H); mass spectrum, m/e (relative intensity) 373 (M^+, 93), 344 (39), 281 (100), 270 (16), 267 (28), 252 (20), and 165 (11). Anal. Calcd for $C_{27}H_{19}NO$: C, 86.84; H, 5.13; N, 3.75. Found: C, 86.63; H, 5.18; N, 3.70.

A similar pyrolysis of **5b** and chromatography of the product gave 10,11-dihydro-10-phenyl-11-(4-tolylimino)-5*H*-dibenzo[*a*,*d*]-cyclohepten-5-one (**19b**, 17%), mp 181–182 °C. Further eluate gave a complex mixture which led to **11** during workup. See the supplementary material for the characterization of **19b**.[15]

A similar pyrolysis of **5e** gave 10-(4-methoxyphenylimino)-anthrone (**7e**, 32%): red needles from benzene–hexane; mp 143–145 °C; R_f 0.32 (benzene); IR 1662 (C=O) cm^{-1}; ^1H NMR δ 3.88 (s, 3 H, OCH_3) and 6.65–8.70 (m, 12 H, aromatic H); mass spectrum, m/e (relative intensity) 313 (M^+, 51), 298 (43), 279 (20), 208 (100), 180 (93), 152 (80), and 126 (14). Anal. Calcd for $C_{21}H_{15}NO_2$: C, 80.49; H, 4.83; N, 4.47. Found: C, 80.42; H, 4.69; N, 4.33.

The iminoanthrone **7e** was prepared independently by the procedure described for **7f** in a 48% yield.

C. Pyrolysis of **3** and **5** in refluxing benzene gave the same products as in xylene, but the reaction was slow. Thermal reaction of **3** with **1a** in refluxing benzene or xylene did not yield **9**.

Photolysis of 3 and 5. A solution of **3** (**5**) (1 mmol) in benzene (30 mL) was irradiated at room temperature under nitrogen with a 100-W high-pressure mercury lamp through a Pyrex filter until gas evolution ceased (~3 h). After irradiation, the resulting solution was concentrated and the residue was chromatographed on silica (benzene as eluant). TLC of the crude photolysate of **3** (**5**) showed spots of compounds which could not be isolated owing to their extreme reactivity in addition to the isolated products shown below. Anthraquinone, which could not be detected prior to workup, was formed during chromatographic separation on silica. The results of analyses of the isolated compounds are as follows. Photolysis of **3a**, **3f–g**, and **3i** gave **1a** (trace) and **11** (20–30%). **3b** and **3e**: **1a** (15–20%) and **11** (3–5%). **5a**: **11** (40%), **19a** (trace), and 10-anilino-11-phenyl-5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (**12a**, 6%). **5b**: **11** (29%). **5e**: **7e** (69%). **12a**: yellow microcrystals from benzene; mp 199–200 °C; R_f 0.35 (benzene); IR 3400 (NH), 1660 (C=O) cm^{-1}; ^1H NMR δ 5.95–8.05 (m, 19 H, aromatic H and NH); mass spectrum, m/e (relative intensity) 373 (M^+, 100), 354 (24), 270 (12), 267 (12), and 252 (12). Anal. Calcd for $C_{27}H_{19}NO$: C, 86.84; H, 5.13; N, 3.75. Found: C, 86.71; H, 5.02; N, 3.78.

Reactions of 3 and 5 in Acetone with Hydrochloric Acid. A. Spiroanthronetriazolines 3. A suspension of **3** (2 mmol) in acetone (30 mL) containing hydrochloric acid (0.2 mL) was stirred at room temperature until gas evolution ceased (~30 min). The resulting solution was poured into water (100 mL), and the precipitate was collected and washed with water. Recrystallization from ethanol gave 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene-5,10-dione (**23**) as colorless needles in 80–95% yield, mp 118 °C (lit.[17] mp 118 °C), identical with an authentic specimen. The filtrate was neutralized with sodium hydrogen carbonate and extracted with ether. The extract was dried and evaporated to give aryl amines (ca. 50–60%).

