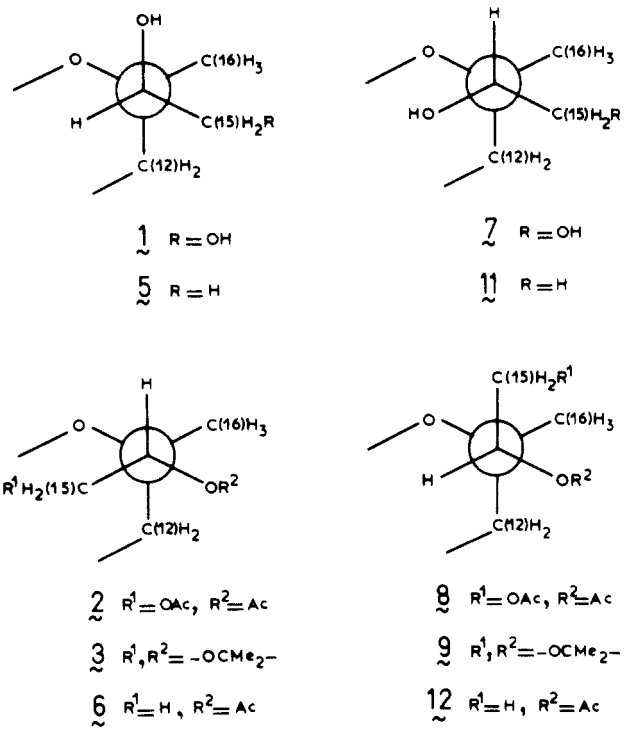
Chart II



(*c* 0.32, $CHCl_3$); IR (KBr) 3600, 3490, 2990, 2940, 1470, 1385, 1215, 1080, 865 cm^{-1}; ^1H NMR δ 4.16–3.45 (4 H, complex signal, H-7, H-14, and 2 H-15), CMe singlets at 1.45 and 1.38 (acetonide), 1.31 (3 H), 1.26 (3 H), 0.92 (3 H), 0.84 (3 H), and 0.81 (3 H); mass spectrum (75 eV, direct inlet), *m/z* (relative intensity) 380 (M^+, 0.3), 365 (7), 347 (4), 279 (100), 261 (54), 243 (16), 203 (14), 141 (34), 123 (40), 95 (30), 81 (23), 69 (37). Anal. Calcd for $C_{23}H_{40}O_4$: C, 72.59; H, 10.60. Found: C, 72.64; H, 10.56.

(14*S*)-8,13-Epoxylabdane-7β,14-diol (11). Treatment of compound **10** as previously described for preparation of compound **5** yielded the derivative **11**: mp 156–158 °C (Me_2CO–*n*-hexane); $[\alpha]^{18}_D$ +10.8° (*c* 1.21, $CHCl_3$); IR (KBr) 3440, 3350, 1145, 1075, 1000, 900 cm^{-1}; ^1H NMR δ 3.55 (2 H, complex signal, H-7 and H-14), 1.04 (3 H, d, J = 6.5 Hz, 3 H-15), CMe singlets at 1.30 (3 H), 1.18 (3 H), 0.87 (3 H), 0.80 (3 H), and 0.77 (3 H); mass spectrum (75 eV, direct inlet), *m/z* (relative intensity) 324 (M^+, 1.2), 309 (1.1), 291 (2.4), 279 (100), 261 (63), 243 (24), 203 (22), 141 (48), 123 (60), 95 (51), 81 (38), 69 (56). Anal. Calcd for $C_{20}H_{36}O_3$: C, 74.02; H, 11.18. Found: C, 73.97; H, 11.29.

(14*S*)-7β,14-Diacetoxy-8,13-epoxylabdane (12). Obtained from compound **11** by Ac_2O–pyridine treatment. Compound **12** was a syrup: IR (NaCl) 1730, 1250, 1105, 1080, 1065, 1035, 980 cm^{-1}; ^1H NMR δ 4.80 (2 H, complex signal, H-7 and H-14), 2.06 and 2.03 (3 H each, s, 2 OAc), 1.10 (3 H, d, J = 7 Hz, 3 H-15), CMe singlets at 1.31 (3 H), 1.17 (3 H), 0.87 (3 H), and 0.80 (6 H).

