Formation of 2,3-Dihydro-1,3,2-benzoxazaphospholes by Cheletropic Reaction of *o*-Quinone Monoimines with Triphenylphosphane. Crystal and Molecular Structures of 2,3-Dihydro-2,2,2-triphenylphenanthro[9,10-*d*]-1,3,2λ^5-oxazaphosphole and 5,7-Di-*tert*-butyl-2,3-dihydro-2,2,2-triphenyl-1,3,2λ^5-benzoxazaphosphole

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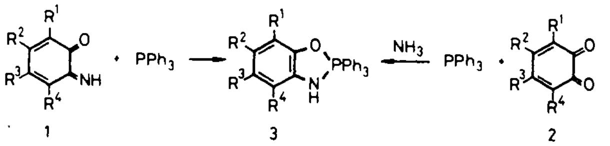
9,10-Phenanthrenequinone monoimine (1c) or 3,5-di-*tert*-butyl-*o*-benzoquinone (2a) in the presence of ammonia undergo cycloaddition with triphenylphosphane to give 2,3-dihydro-1,3,2λ^5-benzoxazaphospholes (3) in good yields. 5,7-Di-*tert*-butyl-2,3-dihydro-2,2,2-triphenyl-1,3,2λ^5-benzoxazaphosphole (3a) shows a tautomeric equilibrium with the iminophosphorane 4a while 2,3-dihydro-2,2,2-triphenylphenanthro[9,10-*d*]-1,3,2λ^5-oxazaphosphole (3c) has a cyclic structure in solution. Both compounds are cyclic in the solid form as confirmed by X-ray structure diffraction studies.

Recently, there has been much interest in the synthesis of five-membered phosphorus-containing heterocycles. Trivalent phosphorus compounds are known as good reaction partners in electrocyclic reactions with conjugated dienes and heterodienes to form phosphole derivatives[1]. Whereas several procedures have been developed for the preparation of five-membered phosphorus heterocycles, access to 2,3-dihydro-1,3,2-benzoxaphospholes is limited to reactions of *o*-aminophenols with halophosphoranes[2] and of 9,10-phenanthrenequinone monoimine with phosphites[3]. In certain cases some (2-hydroxyphenyl)iminophosphoranes undergo cyclization to 2,3-dihydro-1,3,2-benzoxazaphospholes depending on the substituents of the heterocyclic system[4].

Here we describe the synthesis of some 2,3-dihydro-1,3,2-benzoxazaphospholes **3** by a cheletropic reaction of triphenylphosphane with *o*-quinone monoimines **1** or with *o*-quinones **2** and ammonia (eq. 1).

From the series of 3,5-di-*tert*-butyl-*o*-benzoquinone (**2a**), 1,2-naphthoquinone (**2b**), and 9,10-phenanthrenequinone (**2c**) only the latter forms a stable monoimine[5]. 9,10-Phenanthrenequinone monoimine (**1c**) undergoes a facile cheletropic addition reaction by refluxing with triphenylphosphane in acetonitrile under argon or nitrogen to form 2,3-dihydro-2,2,2-triphenylphenanthro[9,10-*d*]-1,3,2λ^5-oxazaphosphole (**3c**, 58%).



(1)

1 3 2

a: $R^1 = R^3 = t\text{-Bu}$; $R^2 = R^4 = H$; b: $R^1R^2 = C_4H_4$, $R^3, R^4 = H$
c: $R^1R^2 = R^3R^4 = C_4H_4$

(2)

3a 4a

The reaction could also be accomplished by starting from the *o*-quinones **2** in the presence of ammonia. The *o*-quinones, pyridine as solvent, liquid ammonia, and triphenylphosphane were placed in a cooled Carius tube or pressure vessel under argon or nitrogen. After heating at 80–90°C for 3 hours, from **2a** and **2c** the 1,3,2λ^5-oxazaphospholes **3a** and **3c** were obtained in good yields.