B. Spiroanthronetriazolines 5. The same reaction of **5** gave arylamines and 10,11-dihydro-11-phenyl-5*H*-dibenzo[*a*,*d*]cycloheptene-5,10-dione (**24**, 90–95%) as colorless needles, mp 135 °C (lit.[13,18] mp 134–135 °C), identical with an authentic specimen.

Reaction of 3 in Methanol with Hydrogen Chloride. A suspension of **3** (1 mmol) in methanol (15 mL) containing hydrogen chloride (0.1 g) was stirred at room temperature until gas evolution was complete (~3 h). The mixture was poured into water and the precipitate was collected. Recrystallization from methanol gave 10-methoxy-5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (**25**) as colorless needles in ca. 85% yield, mp 100–101 °C (lit.[17a] mp 96–97 °C).

Reactions of 3 and 5 in Benzene with Hydrogen Chloride. A solution of **3** (**5**) (1 mmol) in benzene (20 mL) was stirred at room temperature under nitrogen while 3 mL of a saturated solution of hydrogen chloride in benzene was added. The reaction was followed by TLC, which showed disappearance of starting material. The solvent was distilled off under reduced pressure, and the residue was recrystallized from benzene–hexane. The reaction of **3i** and **6a** gave **13i** (55%) and **12a** (63%), respectively. However, isolation or identification of products from other spiroanthronetriazolines could not be achieved owing to their complexity.

Registry No. **1a**, 4159-04-0; **1b**, 14343-92-1; **2a**, 622-37-7; **2b**, 2101-86-2; **2c**, 4113-72-8; **2d**, 31656-92-5; **2e**, 2101-87-3; **2f**, 3296-05-7; **2g**, 3296-06-8; **2h**, 3296-07-9; **2i**, 1516-60-5; **3a**, 73078-95-2; **3b**, 73078-96-3; **3c**, 73078-97-4; **3d**, 73078-98-5; **3e**, 73078-99-6; **3f**, 73079-00-2; **3g**, 73079-01-3; **3i**, 73079-02-4; **5a**, 73079-03-5; **5b**, 73079-04-6; **5e**, 73079-05-7; **7a**, 10019-06-4; **7e**, 73079-06-8; **7f**, 73079-07-9; **7g**, 73079-08-0; **7h**, 73079-09-1; **7i**, 73079-10-4; **8a**, 73079-11-5; **8b**, 73079-12-6; **8c**, 73079-13-7; **8f**, 73079-14-8; **8g**, 73078-83-8; **9c**, 73078-84-9; **9d**, 73078-85-0; **9h**, 73078-86-1; **10**, 65252-95-1; **11**, 84-65-1; **12a**, 73078-87-2; **12g**, 73078-88-3; **12h**, 73078-89-4; **12i**, 73078-90-7; **13i**, 73078-91-8; **19a**, 73078-92-9; **19b**, 73078-93-0; **23**, 16174-24-6; **24**, 73078-94-1; **25**, 40976-22-5; 10,10-dibromoanthrone, 21555-13-5; 4-chloroaniline, 106-47-8.

Supplementary Material Available: Characterization data of the derivatives of **3**, **5**, **7**, **8**, **9**, **12**, and **19** (6 pages). Ordering information is given on any current masthead page.

(17) (a) J. Rigaudy and L. Nédélec, *Bull. Soc. Chim. Fr.*, 659 (1959); (b) W. Tochtermann, K. Oppenlaender, and U. Walter, *Chem. Ber.*, **97**, 1318 (1964).

(18) J. W. Cook, *J. Chem. Soc.*, 58 (1928).