(14*S*)-7β,14-Diacetoxy-8,13-epoxy-15-ethoxylabdane (14). Acetylation of compound **13** gave compound **14**: a syrup; IR (NaCl) 1735, 1240 cm^{-1}; ^1H NMR δ 4.95 (2 H, complex signal, H-7 and H-14), 3.60 (4 H, complex signal, 2 H-15 and OCH_2CH_3), 2.09 and 2.07 (3 H each, s, 2 OAc), 1.15 (3 H, t, J = 7.5 Hz, OCH_2CH_3), CMe singlets at 1.31 (3 H), 1.18 (3 H), 0.88 (3 H), and 0.80 (6 H).

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Registry No. 1, 52591-03-4; 2, 76499-23-5; 3, 76499-24-6; 4, 76499-25-7; 5, 76499-26-8; 6, 76499-27-9; 7, 76549-11-6; 8, 76581-98-1; 9, 76549-12-7; 10, 76549-13-8; 11, 76549-14-9; 12, 76549-15-0; 13, 76499-28-0; 14, 76499-29-1; (14*R*)-7β-acetoxy-8,13-epoxylabdane-14,15-diol, 76499-30-4; (14*R*)-7β-acetoxy-15-(benzoyloxy)-8,13-epoxylabdan-14-ol, 76499-31-5; (14*R*)-7β-acetoxy-14-tosyloxy-15-(benzoyloxy)-8,13-epoxylabdane, 76499-32-6.

Phenolysis of Spiro[(binaphthylenedioxy)cyclophosphazenes]

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During the last few years (aryloxy)cyclophosphazenes containing reactive functional groups have become of great interest due to their relevance to high molecular weight chemistry. Recently series of hexa(*p*-halogenophenoxy)-cyclophosphazenes[1] and hexa(*p*-hydroxymethylphenoxy)cyclophosphazenes[2] have been synthesized as well as a number of cyclophosphazenes with mixed substituents: phenoxy(hydroxyalkoxy),[3] phenoxy(hydroxyphenoxy),[4] and phenoxyisothiocyanato.[5] Kajiwara has prepared a series of cyclolinear spiro-type polymers by the reactions of *gem*-diphenylcyclophosphazene with aromatic *p*-dihydroxy compounds[6] among which the product obtained from hydroquinone was the most interesting.

In our previous paper[7] we reported the synthesis of two isomeric spiro[(binaphthylenedioxy)cyclophosphazenes], **1** and **2**. Both these compounds contain two PCl_2 groups in their molecules. Such a structure (monogem substituted) offers possibilities for the preparation of cyclolinear derivatives. However, it was suspected that the steric hindrance imposed on **1** and **2** by the presence of bulky spiro substituents would significantly restrain, if not prevent completely, substitution of the remaining chlorine atoms in these compounds. In order to establish the possibility of partial (two atoms) and total (four atoms) substitution of chlorine atoms in **1** and **2**, we have studied their reaction with phenol at various molar ratios of reagents.

Results and Discussion

Phenolysis of either $(PNCl_2)_3$ itself[8] or that of its *gem*-diphenyl derivative[8,9] is known to follow a nongeminal substitution pattern due to the steric factors hindering the attachment of the second phenoxy group to the phosphorus atoms already bearing one such a substituent. Therefore, the replacement of chlorine atoms with phenoxy groups in **1** and **2**, which are monogem derivatives could also be expected to follow a nongeminal reaction pattern and to produce diphenoxy derivatives **3** or **4**, respectively, containing two P(OPh)Cl groups as shown in reaction a of Scheme I.