With 1,2-naphthoquinone (**2b**) only a black residue resulted, from which **3b** could not be isolated despite much efforts. This is probably a polymer and its formation suppresses the ring-forming reaction. The compounds **3a** and **3c** are stable under the exclusion of moisture and air, although **3c** darkens somewhat in several weeks. **3c** is sensitive towards oxygen while **3a** can be stored in air for some weeks.

The IR spectra of **3a** and **3c** show ν(NH) frequencies at 3433 and 3383 cm^{-1}, respectively, confirming the existence of the five-membered rings.

The ^1H- and ^{31}P-NMR spectra of **3a** indicate, as shown also previously[4], a tautomeric equilibrium (eq. 2) between the 2,3-dihydro-1,3,2λ^5-benzoxazaphosphole **3a** and the iminophosphorane **4a**. The equilibrium (eq. 2) is solvent-dependent. In C_6D_6 the ratio **3a**:**4a** is 75:25, and in CD_2Cl_2 50:50. The more polar solvent favors the iminophosphorane form. **3c** gives only one signal at $\delta = -31.4$

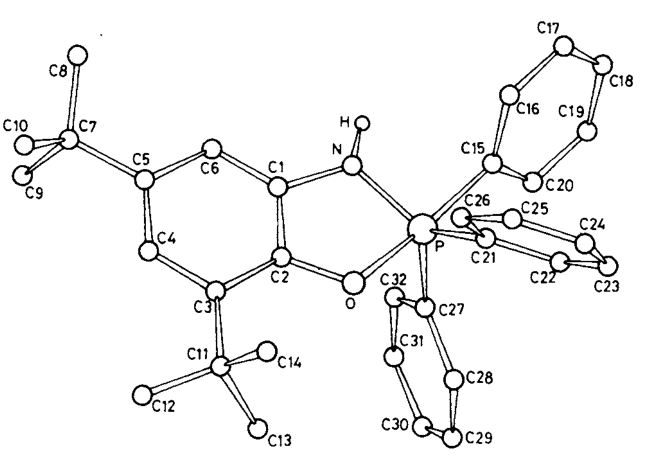


Fig. 1. Molecular structure of **3a** with the numbering of atoms used in the crystal structure analysis

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in C_6D_6 and −28.0 in CD_2Cl_2 in its ^{31}P-NMR spectrum suggesting the nonexistence of the equilibrium (eq. 2) in that case, and confirming its cyclic structure in solution. In order to disclose their structure in the solid state we undertook an X-ray diffraction study of the compounds **3a** and **3c**.

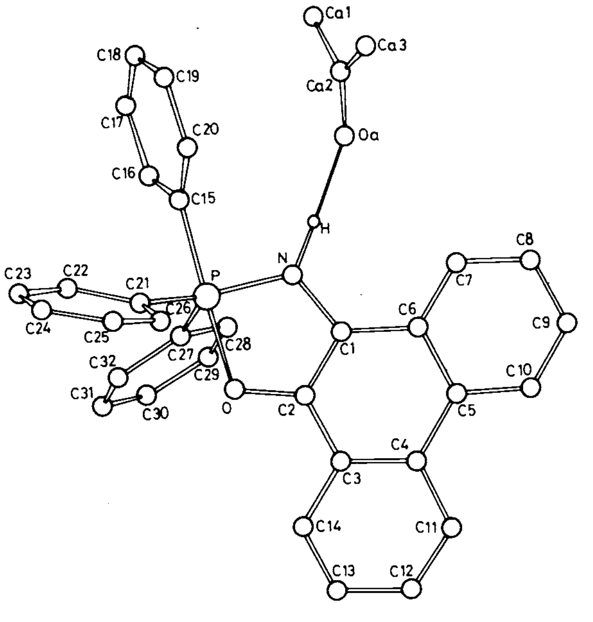

Fig. 2. Molecular structure of **3c** with the numbering of atoms used in the crystal structure analysis

The molecular structures of **3a** and **3c** with the numbering of atoms are depicted in Fig. 1 and 2. Relevant bond distances and angles are given in Tables 1 and 2. The phosphorus atom is five-coordinate in both compounds and sits in the middle of a distorted trigonal bipyramid. The more electronegative atom (oxygen) of the five-membered ring adopts one of the apical positions while the nitrogen atom and two phenyl rings are the equatorial ligands. The phosphorus atom deviates by 0.1399(6) (**3c**) and 0.1057(8) Å (**3a**) from the equatorial plane of the N, C21, and C27 atoms in the direction of C15. The presence of the bulkyl phenyl groups makes the coordination sphere of phosphorus rather crowded.