Synthesis of Spiro[arylenedioxy] Derivatives from Hexachlorocyclotriphosphazene and Dihydroxybinaphthyls

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Monospiro-substituted products prevail when sterically hindered aromatic ortho diols are employed in the reaction with hexachlorocyclotriphosphazene (**1**). Two isomeric monospiro[binaphthylenedioxycyclophosphazenes], **4** and **5**, were isolated in high yields starting from equimolar amounts of **1** and 1,1′-dihydroxy-2,2′-binaphthyl (**2**) and 2,2′-dihydroxy-1,1′-binaphthyl (**3**), respectively. With the latter reagent a small amount of a corresponding bisspiro derivative **6** was also isolated. Differences in the spectral properties of the isomers **4** and **5** can be attributed to the steric and electronic effects. The appearance of a strong K-band UV absorption for (1,1′-dioxy-2,2′-binaphthyl)cyclophosphazene **4** indicates that the naphthalene rings in this compound are in extensive conjugation. The lack of remarkable resonance interaction can be inferred from the UV spectrum of the spirocyclophosphazene derivative (**5**) of 2,2′-dihydroxy-1,1′-binaphthyl.

It has been previously demonstrated that the reaction of hexachlorocyclotriphosphazene (**1**) with aliphatic glycols or ortho diphenols in the presence of a base leads to the formation of spirocyclic products. A number of trisspi-

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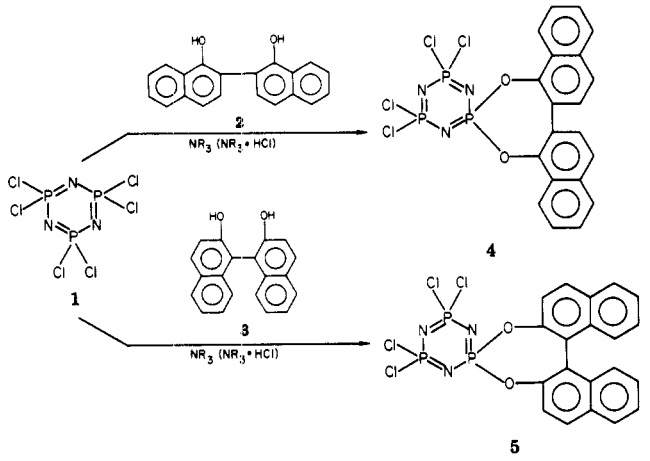
Scheme I



ro[arylenedioxycyclophosphazenes] have been prepared in Allcock's laboratory in which the substituents were 1,1′-dioxyphenylene, 2,3-dioxynaphthylene, 1,8-dioxynaphthylene, or 2,2′-dioxybiphenylene.[1-4] Aliphatic trisspirocyclophosphazene derivatives have also been described.[5-7]

Recently[8-10] a series of mono- and bisspiroalkoxycyclophosphazenes have been obtained in the reaction of 1 with equimolar amounts of aliphatic glycols, their structures being ascertained by mass spectroscopy and ^{31}P NMR.[10] However, attempts to prepare mono- and bis(*o*-phenylenedioxy)cyclophosphazenes failed. A rationale was provided by Allcock[2] in terms of electronic effects. Incorporation of one spiro[arylenedioxy] unit into the phosphazene ring enhances the substitution reactivity of the remaining chlorine atoms and favors exclusive formation of the trisspiro derivatives.

If available, the monospiro[(arylenedioxy)tetrachlorocyclophosphazenes] might potentially be transformed into various derivatives inaccessible from the unreactive trisspirocyclic compounds. In particular, incorporation of the thermodynamically stable[3,11] spiro[arylenedioxycyclophosphazene] units into different polymers may lead to unique material properties such as high thermal and chemical resistance.

This study describes the first successful synthesis of spiro[arylenedioxycyclophosphazenes] from the reaction of 1 with equimolar amounts of *o,o′*-difunctional binaphthols 1,1′-dihydroxy-2,2′-binaphthyl (2) and 2,2′-dihydroxy-1,1′-binaphthyl (3).

