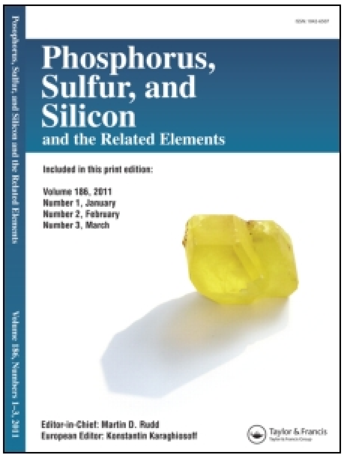

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SYNTHESIS AND CHARACTERIZATION OF NEW 1,1',3,3',5,5'-HEXACHLORO-2,4,6, 1λ^5,3λ^5,5λ^5-TRIAZATRIPHOSPHORINE SPIRO-[ARYLENEDIOXYI-DERIVATIVES

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SYNTHESIS AND CHARACTERIZATION OF NEW 1,1′,3,3′,5,5′-HEXACHLORO-2,4,6, 1λ^5,3λ^5,5λ^5-TRIAZATRIPHOSPHORINE SPIRO-[ARYLENEDIOXY]-DERIVATIVES

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Hitherto reported methods of substitution of 1,1′,3,3′,5,5′-hexachloro-2,4,6,1λ^5,3λ^5,5λ^5-triazatriphosphorine (**1**) with 2,2′-dihydroxy-1,1′-biphenylene (**2**) enabled exclusively the preparation of trisspiro-derivatives, it means fully substituted **1**. We have found that when the reaction of **1** and **2** is carried out in bisolvent system containing THF/H_2O or C_6H_5Cl/H_2O the partial substitution is possible resulting in the corresponding mono- and bisspiro-[2,2′-dioxybiphenyl-1,1′] derivatives of **1**. An efficient method of preparation of novel compounds: 1,1′-spiro-[2,2′-dioxybiphenyl-1,1′]-3,3′,5,5′-tetrachloro-2,4,6,1λ^5,3λ^5,5λ^5-triazatriphosphorine (**3**) and 1,1′,3,3′-bisspiro-[2,2′-dioxybiphenyl-1,1′]-5,5′-dichloro-2,4,6,1λ^5,3λ^5,5λ^5-triazatriphosphorine (**4**) is presented. The dependence of the degree of substitution on the reaction conditions is discussed. In order to ascertain the proposed structures of the obtained compounds: **3** and **4** (Scheme 1) the corresponding phenoxy and 1-aziridinyl derivatives have been synthesized (Scheme 2,3). The structures of all novel compounds have been confirmed by the M.S. and NMR (^1H and ^{31}P) spectroscopies. Owing to the presence of reactive chloride functions the new compounds **3**, **4** might be employed for the synthesis of various derivatives of practical importance.

Key words: 1,1′,3,3′,5,5′-hexachloro-2,4,6,1λ^5,3λ^5,5λ^5-triazatriphosphorine; mono- and bisspiro-[2,2′-dioxybiphenyl-1,1′]-derivatives; phenolysis and aziridinolysis of; fragmentation pattern; structural assignments.

INTRODUCTION

Among the derivatives of 1,1′,3,3′,5,5′-hexachloro-2,4,6,1λ^5,3λ^5,5λ^5-triazatriphosphorine (**1**) the spirocyclic ones are of considerable interest because of their use as reagents in the synthesis of bioactive compounds,[1–3] special polymers, flame resistant resins, pharmaceutics and UV absorbers.[4]

There are reported mono-, bis- and trisspiro derivatives of **1** resulting from the reaction of **1** with aliphatic glycols,[5] *N*-methylethanoloamine,[5,6] and *o*-bis(hydroxymethyl)carborane.[7] Mono- and bisspiro derivatives have been obtained from **1** and biogene diamines.[1,8–10] With regard to spiro[arylenedioxy] derivatives of **1** the tris-(spiro)-substitution was found to be favoured in the reactions of **1** with numerous aromatic ortho-bisphenols, as e.g. catechol,[11] 2,3-dihydroxynaphthalene,[11,12] 1,8-dihydroxynaphthalene and 2,2′-dihydroxybiphenyl-1,1′.[12] Mono- and bisspiro(arylenedioxy) substituted **1** have been obtained so far only in the