In actual fact the reaction of the isomeric 3,3,5,5-tetrachloro(binaphthylenedioxy)cyclotriphosphazenes **1** and **2** with sodium phenolate (**7**) in tetrahydrofuran at molar ratios of 1:2 (Scheme Ia) or 1:4 (Scheme Ib) proceeds quantitatively and leads, depending upon the stoichiom-

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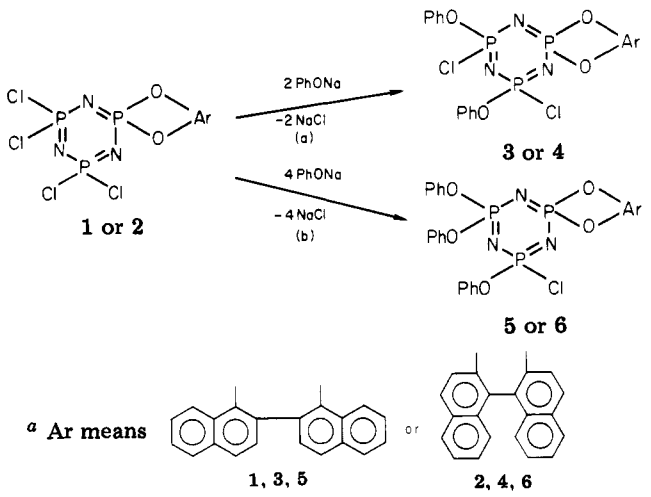
Table I. ^{31}P NMR Data for Phenoxy(binaphthylenedioxy)cyclophosphazenes (A_2B Spin System)[a]

compd	δ_A		δ_B	J_{A-B}, Hz	$\lvert J_{A-B}/(\nu_A - \nu_B)\rvert$	no. of lines[c]
3	18.34		22.64	108.5	≥1	6[d]
4	17.04		22.12	165	1.333	3[d]
5		8.56	28.20	−91.63	0.195	8
6		8.75	26.06	−91.79	0.215	8

[a] Spectra obtained with proton-noise decoupling. Chemical shifts (of $CDCl_3$ solutions) downfield from 85% H_3PO_4. $\delta(\nu)_A$, $\delta(\nu)_B$, and J_{A-B} values were calculated according to ref 11. [b] Ar means 2,2′-binaphthyl-1,1′-diyl (3, 5) or 1,1′-binaphthyl-2,2′-diyl (4, 6) groups, respectively. [c] Number of resonance lines observed in the spectrum. [d] A_2B spin systems decomposed.

Scheme I[a]



etry of the reagents used, to the formation of the corresponding non-*gem*-diphenoxy (3, 4) or tetraphenoxy derivatives (5, 6) as main reaction products. The course of the reaction was controlled by the TLC method; its completion was signaled by the quantity of sodium chloride formed in reactions a or b, respectively. Thus the presence of one dioxybinaphthyl side unit in cyclophosphazenes is not sufficient to prevent substitution at the other phosphorus atoms, at least with groups as bulky as the phenoxy ones.

The retention of the spiro structure was established unequivocally by UV and ^{31}P NMR data. UV spectra of all the new phenoxy derivatives (3–6) closely resemble those of the corresponding parent spiro[(binaphthylenedioxy)cyclophosphazene] 1 or 2, respectively.[7] While λ_{max} remained constant, there was a small increase in the extinction values which could be ascribed to the electronic contributions of the phenoxy substituents.

In our previous paper[7] we postulated resonance stabilization of 1 on the basis of the appearance of a strong K band at λ_{max} 259 nm. The presence of even more intense K bands in the spectra of 3 and 5, which contain 1,1′-dioxy-2,2′-binaphthyl units, is evidence that substitution of the chlorine atoms of 1 by phenoxy groups does not involve destruction of the conjugation between the coupled naphthalene rings (λ_{max} 259 nm: ϵ_{max} 1.06×10^5 (1), 1.18×10^5 (3), 1.14×10^5 (5). This means that the planar conformation of the spirocyclic system postulated for 1[7] is essentially unaffected by the newly incorporated phenoxy substituents.