Results and Discussion

In designing the synthesis of the spiro[arylenedioxycyclophosphazenes], we considered substrate constraints the cyclization process and the possible steric influence of intermediate dioxyarylene products as the principal factors determining the course of the substitution reaction. Accordingly, the isomeric *o,o′*-dihydroxybinaphthyls, 1,1′-dihydroxy-2,2′-binaphthyl (2) and 2,2′-dihydroxy-1,1′-binaphthyl (3), having functional groups in the adjacent positions to the coupled carbon atoms were selected for this reaction.

The arrangement of OH groups in 2 and 3 favors the cyclization reaction at the phosphorus atoms due to the thermodynamic stability of the seven-membered spirocyclic products.[2,3,11] Moreover, significant steric hindrance could be expected after the incorporation of one dioxybinaphthylene side unit into the phosphazene ring. Therefore, it could be anticipated that further substitution of the remaining chlorides by bulky binaphthylenedioxy functions might be sterically inhibited.

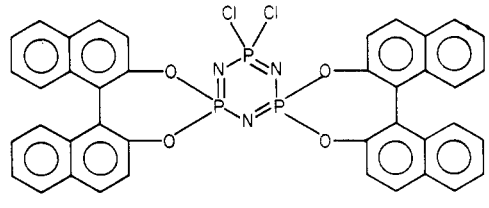
In fact, we observed remarkable steric control of reactivity by the binaphthyl functions, which afford nearly exclusive formation of the monospiro derivatives (Scheme I).

The substitution reactions were carried out in benzene, with triethylamine or pyridine scavenging of the resulting hydrogen chloride. The reactions were monitored by the disappearance of substrates with TLC methodology and by the corresponding formation of amine hydrochloride.

Triethylamine yields cleaner products than pyridine. The latter catalyzes side reactions, like deaquation of binaphthols and further hydrolysis of chlorine atoms.[12]

As anticipated, analytical data confirmed the main products of the reaction of 1 with equimolar amounts of 2 or 3 to be the desired spiro[binaphthylenedioxycyclophosphazenes], 3,3,5,5-tetrachloro-1,1-(1,1′-dioxy-2,2′-binaphthyl)cyclotriphosphazene (4) and 3,3,5,5-tetrachloro-1,1-(2,2′-dioxy-1,1′-binaphthyl)cyclotriphosphazene (5).

In the case of the reaction of 1 with 3, formation of a small amount of the sparingly organic soluble bis-substituted spiro derivative, 5,5-dichloro-1,1:3,3-bis(2,2′-dioxy-1,1′-binaphthyl)cyclophosphazene (6), was also observed. The corresponding bisspiro[1,1′-dioxy-2,2′-binaphthyl] derivative was not isolated.



6

Both isomeric (binaphthylenedioxy)tetrachlorocyclotriphosphazenes 4 and 5 are white crystalline substances with high melting points. They are readily soluble in common organic solvents of medium polarity, such as chloroform or benzene, and less soluble in the nonpolar or highly polar solvents. They appear to be thermally stable up to 200 °C and inert to aqueous hydrolysis in neutral and dilute acidic media.

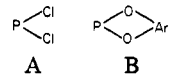
Analytical data readily confirm the isomeric structures of 4 and 5. The presence in the IR spectra of the bands assigned to the P–N stretching mode of the phosphazene ring as well as the absence of the bands corresponding to P–OH or N–H absorptions, which would imply P_3N_3-ring decomposition products, confirms that the phosphazene backbone is unaffected by the chlorine substitution processes. Purified products were free of unreacted substrate