Table 1. Representative bond distances [Å] and bond angles [°] for **3a**

P-O	1.813(2)	O-P-N	85.2(2)
P-N	1.677(2)	O-P-C15	173.5(2)
P-C15	1.895(2)	O-P-C21	86.5(2)
P-C21	1.831(3)	O-P-C27	88.2(2)
P-C27	1.810(3)	N-P-C15	91.0(2)
O-C2	1.354(3)	N-P-C21	126.6(2)
N-C1	1.408(3)	N-P-C27	117.0(2)
		C15-P-C21	91.6(2)
		C15-P-C27	98.1(2)
		C21-P-C27	115.3(2)
		P-O-C2	113.9(2)
		P-N-C1	117.9(3)

The *ipso* carbon atoms of the equatorial phenyl rings form angles larger than 90° (**3c**: 93 and 98°, **3a**: 92 and 98°) with the apical C(15) atoms. The bond angles formed by the equatorial ligands show significant deviations from the ideal 120° (**3c**: 117, 117, and 124°; **3a**: 115, 117, and 127°). There is also a significant difference between the two equatorial P−C bond lengths [**3c**: 1.831(2) and 1.814(2) Å, Δ = 0.017 Å; **3a**: 1.831(3) and 1.810(3) Å, Δ = 0.021 Å]. The *ipso* carbon atoms of the C(27)···C(32) phenyl rings form the shorter P−C bond distances in both cases, and these phenyl rings are fairly coplanar with the planes of the equatorial atoms [dihedral angles are 14.12(8)° (**3c**) and 23.0(1)° (**3a**)]. The apical P−C bond [**3c**: 1.882(1) Å, **3a**: 1.895(2) Å] is much longer than the equatorial one and is slightly longer in **3a** than in **3c** (Δ = 0.013 Å).

Table 2. Representative bond distances [Å] and bond angles [°] for **3c**

P-O	1.879(1)	O-P-N	85.1(1)
P-N	1.678(2)	O-P-C15	175.7(1)
P-C15	1.882(1)	O-P-C21	85.2(1)
P-C21	1.831(2)	O-P-C27	86.1(1)
P-C27	1.814(2)	N-P-C15	92.9(1)
O-C2	1.332(2)	N-P-C21	124.3(1)
N-C1	1.410(2)	N-P-C27	117.4(1)
		C15-P-C21	92.9(1)
		C15-P-C27	98.1(1)
		C21-P-C27	116.5(1)
		P-O-C2	111.8(2)
		P-N-C1	117.3(2)

The P−O bond lengths are inversely related to the apical P−C bonds: the P−O bond observed in **3c** is longer [1.879(1) Å] than in **3a** [1.813(2) Å, Δ = 0.066 Å]. Both of them are, however, longer than in the related dioxazaphospholane modifications[6,7] (1.76 and 1.75 Å). While a considerable π bonding was claimed in equatorial P−O bonds of these compounds with the participation of the phosphorus 3d orbitals, the π character is very small or zero in the apical bonds. The P−O bond with 1.76 Å corresponds to a single bond as predicted by Cruickshank[8]. The P−O bonds in **3c** and **3a** are longer by 0.05−0.12 Å, which must be due to a rather weak interaction. The O−C distances [**3c**: 1.332(2), **3a**: 1.354(3) Å] are identical with those in the dioxaphospholene modifications (1.32 and 1.35 Å) within experimental error. This bond is slightly affected by the extent of the P−O interaction. In compound **3a**, a shorter P−O interaction is observed with a longer C−O bond. The strained five-membered ring is fused with an aromatic ring, therefore steric factors may also play an important role in the molecular geometry.