This is also verified by a comparison of the mass spectra of 5 and 6. The principal fragmentation product of 6 responsible for the base peak at 698 mass units is formed as a result of the loss of one OC_6H_5 group (M − OC_6H_5, *m/e* 698). This observation closely corresponds to the previously reported[1] results for the other totally aryloxy-substituted cyclotriphosphazenes. By contrast, the strongest peak in the mass spectrum of 5 is that of the molecular ion (M, *m/e* 791) and the peak resulting from the loss of one phenoxy substituent is less intense (57.2%). Since the intensity of the molecular ion peak depends on the stability of the parent ion,[10] this observation provides evidence for significant resonance stabilization in 5 which seems to be sufficiently stable to serve as a new high molecular weight standard for mass spectrometry. The mass spectra of the diphenoxy derivatives (3, 4) exhibit parent ions at 675 mass units, each accompanied by two isotope peaks corresponding to the presence of two chlorine atoms in the molecules of these compounds.

^{31}P NMR spectra for all di- and tetraphenoxy-substituted (binaphthylenedioxy)cyclophosphazenes 3–6 show A_2B spin systems. This verifies the presence of two magnetically equivalent phosphorus atoms in the phosphazene rings of 3 and 4 and of 5 and 6. To facilitate their comparison, ^{31}P NMR data have been presented in Table I. The structure of an A_2B spectrum depends only on the ratio of J_{A-B} to $\nu_A - \nu_B$[11] and when $0.15 < |J_{A-B}/(\nu_A - \nu_B)| < 0.5$ eight fundamental A_2B transitions can be resolved. All eight resonance lines have been identified in the spectra of 5 and 6, just as for the parent tetrachloro compounds 1 and 2.[7] In the case of 3 and 4, a number of transitions are degenerate, owing to the fact that $J_{AB}/(\nu_A - \nu_B)$ exceeds 1 (see Table I). Thus the spectrum of 3 consists of six lines, and that of 4 collapses into a triplet, with the middle peak showing the highest intensity. The calculated chemical shifts of the P(OPh)Cl or $P(OPh)_2$ groups in all the newly synthesized compounds 3–6 are similar to the corresponding values for P(OPh)Cl or $P(OPh)_2$ in other cyclophosphazenes containing such units.[8,12] The presence of two equivalent phosphorus atoms with chemical shifts characteristic of P(OPh)Cl groups in the diphenoxy derivatives 3 and 4 confirms the assumed nongeminal substitution pattern in the products resulting from phenolysis of 1 and 2. The elucidation of the questions of stereochemistry relating to these compounds is one of our present goals.[13] Owing to the ease with which all chlorine atoms of 1 and 2 can be replaced by phenoxy groups, 3 and

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(13) Only one crystalline form has been isolated chromatographically for each of the isomers 3 and 4. We intend to establish their cis or trans configuration by replacing the chlorine atoms by methoxy groups and comparing the products with those obtained by phenolysis of chlorodimethoxy derivatives of 1 and 2 by NMR technique. These studies are under way.

4 can be considered as reactive difunctional (two atoms of Cl) monomers useful in polycondensation processes leading to the linear-chain polymers (for example by reaction with diphenols). The parent tetrachloro compounds 1 and 2 can in turn be expected to yield cyclolinear polymers by direct reaction with aromatic, *p*-diols in a manner similar to the case reported by Kajiwara.[6]

Experimental Section

General Methods. All substitution experiments were carried out in an atmosphere of dry argon in a standard glass apparatus. Moisture was excluded by calcium chloride drying tubes.

Melting points were measured on a Boetius microscope hot stage and are uncorrected.