(1) H. R. Allcock, *J. Am. Chem. Soc.*, **85**, 4050 (1963).
(2) H. R. Allcock, *J. Am. Chem. Soc.*, **86**, 2591 (1964).
(3) H. R. Allcock and R. L. Kugel, *Inorg. Chem.*, **5**, 1016 (1966).
(4) H. R. Allcock and E. J. Walsch, *Inorg. Chem.*, **10**, 1643 (1971).
(5) J. Parrod and R. Pornin, *C. R. Hebd. Seances Acad. Sci.*, **258**, 3022 (1964).
(6) R. Pornin, *Bull. Soc. Chim. Fr.*, **9**, 2861 (1961).
(7) A. J. Matuszko and M. S. Chang, *J. Org. Chem.*, **31**, 2004 (1966).
(8) H. Manns and H. Specker, *Z. Anorg. Allg. Chem.*, **425**, 127 (1976).
(9) H. Rose and H. Specker, *Z. Anorg. Allg. Chem.*, **426**, 275 (1976).
(10) H. Manns and H. Specker, *Z. Anal. Chem.*, **275**, 103 (1975).
(11) H. R. Allcock, *Inorg. Chem.*, **5**, 1321 (1966), and references therein.
(12) B. I. Stepanov and G. I. Migachev, *Z. Obshch. Khim.*, **36**, 1447 (1966).

Table I. ^{31}P NMR Spectral Data for Spiro[binaphthylenedioxycyclophosphazenes][a]

compd	spin system	δ_A,[d] ppm	δ_B,[d] ppm	J_{AB}, Hz	$J_{AB}/(\nu_A - \nu_B)$[b]	A/B[c]
4	A_2B	24.29	13.61	70.96	0.275 (8)	2:1
5	A_2B	23.48	14.98	70.96	0.342 (8)	2:1
6	AB_2	28.56	20.26	57.30	0.351 (8)	1:2

[a] δ_A, ν_A, δ_B, ν_B, and J_{AB} values were calculated according to ref 22. [b] Values in parentheses show the number of resonance lines observed in the spectra. [c] The ratio of the integrated area of the A portion of the spectrum to the B portion. [d] Structures for A and B:



A B

Table II. Comparison of the Fragmentation Patterns for the Isomeric (Binaphthylenedioxy)tetrachlorocyclophosphazenes

m/e	fragment	% of base peak 4	% of base peak 5
567 (M + 8)	$P_3N_3{}^{37}Cl_4(O_2C_{20}H_{12})$	1.0	0.8
565 (M + 6)	$P_3N_3{}^{37}Cl_3Cl(O_2C_{20}H_{12})$	11.1	10.1
563 (M + 4)	$P_3N_3{}^{37}Cl_2Cl_2(O_2C_{20}H_{12})$	49.2	45.0
561 (M + 2)	$P_3N_3{}^{37}ClCl_3(O_2C_{20}H_{12})$	100.0	91.9
559 (M)	$P_3N_3Cl_4(O_2C_{20}H_{12})$	76.1	71.0
526	$P_3N_3Cl_3(O_2C_{20}H_{12})$	3.0	3.8
489	$P_3N_3Cl_2(O_2C_{20}H_{12})$	2.3	5.9
284	$C_{20}H_{12}O_2$	0.6	3.6
268	$C_{20}H_{12}O$	26.6	100.0
267	$C_{20}H_{11}O$	18.0	75.4
266	$C_{20}H_{10}O$	13.8	21.4
265	$C_{20}H_9O$	2.8	22.7
264	$C_{20}H_8O$	2.4	25.2
256	$P_3N_3OCl_3$	2.9	4.3
240	$P_3N_3Cl_3$	4.0	25.5

hydroxyls, and no oligomeric byproducts were evident. Thus, reactions of 1 with 2 or 3 appear to yield only the exocyclic derivatives.

The spiro structures of the compounds 4 and 5 were confirmed by their ^{31}P NMR spectra (Table I) and mass spectral correlations (Table II). The ^{31}P NMR spectra show well-resolved A_2B spin systems corresponding to an equivalency of two phosphorus atoms in the phosphazene rings. Chemical shifts and coupling constants correspond closely to previously reported values[10] of compounds containing two PCl_2 groups and one spiro[alkylenedioxy] unit.