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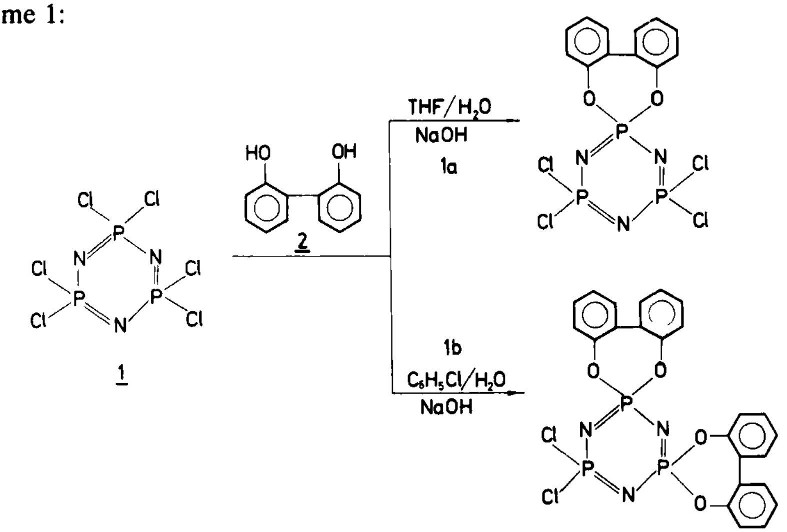
reactions of **1** and sterically hindered *o*-diols, such as 1,1′-dihydroxy-2,2′-binaphthylene.[13]

In this paper the synthesis and structure determination of novel hitherto unreported mono- and bisspiro (arylene) derivatives by the reaction of **1** with 2,2′-dihydroxy-1,1′-biphenylene are described (Scheme 1).

RESULTS AND DISCUSSION

It is known that the reaction of **1** with **2** in the presence of triethylamine in a dry THF solution yields exclusively the trisspirosubstituted derivative.[12] Partly substituted derivatives: 1,1′-spiro-[2,2′-dioxybiphenyl-1,1′]-3,3′,5,5′tetrachloro-2,4,6,$1\lambda^5,3\lambda^5,5\lambda^5$-triazatriphosphorine (**3**) and 1,1′,3,3′-bisspiro[2,2′-dioxybiphenyl-1,1′]-5,5′-dichloro-2,4,6,$1\lambda^5,3\lambda^5,5\lambda^5$-triazatriphosphorine (**4**) have been obtained by the reaction of **1** with 2,2′-dihydroxybiphenyl-1,1′ (**2**) in heterogeneous systems containing water and suitable organic solvent (THF—for **3** or chlorobenzene—for **4**), in the presence of NaOH as HCl acceptor, according to Scheme 1:

