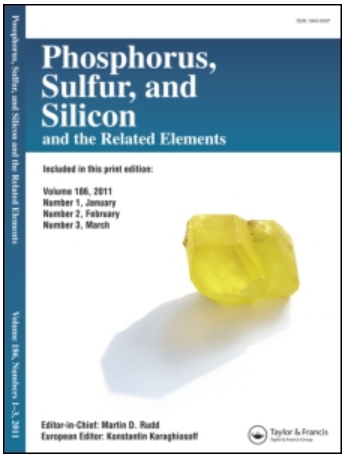

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Synthesis of 6-Alkyl Carbamato/Alkyl Thiocarbamato-2,10-dichloro-12-trichloromethyl-12 H -dibenzo[d,g][1,3,2]-dioxaphosphocin 6-Oxides

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SYNTHESIS OF 6-ALKYL CARBAMATO/ALKYL THIOCARBAMATO-2,10-DICHLORO-12-TRICHLOROMETHYL-12*H*-DIBENZO [d,g][1,3,2]-DIOXAPHOSPHOCIN 6-OXIDES

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*6-Alkylcarbamato/alkylthiocarbamato-2,10-dichloro-12-trichloromethyl-12*H*-dibenzo [d,g][1,3,2]-dioxaphosphocin 6-oxides have been synthesized by the condensation of 2,2-bis(2-hydroxy-5-chlorophenyl)-1,1,1-trichloroethane with dichlorophosphinyl carbamates of different alcohols/thiols in the presence of triethylamine in dry toluene and were characterized by different spectral studies.*

Keywords: 6-Alkyl carbamato/alkylthiocarbamato-2,10-dichloro-12-trichloromethyl-12*H*-dibenzo[d,g][1,3,2]-dioxaphosphocin 6-oxides, IR and NMR (^{1}H&^{31}P) spectral analyses

INTRODUCTION

Large numbers of organocarbamates are reported to be highly anticholinergic and found to be potential fungicides and insecticides.[1] In search of our studies for the synthesis of effective and eco-friendly pesticides, we have accomplished the synthesis of some new 6-alkylcarbamato/alkylthiocarbamato-2,10-dichloro-12-trichloromethyl-12*H*-dibenzo[d,g][1,3,2]-dioxaphosphocin 6-oxides.

RESULTS AND DISCUSSION

The synthesis (Scheme 1) involves the addition of isocyanatophosphonic dichloride (**1**)[2] with various alcohols/thiols at –10°C in dry toluene to afford the corresponding dichloroisocyanatophosphinyl

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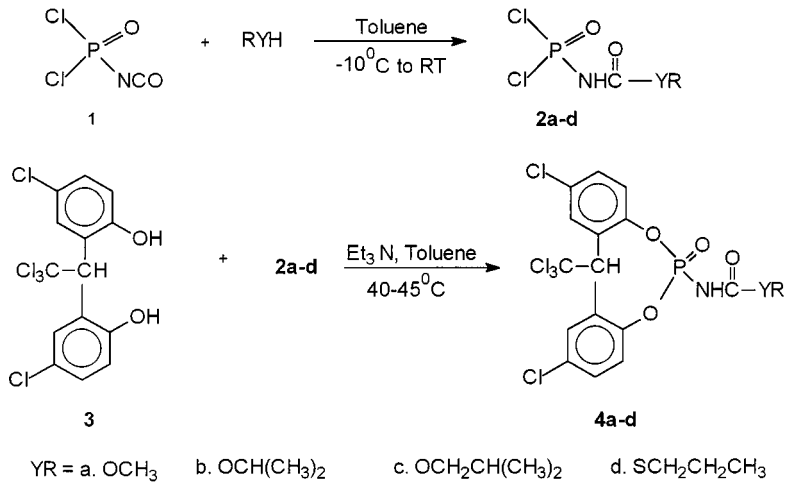

SCHEME 1

carbamates/thiocarbamates (**2a–d**). Condensation of **2a–d** *in situ* with 2,2-bis(2-hydroxy-5-chlorophenyl)-1,1,1-trichloroethane (**3**)[3] in the presence of triethylamine at 40–45°C yielded the title compounds (**4a–d**). Interestingly, primary and secondary alcohols/thiols reacted readily with isocyanatophosphonic dichloride (**1**) to give their respective carbamates/thiocarbamates (**2a–d**), but tertiary alcohols/thiols failed under the same conditions, obviously due to steric factors.