The acetone molecule in the lattice of **3c** is linked to the phospholene molecule by an N−H···O hydrogen bond [N−H(N): 1.058; N···O(a): 3.027(2); H(N)···O(a): 2.019 Å; N−H(N)···O(a): 158.0°].

We thank Dr. *G. Szalontai* for help and recording the NMR spectra.

Experimental

All experiments were carried out under argon or nitrogen using Schlenk-type inert gas techniques. The solvents were dried and degassed in the usual manner.

9,10-Phenanthrenequinone monoimine (**1c**) was prepared according to the literature[5]. − ^{1}H and ^{31}P NMR: Varian CFT 20. − IR: Specord 75 IR. − MS: Jeol MS 01 SG 2.

X-Ray Structure Analysis of **3a** *and* **3c**[9]: The determination of the unit cell parameters and the collection of the intensity data were performed on an Enraf-Nonius CAD 4 four-circle computer-controlled diffractometer.

Compound **3c** crystallized from acetone containing equimolar amounts of 9,10-phenanthrenequinone and triphenylphosphane in the space group $P2_1/c$ with cell dimensions $a = 9.889(1)$, $b = 32.206(2)$, $c = 10.094(1)$ Å, $\beta = 117.75(1)°$, $V = 2845.0$ Å^3, $Z = 4$, $D_{calc} = 1.23$ g cm^{-3}, for $\pm h, +k, +l$ in the range $3.0 < 2\Theta < 150°$. The structure was solved by direct methods (MULTAN)[10] using 6258 independent reflexions and refined with the use of 5701 intensities $[I \geq 3\Theta(I)]$ to $R = 0.049$ and $R_w = 0.047$. The acetone molecule and H(N) were located in a difference map.

Table 3. Positional parameters and their estimated standard deviations for **3c**

Atom	x/a	y/b	z/c	8(eq)
P	0.93020(5)	0.09598(1)	0.13781(5)	2.92(1)
O	0.7314(1)	0.11795(4)	0.0522(1)	3.76(3)
N	0.9722(1)	0.13345(5)	0.2666(1)	3.42(4)
C(1)	0.8494(2)	0.15682(6)	0.2616(2)	2.65(4)
C(2)	0.7170(2)	0.14693(6)	0.1389(2)	2.85(4)
C(3)	0.5758(2)	0.16680(6)	0.1047(2)	3.03(5)
C(4)	0.5758(2)	0.19808(7)	0.2025(2)	3.21(5)
C(5)	0.7164(2)	0.20928(6)	0.3325(2)	2.78(5)
C(6)	0.8568(2)	0.18860(6)	0.3631(2)	2.73(4)
C(7)	0.9946(2)	0.20033(7)	0.4876(2)	3.39(5)
C(8)	0.9962(3)	0.23148(7)	0.5819(2)	4.29(6)
C(9)	0.8590(3)	0.25130(8)	0.5528(2)	4.15(7)
C(10)	0.7256(3)	0.24059(7)	0.4334(2)	3.83(6)
C(11)	0.4329(2)	0.21712(9)	0.1655(3)	4.57(7)
C(12)	0.3033(3)	0.2058(1)	0.0400(3)	6.11(9)
C(13)	0.3050(2)	0.1750(1)	-0.0550(3)	5.85(9)
C(14)	0.4400(2)	0.15565(8)	-0.0232(2)	4.27(6)
C(15)	1.1343(2)	0.07781(6)	0.2211(2)	3.07(4)
C(16)	1.1846(2)	0.03836(7)	0.2761(2)	3.58(5)
C(17)	1.3342(2)	0.02612(8)	0.3248(2)	4.76(6)
C(18)	1.4379(2)	0.0533(1)	0.3197(2)	5.39(7)
C(19)	1.3927(2)	0.0927(1)	0.2667(2)	4.78(7)
C(20)	1.2428(2)	0.10492(8)	0.2176(2)	4.09(6)
C(21)	0.9174(2)	0.10399(6)	-0.0473(2)	3.05(4)
C(22)	0.9513(2)	0.07205(7)	-0.1194(2)	3.41(5)
C(23)	0.9426(2)	0.07852(8)	-0.2590(2)	4.11(6)
C(24)	0.9066(2)	0.11703(9)	-0.3235(2)	4.67(7)
C(25)	0.8777(2)	0.14917(8)	-0.2527(2)	4.60(6)
C(26)	0.8811(2)	0.14292(7)	-0.1149(2)	3.79(5)
C(27)	0.8463(2)	0.04854(6)	0.1636(2)	3.01(4)
C(28)	0.8655(2)	0.03963(8)	0.3059(2)	3.93(6)
C(30)	0.7227(3)	-0.02270(9)	0.2172(3)	4.89(8)
C(31)	0.7009(3)	-0.01399(9)	0.0750(3)	5.15(7)
C(32)	0.7615(2)	0.02154(7)	0.0483(2)	3.92(5)
O(a)	1.2644(2)	0.12266(8)	0.5566(2)	7.41(7)
C(a1)	1.5144(3)	0.0963(1)	0.6680(3)	5.81(8)
C(a2)	1.3986(3)	0.1290(1)	0.5946(2)	5.84(8)
C(a3)	1.4516(4)	0.1700(1)	0.5703(5)	9.4(1)