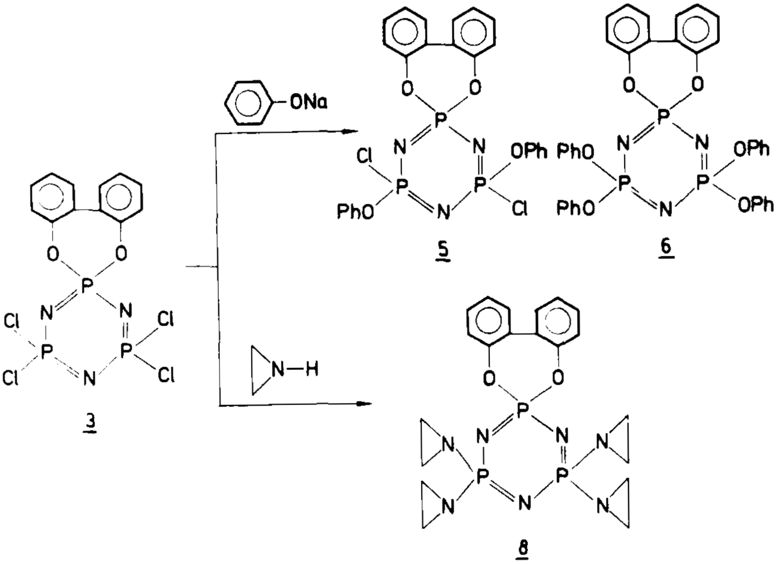


SCHEME 1

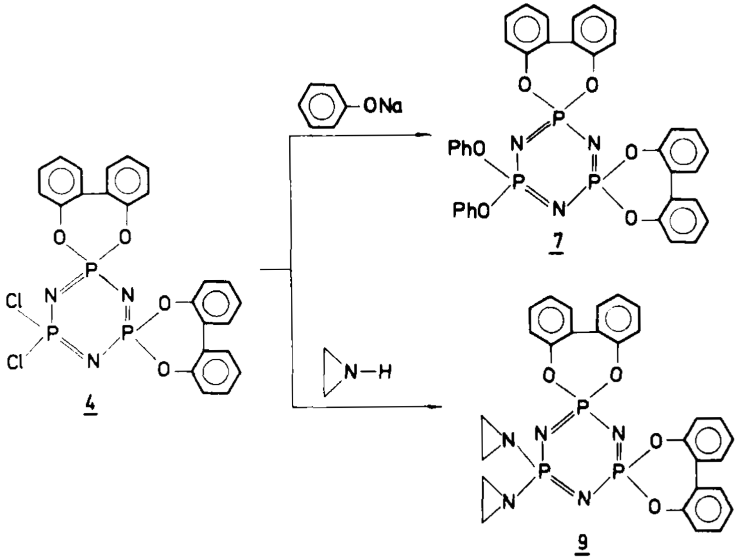
In the case of mono-spiro-substitution (Scheme 1a) the reaction was found to be completed after 5–10 minutes of stirring the reagents at 10–20°C. The presence in the reaction mixture of salting-out and reducing agents allowed to suppress side reactions e.g. hydrolysis of chlorine atoms and the oxidation of phenolic hydroxyl groups. Under above mentioned conditions no traces of higher, i.e. bis (**4**) or tris-spiro-substituted derivatives have been detected in the crude reaction product. Therefore this method provides a convenient way of the selective mono-spiro-substitution of **1** with **2** and might be applied also for the synthesis of other monospiro [arylenedioxy] derivatives.[14] Bis-spiro-derivative **4** was prepared by the typical interfacial condensation of **1** and **2** (Scheme 1b) in the presence of a phase-transfer catalyst. Both **3** and **4** compounds are white crystalline substances with high melting points, well soluble in $CHCl_3$ and THF, readily soluble in benzene and sparingly soluble in nonpolar solvents.

DTA shows that **3** is thermally stable up to 250°C and **4** up to 350°C. In the Table I there are presented ^1H NMR, ^{31}P NMR, UV, IR spectral data for **3**, **4**. UV spectra reveal two characteristic bands of absorption in both compounds (**3**, **4**), at λ_1 215 nm and λ_2 245 nm. In the IR spectra, there are bands assigned to the P–N stretching mode and bands corresponding to biphenyl stretching mode. ^1H NMR spectra show one region of absorption as a large multiplet, which can be assigned to the protons of biphenyl groups. ^{31}P NMR spectra are of A_2B (**3**) and AB_2 (**4**) type corresponding to the two differently substituted phosphorus atoms in the respective P_3N_3 rings.

Table II shows the respective MS spectral data. Spectroanalytical data are consistent with the proposed structures **3** and **4**.



SCHEME 2



SCHEME 3

TABLE I

Analytical data of **3,4** compounds

Comp.	m.p. [°C] DSC	H kJ/mol	UV(in Dioxane)		IR (KBr pellet) ν [cm^{-1}]			
			λ_{max} [nm]	ε_{max} $l\,mol^{-1}cm^{-1}$	P=N	P—OC_{ar}	O—C_{ar}	HC_{ar}
3	192.5	32.8	215 245	2.76×10^4 2.10×10^4	1205 1190	1160 1100	1260	3075 1500 1480 1460
4	325.7	43.5	215	3.81×10^4	1205 1190	1100	1280	3080 1500 1475 1455