The mass spectra of 4 and 5 exhibited parent peaks at 559 mass units and appropriate isotope contributions from four chlorides.[13]

The intensities of the fragmentation peaks—corresponding to the loss of oxybinaphthylene units—relative to the molecular ion are greater in the case of bis(β-naphthol) 5 than bis(α-naphthol) 4 derivatives. These differences are probably due to greater steric strain in 5 compared to a more strain free planar conformation of 4 which would enhance its resonance stabilization. The resonance interactions of 4 can be seen by comparison of its UV spectrum to those of 1-hydroxynaphthylene (7) and 1,1′-dihydroxy-2,2′-binaphthyl (2). In the spectrum of 2, a new absorption band (ϵ_{max} 2.85 × 10^4), absent in 7, appears at 259 nm, which is attributable to the resonance interaction between two conjugated naphthalene rings.[14] In the case of 4 the significant increase of this band [λ_{max} 259 nm (ϵ_{max} 1.06 × 10^5)] indicates the effect of forcing the 2,2′-binaphthyl rings to coplanarity as a result of the spiro structure. In the UV spectra of all previously reported trisspiro[arylenedioxycyclophosphazenes], including that of seven-membered tris(2,2′-dioxybiphenyl)cyclophosphazene,[3,4] no evidence for enhanced resonance interaction within the side groups or between the side groups and the phosphazene ring system has been observed.

The remarkable lack of resonance interaction between the naphthalene rings in 3 and 5 can be inferred from the absence of any new absorption band in their UV spectra compared to that of 2-naphthol (8). The formation of the spirocyclic derivative 5 from 1 and 3 is influenced on the one hand by the permissible cyclophosphazene O–P–O bond angle[11] and, on the other hand, by the steric barrier to the restricted rotation in 1,1′-binaphthyl.[15,16] Compromising these two factors results in forming the strained nonplanar structure 5.

The nonplanar conformation of 5 makes it possible to introduce the second 2,2′-dioxy-1,1′-binaphthyl group into the phosphazene ring. The resulting bisspiro derivative, 6, was unambiguously identified. On the other hand, the spatial arrangement of the 1,1′-dioxy-2,2′-binaphthyl unit in 4 hinders the substitution of the remaining chlorine atoms with such additional bulky groups. Thus, reacting 1 and 2 is practically limited to the stage of monospiro derivative formation.

Experimental Section

General Methods. All substitution experiments were carried out under a dry argon atmosphere in a standard glass apparatus with the exclusion of moisture by calcium chloride drying tubes.

Melting points were measured on a Boetius microscope hot stage and are uncorrected. The IR spectra were measured as Nujol or halocarbon mulls on a UR-120 Carl Zeiss Jena spectrophotometer. The UV spectra were recorded with a Specord UV–Vis 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 performed on a JEOL FX-60 spectrometer at 24.3 MHz using 85% H_3PO_4 as an external standard. The mass spectra were recorded on an LKB-9000 mass spectrometer at a 70-eV electron energy and at an ion-source temperature of 290 °C.

TLC was performed on Merck precoated silica gel 60 plates, and pyridine–*m*-toluidine (1:1) reagent[17] was used for visualization of all chlorine-containing cyclophosphazenes.[18] Column chro-

(13) R. M. Silverstein, G. C. Bassler, and C. Morrill, "Spectrometric Identification of Organic Compounds", Wiley, New York, Sydney, and Toronto, 1974, p 36.

(14) Reference 13, pp 250–2.

(15) S. Singh, *Curr. Sci.*, 44, 873 (1975).

(16) J. Hanazaki and H. Akimoto, *J. Am. Chem. Soc.*, 94, 4101 (1972).

(17) V. Novobilsky, V. Kolsky, and W. Wanek, *Z. Anorg. Allg. Chem.*, 423, 273 (1976).

(18) The reagent described in ref 17 was used to visualize spots of chlorophosphazenes $(PNCl_2)_n$ with different ring sizes (n = 3–8). We have found it to form colored complexes with all the chlorine-containing cyclophosphazenes, in particular, with mono- and bisspiro[arylenedioxy] with all the 4, 5, and 6.

matography was done with silica gel (70–230 mesh, product of E. Merck, Darmstadt).

