Preparation of Alkyl Diphenylphosphinates

JAMES E. QUICK and DAVID L. VENEZKY
Chemistry Division, Naval Research Laboratory, Washington, D. C. 20390

Diphenylchlorophosphine, dissolved in carbon tetrachloride, was oxidized with dimethyl sulfoxide and the resulting acid chloride, which was neither isolated nor purified, was treated with the appropriate alcohol to form the ester of diphenylphosphinic acid. Melting point, boiling point, per cent yield, and characteristic infrared and PMR data are given for the methyl, ethyl, isopropyl, and *n*-butyl esters.

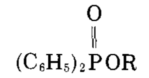
ESTERS of diphenylphosphinic acid have been prepared by various methods in low yields (*5, 6*) or in good yields by the reaction of diphenylphosphinic chloride, $(C_6H_5)_2P(O)Cl$, with the appropriate alcohol in the presence of a tertiary amine (*3*). As reported here, diphenylchlorophosphine, $(C_6H_5)_2PCl$, is used as the starting material and is oxidized to diphenylphosphinic chloride, with dimethyl sulfoxide (*1, 2*). In the absence of a tertiary amine, the acid chloride, which is neither isolated nor purified, reacts with the appropriate alcohol to form the ester. A stream of dry nitrogen removes most of the volatile by-products of the reaction, dimethyl sulfide and hydrogen chloride. To purify the esters, either precipitation from acetone solution with water or a vacuum distillation is used. For the methyl and ethyl esters, either method of purification yielded oils that crystallized after the liquid was poured into another vessel or the cold glass was warmed.

Table I lists the four esters prepared. The high yields reported are attributed to the minimum handling of the reactive intermediate, the acid chloride. Since dialkylchlorophosphines are commercially available, the method could be readily extended to esters of dialkylphosphinic acids.

Infrared spectra (Table II) of the esters show the expected absorption bands near 1225 cm^{-1} (P=O stretching) and 980 to 1030 cm^{-1} (P—O—C) (*3, 7*). The strong absorption at 1180 cm^{-1}, attributed to P=O stretching associated with diphenylphosphinic acid, was used to determine the absence of acid in the purified esters.

The PMR spectra of the esters in acetone-d_6 solutions showed the expected multiplets between 7.5 and 7.8 ppm, downfield from TMS, attributed to protons on the phenyl groups attached to the phosphorus. The observed splittings in the PMR spectral regions of alkyl-group protons is caused by coupling between phosphorus and hydrogen nuclei—for example, a doublet centered at 3.68 ppm, instead of a singlet, is observed for the methyl protons of the methyl ester. Esters formed from alcohols containing one or two protons in the group next to the oxygen exhibit even more complex spectra due to the coupling between the phosphorus and hydrogen (J_{P-H}) in addition to the coupling between hydrogen and hydrogen (J_{H-H}) (*4*). The chemical shifts and the coupling constants are shown in Table III.

Table II. Infrared Data for Alkyl Diphenylphosphinates


$(C_6H_5)_2\overset{\overset{O}{\|}}{P}OR$

R	Infrared Frequencies, Cm^{-1}	
	P=O	P—O—C
CH_3-	1228	1030 (doublet)
CH_3CH_2-	1227	1031
$(CH_3)_2CH$-	1218	980
$CH_3(CH_2)_3$-	1220	1033

EXPERIMENTAL

The infrared spectra of solids were run as potassium bromide pellets and liquids were run as thin films between sodium chloride windows. A Perkin-Elmer Model 457 spectrometer was used for infrared measurements. PMR spectra

Table I. Esters of Diphenylphosphinic Acid, $(C_6H_5)_2P(O)OR$

R	Crude Yield, %	M.P.[a], °C	B.P.[a], °C (2.5-torr)	n_D^{25} [b]	Analyses					
					Calculated, %			Found, %[c]		
					C	H	P	C	H	P
CH_3-	74	59-61	180-90	1.5846	67.24	5.64	13.34	67.21	5.71	13.31
C_2H_5-	94	43.5	195-200	1.5716	68.29	6.14	12.58	68.51	6.34	12.36
$(CH_3)_2CH$-	87	95-6	...	...	69.22	6.58	11.90	68.75	6.53	11.92
$CH_3(CH_2)_3$-	96	92.5-3.5	...	...	70.06	6.98	11.29	70.36	7.08	11.02

[a] All temperatures uncorrected. [b] Obtained on oils. [c] Analyses performed by Aldridge Associates, Inc., Washington, D. C.

Table III. PMR Data for Alkyl Diphenylphosphinates in Acetone-d_6 Solutions

Group	Chemical Shifts[a], PPM	Coupling Constants, Hz	
		J_{P-H}	J_{H-H}
1. $(C_6H_5)_2P(O)OCH_3$			
$-CH_3$	3.68 (doublet)	11.14 ± 0.03	
2. $(C_6H_5)_2P(O)OCH_2CH_3$			
$>CH_2$	4.03 (quintet)	7.95 ± 0.03	
$-CH_3$	1.27 (triplet)		7.03 ± 0.05
3. $(C_6H_5)_2P(O)OCH(CH_3)_2$			
$\geqslant CH$	4.56 (double-heptet)	8.28 ± 0.05	
$-CH_3$	1.32 (doublet)		6.13 ± 0.08
4. $(C_6H_5)_2P(O)O\overset{\alpha}{C}H_2\overset{\beta}{C}H_2\overset{\gamma}{C}H_2CH_3$			
$>CH_2(\alpha)$	3.99 (quartet)	7.07 ± 0.04	
$>CH_2(\beta, \gamma)$	[b]		
$-CH_3$	0.88 (triplet)		6.28 ± 0.04

[a] Downfield from TMS. [b] Complex set of multiplets between 1 and 2 ppm.

were run on a Varian HA-100 spectrometer. Tetramethylsilane was used as an internal reference. Copies of the infrared and PMR spectra are available for those desiring comparative data.

The general method used to prepare the esters is illustrated by ethyl diphenylphosphinate. In a flask fitted with a dry-nitrogen bubbler and containing a magnetic stirrer, diphenylchlorophosphine (Stauffer Chemical Co., Victor Division) (18.4 ml, 0.10 mole) was diluted with 50 ml of dried carbon tetrachloride. After the slow addition of dimethyl sulfoxide (7.3 ml, 0.10 mole), the reaction mixture was refluxed 3 hours. The volatile product, dimethyl sulfide, was collected in a trap cooled to liquid nitrogen temperature. When the reaction mixture had cooled to room temperature, absolute ethanol (6.2 ml, 0.11 mole) was slowly added; the solution was stirred at room temperature for approximately 2 hours. The solvent and other remaining volatiles were removed by flash evaporation. The crude ethyl diphenylphosphinate was isolated as an oil (23.8 grams, 94% yield) and was purified by vacuum distillation at 195° to 200° C under 2,5-torr pressure. The clear liquid distillate crystallized when the purified ester was transferred to a bottle.

Although the methyl ester was also purified by vacuum distillation, the isopropyl and *n*-butyl esters were more conveniently purified by precipitating the esters from acetone solutions by the addition of water. The purified esters did not appear to hydrolyze readily in the presence of water at room temperature.

Attempts to prepare the *o*-cresyl ester yielded only diphenylphosphinic chloride and unreacted *o*-cresol.

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