TABLE II

Fragmentation pattern of **3** and **4**

M/e	Fragment	% of base peak	*M/e*	Fragment	% of base peak
465 (M + 6)	$P_3N_3{}^{37}Cl_3ClC_{12}H_8O_2$	23.6	577 (M + 4)	$P_3N_3{}^{37}Cl_2(C_{12}H_8O_2)_2$	13.72
463 (M + 4)	$P_3N_3{}^{37}Cl_2Cl_2C_{12}H_8O_2$	64.7	575 (M + 2)	$P_3N_3{}^{37}ClCl(C_{12}H_8O_2)_2$	71.1
461 (M + 2)	$P_3N_3{}^{37}ClCl_3C_{12}H_8O_2$	94	573 (M)	$P_3N_3Cl_2(C_{12}H_8O_2)_2$	100
459 (M)	$P_3N_3Cl_4C_{12}H_8O_2$	100	538	$P_3N_3Cl(C_{12}H_8O_2)_2$	7.14
424	$P_3N_3Cl_3C_{12}H_8O_2$	6.8	368	$(C_{12}H_8O_2)_2$	0.17
389	$P_3N_3Cl_2C_{12}H_8O_2$	1.3	205	$P_3N_3Cl_2$	0.51
240	$P_3N_3Cl_3$	3.3	184	$C_{12}H_8O_2$	10.2
184	$C_{12}H_8O_2$	0.8	168	$C_{12}H_8O$	20.17
168	$C_{12}H_8O$	28.8	76	C_6H_4	15.6
152	$C_{12}H_8$	2.8			
76	C_6H_4	10.7			

In order to confirm the proposed structures of **3** and **4** corresponding phenoxy (**5**–**7**) and aziridinyl (**8**, **9**) derivatives have been synthesized, according to the Schemes 2 and 3 respectively. Table III presents the analytical data of the obtained derivatives **5**–**9**.

The revealed ease of substitution of chlorine atoms in both **3** and **4** compounds with phenolate anions and aziridinyl groups indicates the possibility of other Cl-substitution reactions with various mono- and difunctional nucleophiles, the latter being the route to the respective polymers. Incorporation of thermodynamically stable spirocyclic units derived from **3** or **4** into various polymer structures might result in polymer materials with high thermal and chemical stability.

EXPERIMENTAL SECTION

Melting points were measured using the Boethius hot stage and the Thermal Analyzer [du Pont 1090]. IR spectra were recorded with Specord UR-120 spectrophotometer Carl Zeiss Jena. UV spectra were recorded with UV/VIS-Carl Zeiss Jena. ^1H NMR were recorded with Varian VXR300 spectrometer. Chemical shifts are expressed in ppm, relative to the internal reference TMS. ^{31}P NMR proton decoupled spectra were taken with Varian VXR-300 spectrometer at 121 MHZ. Chemical shifts were determined relative to 80% H_3PO_4 serving as an external reference. Mass spectra were recorded with LKB-GCMS-2091 apparatus. TLC experiments were performed on E. Merck precoated (0.2 mm) silica gel 60 plates, using the mixture of hexane and THF as an eluent. The pyridine-toluidine reagent[16] was used for visualization of all chlorine containing derivatives, and J_2—vapours for the others.

Materials

THF, hexane were distilled over KOH and CaH_2, under an argone atmosphere. Chlorobenzene was distilled over $CaCl_2$. Pyridine and toluidine were used as obtained from E. Merck, Germany. 1,1′,3,3′,5,5′-hexachloro-2,4,6,1λ^5,3λ^5,5λ^5-triazatriphosphorine was synthesized and purified by previously described method.[17] 2,2′-dihydroxy-1,1′-biphenylene reagent was supplied from Loba, France.