The IR spectra were performed as Nujol or halocarbon mulls on a UR-120 Carl Zeiss Jena spectrophotometer. The ^1H NMR spectra were recorded on a Varian XL-100 spectrometer using Me_4Si as an internal standard. The proton-noise-decoupled ^{31}P NMR spectra were obtained on a JEOL FX-60 spectrometer at 24.3 MHz by using 85% H_3PO_4 as an external standard. The mass spectra were recorded on a LKB 9000 mass spectrometer at a 70-eV electron energy and at an ion source temperature of 290 °C. TLC experiments were carried out on Merck Precoated silica gel 60 plates (solvent system 1:1 benzene–hexane). Visualization was performed by pyridine–*m*-toluidine (1:1) reagent for all chlorine-containing cyclophosphazenes (**1–4**)[13] and by Millon's reagent[14] for all aryloxy-substituted cyclophosphazenes (**1–6**).

Materials. 3,3,5,5-Tetrachloro-1,1-(1,1′-dioxy-2,2′-binaphthyl)cyclotriphosphazene (1) and 3,3,5,5-tetrachloro-1,1-(2,2′-dioxy-1,1′-binaphthyl)cyclotriphosphazene (2) were obtained and purified according to the method described previously:[7] mp 310 °C (**1**), 283 °C (**2**). **Sodium phenolate (7)** was prepared by the reaction of sodium and phenol carried out in tetrahydrofuran solvent. Phenol was freshly distilled before use; mp 41 °C. Tetrahydrofuran was distilled from potassium hydroxide pellets and then dried over calcium hydride. Argon was passed through concentrated sulfuric acid and then through 4-Å molecular sieves.

Synthesis. 3,5-Diphenoxy-3,5-dichloro-1,1-(1,1′-dioxy-2,2′-binaphthyl)cyclotriphosphazene (3) and 3,5-Diphenoxy-3,5-dichloro-1,1-(2,2′-dioxy-1,1′-binaphthyl)cyclotriphosphazene (4). Under an argon atmosphere a solution of 0.02 M C_6H_5ONa in tetrahydrofuran (50 mL) was added dropwise over a 1-h period to a stirred solution of 0.01 mol (5.61 g) of **1** or **2** in 100 mL of THF at 30–40 °C. The substitution was found to proceed almost quantitatively on addition of phenolate as no traces of base were indicated in the reaction mixture immediately after the addition was completed. To ensure completion, we refluxed the mixture for 2–3 h. The sodium chloride formed in the reaction was removed by centrifugation and determined by titration with 0.01 N $AgNO_3$. The cold solution was poured into excess H_2O to yield a white solid, which was isolated by filtration, washed on the filter with water, dried in air, and finally dried under vacuum (yield of the crude product 6.32 g from **1** or 6.48 g from **2**). The product was purified by column chromatography on silica with hexane–benzene (2:1). When the eluted fractions were allowed to stand overnight, compound **3** or **4** crystallized directly in the form of white crystals: mp 202 °C (**3**), 213 °C (**4**); yield 5.60 g (82.8%) of **3**, 5.42 g (80.3%) of **4**; IR (Nujol mull) 3070 (CH_{Ar}), 1590, 1485 (Ar skeleton) 1265, 1255, 1185, 1160, and 1085 (POC_{Ar} and P=N) cm^{-1} (**3**); 3070, 1620, 1590, 1500, 1270, 1250, 1210 (**4**); UV (cyclohexane) λ_{max} 215 nm (ϵ 5.2×10^4), 259 (1.18×10^5), 272 (3.6×10^4) (**3**); 216 (1.4×10^5), 262 (1.0×10^4), 305 (1.8×10^4) (**4**); ^1H NMR ($CDCl_3$) δ 7.0–7.9 (m, 20 H), 8.0–8.1 (m, 2 H) ppm (**3**); 6.9–7.4 (m, 17 H), 7.6–8.0 (m, 5 H) ppm (**4**); ^{31}P NMR, Table I; mass spectrum, *m/e* (relative intensity) 679 [17.1, $(M + 4)^+$], 677 [75.1, $(M + 2)^+$, 675 [100, M^+], (**3**); 679 [15.2, $(M + 4)^+$], 677 [69.5, $(M + 2)^+$], 675 [100, M^+] (**4**). Anal. Calcd for $C_{32}H_{22}O_4Cl_2N_3P_3$: C, 56.70; H, 3.26; Cl, 10.50; N, 6.21; P, 13.75. Found (for **3**): C, 56.54; H, 3.76; Cl, 10.3; N, 6.14; P, 13.40. Found (for **4**): C, 56.32; H, 3.78; Cl, 10.45; N, 6.17; P, 13.54.