Materials. Hexachlorocyclotriphosphazene (1) was obtained by ammonolysis of phosphorus pentachloride as previously reported[19] and purified by vacuum resublimation at 90–95 °C (0.5 mm); mp 113 °C.

1,1′-Dihydroxy-2,2′-binaphthyl (2) was synthesized and separated according to the method reported by Joffe[20] and recrystallized from benzene; mp 220 °C.

2,2′-Dihydroxy-1,1′-binaphthyl (3) was obtained by oxydation of 2-naphthol with ferric chloride[21] and purified by recrystallization from toluene; mp 219 °C.

Synthesis. (A) 3,3,5,5-Tetrachloro-1,1-(1,1′-dioxy-2,2′-binaphthyl)cyclotriphosphazene (4). A 34.8-g (0.1 mol) sample of hexachlorocyclotriphosphazene (1) and 28.6 g (0.1 mol) of 1,1′-dihydroxy-2,2′-binaphthyl (2) were dissolved on heating in dry benzene (700 mL). Then 50 mL (36.5 g, 0.36 mol) of triethylamine diluted with 50 mL of benzene was added dropwise over a 1-h period to the stirred solution of 1 and 2 at 50 °C. The reaction mixture was refluxed for 3–5 h to complete the reaction. The course of the reaction was followed by TLC analysis of aliquots with hexane–benzene (2:1) solvent, until the disappearance of the spot corresponding to 1. The complete conversion of 1 was then confirmed from the quantity of triethylamine hydrochloride formed in the reaction. The latter was filtered off hot under vacuum and determined by titration with 0.01 N $AgNO_3$. Removal of the solvents from the filtrate left a solid residue, which was washed several times with distilled water to remove traces of the amine hydrochloride, dried, and washed with cold acetone to remove traces of unreacted 2. Pure 4 was obtained by crystallization from benzene–hexane (1:1) to yield 43.7 g (76.3%) of white crystals: mp 310 °C; IR (Nujol mull) 3075 ($C_{Ar}H$), 1600, 1500 (Ar), 1250 (OC_{Ar}), 1205, 1185 (P=N), 1155, 1090 (POC_{Ar}), 950, 900, 840 (Ar), 880 (P=N) cm^{-1}; ^1H NMR ($CDCl_3$) 7.5–7.7 (m, 6 H), 7.8–8.0 (m, 4 H), 8.2–8.4 (m, 2 H) ppm; ^{31}P NMR (see Table I); UV (cyclohexane) λ_{max} 215 nm (ϵ 3.9 × 10^4), 259 (1.06 × 10^5), 272 (3.1 × 10^4), 283 (2.1 × 10^4); mass spectrum (see Table II).

Anal. Calcd for $C_{20}H_{12}O_2Cl_4N_3P_3$: C, 42.80; H, 2.14; Cl, 25.30; N, 7.48; P, 16.30. Found: C, 42.63; H, 2.30; Cl, 25.50; N, 7.38; P, 16.45.

(B) 3,3,5,5-Tetrachloro-1,1-(2,2′-dioxy-1,1′-binaphthyl)cyclotriphosphazene (5). A 34.8-g (0.1 mol) sample of hexachlorocyclophosphazene (1) and 28.6 g (0.1 mol) of 2,2′-dihydroxy-1,1′-binaphthyl (3) were subjected to the same procedure as described above for 4. The benzene-soluble product of the reaction was washed with distilled water and then dried to yield a pale yellow solid (49.2 g, 87.7%). This crude material was purified by column chromatography on silica with hexane–benzene (3:1). When the eluted fractions were allowed to stand overnight, compound 5 crystallized directly in the form of white, needlelike crystals: mp 283 °C; IR (Nujol mull) 3065 ($C_{Ar}H$), 1590, 1510 (Ar), 1260 (OC_{Ar}), 1215, 1190 (P=N), 1160, 1070 (POC_{Ar}), 995, 955, 915, 815 (Ar), 890 (P=N) cm^{-1}; UV (in cyclohexane) λ_{max} 216 nm ϵ 1.20 × 10^5), 263 (7.4 × 10^3), 305 (1.36 × 10^4); ^1H NMR ($CDCl_3$) 7.2–7.6 (m, 8 H), 7.8–8.1 (m, 4 H) ppm; ^{31}P NMR (see Table I); mass spectrum (see Table II).