Synthesis

1,1′-spiro-[2,2′-dioxybiphenyl-1,1′]-3,3′,5,5′-tetrachloro-2,4,6,1λ^5,3λ^5,5λ^5-triazatriphosphorine (**3**). A three-necked, 250 ml round-bottomed flask equipped with mechanical stirrer., thermometer and dropping funnel was charged with 100 ml of water, 1.3 g (0.007 mol) of **2**, 6 g of $Na_2S_2O_4$. The flask was put

TABLE III

Analytical data of phenoxy and (1-azirdynyl) derivatives

Comp.	m.p. [°C] DSC	H kJ/mol	UV (in Dioxane) λ_{max} [nm]	UV (in Dioxane) ε_{max} $l\,mol^{-1}cm^{-1}$	IR (KBr pellet) ν [cm^{-1}] P=N	P—OC_{ar}	CH_2	HC_{ar}	^{1}H CH_{ar}
5	197.0	32.8			1180 1210	1260	3000 1440	3070 1500	7.5–7.1 m
6	190.0	29.2			1200 1180	1270	2995 1435	3065 1498	7.5–7.1 m
7	132.0	41.3			1210 1180	1260	3000 1440	3070 1498	7.5–7.1 m
8	259.0[1]	124.7[2]	248 270	1.28×10^4 3.30×10^4	1216 1196	1264 944	2992 1440 1476	3064 1500	7.6–7.1 m
9	146.0	36.8	247 270	2.56×10^4 4.40×10^4	1212 1196	1264 944	2996 1436	3070 1500	7.6-7.3 m

[1] Associated with an exothermic effect (DSC), probably due to the polymerization of aziridinyl groups.

[2] Heat enthalpy of the polymerization reaction.

[3] A_2B spin system.

[4] X = OPh, Y = Cl for **5**. X = Y = OPh for **6**, **7**.

into a kryostat bath. The solution of 2.1 g (0.006 mol) of **1** in 120 ml THF was added dropwise into a vigorously stirred mixture of the above reagents. The reaction was carried out on stirring at 2–5°C for the next 10 min and was quenched by the addition of 5 ml of conc. HCl. Content of the flask was poured into 1 L of boiling water containing 30 g NaCl, to distill off THF. Precipitate was filtered off, washed with H_2O, acetone and dried under vacuum, to give 1.84 g (y. 66%) of product **3**.
Anal. Calcd for $C_{12}H_8O_2P_3N_3Cl_4$ (**3**): C 31.2%, H 1.7%, P 20.2%, N 9.1%, Cl 30.9%. Found: C 31.0%, H 1.7%, P 19.9%, N 9.4%, Cl 31%.

1,1'3,3'-bisspiro[2,2'-dioxybiphenyl-1,1']-5,5'dichloro-2,4,6,$1\lambda^5,3\lambda^5,5\lambda^5$*-triazatriphosphorine* (**4**). A two-necked, 250 ml round-bottomed flask equipped with mechanical stirrer and condenser was charged with 25 ml of chlorobenzene, 50 ml of water 3 g (0.0086 mol) of **1**, 3.5 g (0.019 mol) of **2**, 1.1 g (0.038 mol) of NaOH and 0.28 g (0.0009 mol) of tetrabutylammonium bromide, as PTC catalyst.[15] The reaction mixture was rapidly stirred at room temperature for 3 hrs. Then the mixture was heated to 70°C for another 3 hrs. Reaction was quenched with 7 ml of conc. HCl. The residue was filtered off, washed with chlorobenzene, acetone and dried, to yield 3.95 g (80%) of **4**.
Anal. calcd for $C_{24}H_{16}O_4P_3N_3Cl_2$ (**4**): C 50.2%, H 2.8%, P. 16.2%, N 7.3%, Cl 12.4%. Found: C 50.5%, H 2.9%, P 16.4%, N 7.1, Cl 12.2% (Tables I, II).

1,1'-spiro-[2,2'-dioxybiphenyl-1,1']-3,5-diphenoxy-3,5-dichloro-2,4,6,$1\lambda^5,3\lambda^5,5\lambda^5$*-triazatriphosphorine* (**5**). *1,1'-spiro-[2,2'-dioxyphenyl-1,1']-3,3',5,5'-tetraphenoxy-2,4,6,*$1\lambda^5,3\lambda^5,5\lambda^5$*-triazatriphosphorine* (**6**). A two-necked round-bottomed flask equipped with mechanical stirrer and condenser was charged with 20 ml of THF, 0.9 g (0.0095 mol) of phenol, 0.21 g (0.0095 mol) of sodium and stirred under Ar-atm. until sodium reacted. Then 1 g (0.002 mol) of **3** was added and the reaction mixture was stirred under reflux. The course of the reaction was followed by TLC analysis. When the reaction was over the precipitate was filtered off and the organic liquid was poured into hexane.