3,3,5,5-Tetraphenoxy-1,1-(1,1′-dioxy-2,2′-binaphthyl)-cyclotriphosphazene (5) and 3,3,5,5-Tetraphenoxy-1,1-(2,2′-dioxy-1,1′-binaphthyl)cyclotriphosphazene (6). Under an argon atmosphere a solution of 0.042 mol of sodium phenolate in 50 mL of tetrahydrofuran was added dropwise with stirring to a boiling solution of 5.59 g (0.01 mol) of **1** and **2** in 100 mL of THF. When the addition was completed, the mixture was refluxed for 4–5 h until TLC showed complete reaction of the chlorine atoms in **1** or **2**. This could be deduced from the absence of any colored spots after the developed TLC plates were sprayed with pyridine–*m*-toluidine (1:1) detecting reagent.[14] After the precipitate was centrifuged free of sodium chloride, the slightly alkaline filtrate was poured into an excess of cold 5% aqueous HCl to yield a gray solid which was isolated and purified by recrystallization from benzene-heptane (1:2). The white crystals formed by crystallization were heated under vacuum at 100 °C to remove retained solvent: yield 7.05 g (89.1%) of **5** (mp 185 °C) or 6.78 g (85.7%) of **6** (mp 158 °C); IR (Nujol mull) 3075 (CH_{Ar}), 1590, 1485 (Ar skeleton), 1265, 1185, 1160 (PCC_{Ar} and P=N) cm^{-1} (**5**); 3070, 1590, 1485, 1260, 1230, 1200, 1180, 1160 cm^{-1} (**6**); UV (cyclohexane) λ_{max} 215 (ϵ 5.0×10^4), 259 (1.14×10^5), 272 (3.8×10^4) (**5**); 216 (1.43×10^5), 263 (1.1×10^4), 305 (1.5×10^4) (**6**); ^1H NMR δ 7.05–7.30 (m, 8 H), 7.35–7.70 (m, 4 H), 7.75–7.90 (m, 20 H) (**5**); 6.62–7.42 (m, 28 H), 7.65–7.85 (m, 4 H) (**6**); ^{31}P NMR, Table I; mass spectrum, *m/e* (relative intensity) 791 [100, M^+], 698 [57.2, $(M - OC_6H_5)^+$] (for **5**); 791 [67.0, M^+], [100, 698 $(M - OC_6H_5)^+$] (for **6**). Anal. Calcd for $C_{44}H_{32}O_6N_3P_3$: C, 66.68; H, 4.03; N, 5.32; P, 11.75. Found (for **5**): C, 66.90; H, 4.31; N, 5.54; P. 11.61. Found (for **6**): C, 66.15; H, 4.27; N, 5.52; P, 11.82.

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Reaction of Methyl Iodide with Gramine and with Nitro-Substituted Gramines

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Gramine methiodides are important intermediates in the synthesis of tryptamines, tryptophans, indoleacetic acids, and other indole derivatives having a two-carbon side chain at the 3-position.[1,2] Preparation of gramine methiodide (**2a**) by alkylation of gramine (**1a**) with methyl iodide is complicated by formation of bis[(indol-3-yl)methyl]dimethylammonium iodide (**3a**),[3,4] as shown in Scheme I. The same problem exists when other alkylating agents are used.[3,5] Schöpf and Thesing[3] and Geissman and Armen,[4] who first elucidated this reaction sequence, suggested several ways to suppress the formation of **3a**.

We have found that controlling the product ratio in this set of reactions is more difficult than previously recognized. Although Geissman and Armen generated gramine methiodide (**2a**) in neat methyl iodide,[4] others[6] have interpreted their results to mean that a large excess of methyl iodide in ethanol is sufficient. We find, however, that the product

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