The IR (Table I), ^{1}H and ^{31}P NMR Spectra (Table II) of **4a–d** confirmed their proposed structures.[4–7]

TABLE I Physical Properties[a] and IR Spectral (Cm^{-1}) Data of Compounds (**4a–d**)

Compd.	Mol. Formula (Mol. wt)	M.P. °C	Yield %	Found (calcd.)% C	Found (calcd.)% H	IR (Cm^{-1}) C=O	IR (Cm^{-1}) P=O	IR (Cm^{-1}) P–NH
4a	$C_{16}H_{11}O_5Cl_5P$ (491.47)	118–20	61	38.92 (39.10)	2.18 (2.26)	1750	1227	3210
4b	$C_{18}H_{15}O_5Cl_{15}P$ (519.53)	140–43	55	41.30 (41.61)	2.78 (2.91)	1762	1222	3203
4c	$C_{19}H_{17}O_5Cl_{15}P$ (533.55)	130–34	48	42.82 (42.77)	3.18 (3.21)	1766	1213	3192
4d	$C_{18}H_{15}O_4Cl_{15}PS$ (535.60)	135–38	55	40.48 (40.37)	2.85 (2.82)	1647	1234	3195

[a]Triturated with 2-propanol.

TABLE II ^{1}H and ^{31}P NMR Data[a,b] of Compounds **4a–d**

Compd.	Ar—H	H(12)	R—H	—NH	^{31}P NMR[c]
4a	7.12–7.75 (m, 6H)	6.32	3.48 (s, 3H, OCH_3)	5.95 (d, J = 5.4 Hz)	−19.30
4b	7.05–8.02 (m, 6H)	6.40	2.98–3.05 (m, 1H, OCH) 1.19–2.25 (m, 6H, $2CH_3$)	6.18 (d, J = 7.9 Hz)	−23.54
4c	7.62–8.28 (m, 6H)	6.22	3.92 (d, 2H, OCH_2) 1.08–1.15 (m, 1H, CH) 0.85–0.92 (m, 6H, $2CH_3$)	5.99 (d, J = 8.2 Hz)	−25.45
4d	7.12–8.22 (m, 6H)	6.30	2.89 (t, 2H, SCH_2) 1.64–1.69 (m, 2H, CH_2) 1.01 (t, 3H, CH_3)	6.19 (d, J = 6.0 Hz)	−20.15

[a]Chemical shifts in J from TMS, J(Hz) given in parenthesis.
[b]Recorded in $CDCl_3$.
[c]Chemical shifts in J from 85% H_3PO_4.

EXPERIMENTAL

All melting points were determined in open capillary tubes on a Mel-Temp apparatus and are uncorrected. IR spectra (ν_{max} in Cm^{-1}) were recorded in KBr pellets on a Perkin-Elmer 1000 unit. All ^{1}H and ^{31}P NMR spectra were recorded from varian AMX-400 MHz spectrometer in solutions in $CDCl_3$, and chemical shifts were referenced from TMS for ^{1}H and 85% H_3PO_4 for ^{31}P NMR. Microanalytical data were obtained from Central Drug Research Institute, Lucknow, India.

6-Isobutylcarbamato-2,10-dichloro-12-trichloromethyl-12*H*-dibenzo[d,g][1,3,2]-dioxaphosphocin 6-Oxide (4c)

A solution of isobutyl alcohol (0.37 g, 0.005 mol) in 10 mL of dry toluene was added dropwise over a period of 20 minutes to a cold solution (−10°C) of 1 (0.8 g, 0.005 mol) in 15 mL of dry toluene. After the addition, the reaction mixture was warmed to room temperature with stirring for an additional 2 hours and then added *in situ* to a cold solution (0°C) of **3** (1.92 g, 0.005 mol) and triethylamine (1.4 g, 0.01 mol) in 15 mL of dry toluene. The temperature of the reaction mixture was allowed to rise to room temperature, and stirring was continued

for an additional 5 hours at 40–45°C. Progress of the reaction was monitored by TLC analysis. The mixture was filtered and the solvent on evaporation afforded crude product, which on trituration with warm 2-propanol gave an analytically pure compound, 0.38 g (48%) of **4c**, m.p. 130–34°C.

Other compounds **4a**, **4b**, and **4d** were synthesized by adopting the same procedure.

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