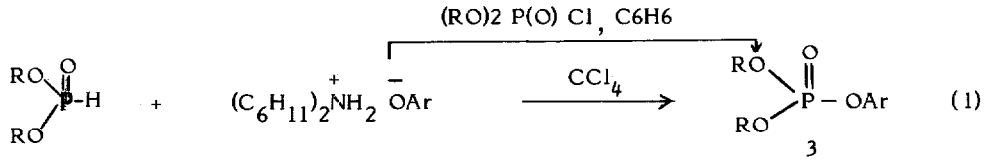
A CONVENIENT SYNTHETIC ROUTE TO PHOSPHATE ESTERS FROM PHOSPHITES

Purnanand*, B.S.Batra and B.P.Pant
Defence Research and Development Establishment
Gwalior 474002 (MP) India

Abstract: Dialkyl arylphosphate esters have been synthesized in improved yields by the reaction of dicyclohexylamine salts of substituted phenols with dialkyl hydrogen phosphite and carbon tetrachloride. The reaction proceeds through the corresponding phosphorochloridates.

Dialkyl arylphosphate esters form an important class of insecticides and are synthesized by well known methods[1,2]. Reaction between phosphorochloridate and sodium salt of substituted phenols is the most attempted method, but isolation of sodium salt of phenols having pka above 7.15 are not readily accessible.

Recently we observed that a wide variety of phenols having pka values between 7.15 and 10.26 react with dicyclohexylamine (DCHA) to give the crystalline salts, which are soluble in organic solvents. We investigated the reactivity of these salts with dialkyl phosphorochloridates and dialkyl phosphites in benzene and carbon tetrachloride respectively. In both cases dialkyl arylphosphates are obtained in good yields (equation 1).



(1)

1a:R=CH_3 **2a**:Ar=C_6H_5 , **2b**:Ar=3-$CH_3C_6H_4$
1b:R=C_2H_5 **2c**:Ar=4-ClC_6H_4 , **2d**: Ar=4-$NO_2C_6H_4$
2e:Ar=6-Cl-2-C_5H_3N , **2f**:Ar=2,4-$Cl_2C_6H_3$

In a typical experiment, phenol (9.4g, 0.1mol) and DCHA (19g,~0.1mol) were refluxed in acetone (50ml) for an hour. The reaction mixture was cooled, diluted with hexane (200ml) and allowed to crystallize. Crystallized salt **2a** gave yield 80% and mp 66°C. Salts **2b-f** were prepared by similar procedure, their yields and melting points are described as follows: **2b**:70% mp 58°C; **2c**:75% , mp 90-92°C; **2d**: 90% , mp 156-57°C; **2e**:80% , mp 129-30°C; 2f:90% , mp 180°C.

To **1a** (2.4g,~0.01mol) and carbon tetrachloride (50ml), **2a** (5.50g, 0.02mol) was added at room temperature with stirring. The resulting solution was refluxed with stirring upto 3-4 hours. The reaction mixture was then cooled, filtered and solvent removed under vacuum. The residual liquid on distillation at 120°C (1.0 Torr) yielded dimethyl phenyl phosphate ester (entry 3a). Representative esters of this series (entry 3b-i) were prepared by similar procedure. The reaction conditions and results are summarised in the table.

Table: Synthesis of Dialkylarylphosphate Esters, $(RO)_2P(O)OAr$

Entry	R	Ar	Reaction conditions	bp[a] (°C/Torr)	Yield[b] (%)
3a	CH_3	C_6H_5	CCl_4, reflux, 3.5h	120/1.0	55(30)
3b	C_2H_5	C_6H_5	CCl_4, reflux, 3.5h	108/0.2	65(37)
3c	C_2H_5	3-$CH_3C_6H_4$	CCl_4, reflux, 3.0h	106–8/0.1	58(25)
3d	CH_3	2-$C_{10}H_7$	CCl_4, reflux, 4.0h	142/0.2	50(30)
3e	CH_3	4-ClC_6H_4	CCl_4, reflux, 4.0h	102/0.1	63(36)
3f	CH_3	4-$NO_2C_6H_4$	CCl_4, reflux, 4.0h	144–46/0.1	62(30)
3g	C_2H_5	4-$NO_2C_6H_4$	CCl_4, reflux, 4.0h	156/0.1	70(46)
3h	CH_3	2,4-$Cl_2(C_6H_3)$	CCl_4, reflux, 4.0h	116/0.2	65(40)
3i	CH_3	6-Cl-2-C_5H_3N	CCl_4, reflux, 4.0h	128/0.1	60(25)

[a] uncorrected

[b] The structure of these esters were confirmed by IR and ^1H NMR spectra and comparison with authentic samples. Yields obtained from synthesis by known methods[3] are given in parenthesis.

These results suggest that the transformation of phosphites occurs exclusively through generation of phosphorochloridates[4,5]. The catalytic amounts of base needed for the progress of reaction was obtained from the decomposition of salts. All salts decomposed fast under chromatographic conditions: TLC, on silicagel with benzene–acetone (8:2); GLC, on OV-17 column, temperature 200°C and detector FID.

A likely reaction path based on these observations is as follows:

$$(C_6H_{11})_2\overset{+}{N}H_2\ \overline{O}Ar \rightleftharpoons (C_6H_{11})_2NH + ArOH \quad \ldots \quad (2)$$

$$(C_6H_{11})_2\ddot{N}H + H\text{-}O\text{-}\underset{\displaystyle OR}{\overset{\displaystyle OR}{\overset{|}{\underset{|}{P}}}}\text{:} + Cl\text{-}CCl_3 \longrightarrow (RO)_2\overset{O}{\overset{\|}{P}}\text{-}Cl + (C_6H_{11})_2NH + CHCl_3 \quad \ldots \quad (3)$$

$$(RO)_2\overset{O}{\overset{\|}{P}}\text{-}Cl + ArOH + (C_6H_{11})_2NH \longrightarrow (RO)_2\overset{O}{\overset{\|}{P}}\text{-}OAr + (C_6H_{11})_2NH.HCl \quad \ldots \quad (4)$$

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