Crude product containing the mixture of compound **5** and **6** was separated by chromatography on silica gel, using as an eluent hexaneTHF = 10:3. (Yield **5**: 0.345 g 30%, **6**: 0.442 g 32%).
Anal. Calcd for $C_{24}H_{18}O_4P_3N_3Cl_2$ (**5**): C 50.0%, H 3.1%, P 16.1%, N 7.3%, Cl 12.4%. Found: C 49.8%, H 3.3%, P 16.3%, N 7.5, Cl 12.2%.
Anal. Calcd for $C_{36}H_{28}O_6P_3N_3$ (**6**): C 62.5%, H 4.2%, P 13.5%, N 6.1%. Found: C 62.1%, H 4.2%, P 13.3%, N 6.5 (Table III).

1,1',3,3'-bisspiro[2,2'-dioxybiphenyl-1,1']-5,5'-diphenoxy-2,4,6,$1\lambda^5,3\lambda^5,5\lambda^5$*-triazatriphosphorine* (**7**). 0.5 g (0.35 mol) of phenol, 0.1 g (0.08 mol) of sodium, 1 g (0.0015 mol) of **4** were subjected to the same procedure as described above. Yield of **7**: 0.373 g, 30%.
Anal. Calcd for $C_{36}H_{25}O_6P_3N_3$ (**7**): C 62.7%, H 3.8%, P 13.5%, N 6.1%. Found: C 62.3%, H 4.1%, P 13.8%, N 6.1% (Table III).

1,1-spiro-[2,2'-dioxybiphenyl-1,1']-3,3,5,5-tetrakis(1-aziridinyl)-2,4,6,$1\lambda^5,3\lambda^5,5\lambda^5$*-triazatriphosphorine* (**8**). To a stirred solution of 0.922 g (0.002 m) of **3** in 15 ml of dry benzene containing active carbon a solution of 1.50 ml (1,25 g. 0.029 mol) of aziridine in 10 ml of dry benzene was added slowly dropwise at room temperature. When the addition was completed, the reaction solution was decanted over the formed precipitate (aziridinium hydrochloride adsorbed on active carbon) and placed into an another reaction flask. A new portion of active carbon and 0.6 ml (0.5 g, 0.013 m) of aziridine were added and the reaction was carried out on stirring for the next 4 hours. The course of the substitution was controlled by means of TLC analysis.

The reaction was considered to be completed when only the single spot ($Rf = 0.35$) of the fully aziridinyl-substituted derivative **8** was revealed with J_2 vapour in the sample of the reaction mixture subjected to the TLC on silicagel (eluent: THF). After final filtration the solvent and the excess of aziridine were distilled off under reduced pressure to give the crude product, 0.82 g (84.1%) which was then recrystallized from a mixture of benzene–hexane (1 : 1), yielding the pure product **8** in the form of colourless crystals.
Anal. Calcd for $C_{20}H_{24}O_2P_3N_7$ (**8**): C 49.3%, H 4.9%, P 19.1%, N 20.1%. Found: C 49.0%, H 4.6%, P 19.3%, N 20.4%.

1,1,3,3-bisspiro-[2,2'-dioxybiphenyl-1,1']-5,5-bis-(1-aziridinyl)-2,4,6,$1\lambda^5,3\lambda^5,5\lambda^5$*-triazatriphosphorine* (**9**). The product **9** was obtained from **4** (1.147 g; 0.002 m) and aziridine (1 ml; 0.832 g; 0.019 m) according to the same procedure as described above for the preparation of compound **8**. Yield of **9**: 0.73 g (62.18%).
Anal. Calcd for $C_{28}H_{24}O_4P_3N_5$ (**9**): C 57.0%, H 4.1%, P 15.8%, N 11.2%. Found: C 57.0%, H 4.2%, P 15.6%, N 11.7%.

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