Anal. Calcd for $C_{20}H_{12}O_2Cl_4N_3P_3$: C, 42.80; H, 2.14; Cl, 25.30; N, 7.48; P, 16.30. Found: C, 42.64; H, 2.72; Cl, 25.20; N, 7.27; P, 16.50.

The precipitate separated by the filtration of the reaction mixture (30.7 g) left a solid residue (3.2 g) after the amine hydrochloride was washed away. This was subsequently extracted with acetone, DMF, and chloroform. The remaining insoluble material (2.5 g, mp 313–320 °C) was found to consist mainly of **5,5-dichloro-1,1:3,3-bis(2,2-dioxy-1,1′-binaphthyl)cyclotriphosphazene (6).**

Analytically pure 6 was isolated chromatographically (0.2 g) from the main solvent-soluble fraction of the reaction products by stripping the chromatography column with benzene solvent: mp 330 °C; IR 3065, 1590, 1510, 1275, 1245, 1205, 1190, 1170, 1155, 1075, 995, 980, 955, 935, 900, 885, 835, 820 cm^{-1} (the assignments are the same as for 5); UV (in cyclohexane) λ_{max} 219 nm (ϵ 2.21 × 10^5), 263 (1.5 × 10^4), 305 (2.8 × 10^4); ^{31}P NMR (see Table I); mass spectrum (70 eV), *m/e* (relative intensity) 773 (M^+, 60.96), 775 ($(M + 2)^+$, 40.96).

Anal. Calcd for $C_{40}H_{24}O_4Cl_2N_3P_3$: C, 61.80; H, 3.09; Cl, 9.17; N, 5.42; P, 12.0. Found: C, 61.30; H, 3.27; Cl, 9.13; N, 5.72; P, 11.83.

(19) S. M. Zhivukhin, V. V. Kireev, V. P. Popilin, and C. S. Kolesnikov, *Zh. Neorg. Khim.*, **14**, 1051 (1969).
(20) J. S. Joffe, *Zh. Obshch. Khim.*, **9**, 1136 (1939).
(21) Z. Dianin, *Ber. Dtsch. Chem. Ges.*, **6**, 1252 (1873).
(22) P. Diehl, E. Fluck, and R. Kosfeld, "NMR—Basic Principles and Progress", Springer-Verlag, Berlin, Heidelberg, and New York, 1971, p 104.

Registry No. 1, 940-71-6; 2, 604-60-4; 3, 602-09-5; 4, 72881-41-5; 5, 72866-26-3; 6, 72866-27-4.

New Synthesis of Diazepam

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An efficient preparation of 7-chloro-1-methyl-3,4-dihydro-1*H*-1,4-benzodiazepine-2,5-dione from 5-chloro-*N*-methylisatoic anhydride and glycine has been devised, and from it, by the action of phenylmagnesium chloride on its *N*-acetyl derivative followed by treatment with hydroxylamine and cleavage of the resulting desacetyl oxime with sodium bisulfite, diazepam has been synthesized. The overall yield is about 50% from 5-chloroisatoic anhydride.

A new synthesis of diazepam has been devised. It depends critically on three new findings.

(1) 3,4-Dihydro-1*H*-1,4-benzodiazepine-2,5-diones, hitherto difficultly accessible,[1] can be made easily and in high yield directly from isatoic anhydrides and glycine. Intermediate in this preparation are *o*-aminohippuric acids, which can be isolated as their difficultly soluble potassium salts or can be cyclized without isolation to the benzo-1,4-diazepine-2,5-diones.

To achieve these yields it is only necessary to add 1 equiv of a weak base (Na_2CO_3 or triethylamine) to convert the glycine into its anion in which the amino group is present

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