Compound **3a** crystallized from toluene/hexane in the space group $P2_1/n$ with cell dimensions $a = 11.919(2)$, $b = 9.700(2)$, $c = 23.487(4)$ Å, $\beta = 90(1)°$, $V = 2715.1$ Å^3, $Z = 4$, $D_{calc} = 1.18$ g cm^{-3}, for $+h, +k, \pm l$ in the range $3.0 < 2\Theta < 150°$. The structure was solved by direct methods (MULTAN)[10] using 5765 independent reflexions and refined with the use of 3257 intensities $[I \geq 5\sigma(I)]$ to $R = 0.038$ and $R_w = 0.038$.

2,3-Dihydro-2,2,2-triphenylphenanthro[9,10-d]-1,3,2λ⁵-oxazaphosphole (**3c**)

Method a: A solution of 9,10-phenanthrenequinone monoimine (**1c**) (5.18 g, 25 mmol), triphenylphosphane (6.56 g, 25 mmol), and acetonitrile (200 ml) was refluxed under argon for 2 h. After cooling pale yellow crystals deposited, which were filtered off and dried in vacuo to give **3c**. Yield 6.80 g (58%), m.p. 153–155°C (benzene/hexane). – IR (KBr): ν = 3383 cm^{-1}, 3050, 1583, 1434, 1396, 1363, 1350, 1286, 1203, 1136, 1103, 763, 747, 763, 717, 694, 537, 523. – MS (70 eV): *m/z* (%) = 469 (M$^+$, 30), 392(8), 277(22), 262(100), 183 (35), 108(20). – ^{1}H NMR (CDCl$_3$): δ = 7.3 (br). – ^{31}P NMR (C$_6$D$_6$): δ = −31.4; (CD$_2$Cl$_2$) −28.0.

$C_{32}H_{24}NOP$ (469.5) Calcd. C 81.86 H 5.15 N 2.98
Found C 82.11 H 5.01 N 2.97

Table 4. Positional parameters and their estimated standard deviations for **3a**

Atom	x/a	y/b	z/c	B(eq)
P	0.68709(5)	0.20319(7)	0.97042(2)	2.82(2)
O	0.7390(1)	0.1177(1)	0.90747(6)	3.08(6)
N	0.5604(1)	0.1871(2)	0.93908(8)	3.20(8)
C(1)	0.5557(1)	0.1466(2)	0.88153(9)	2.81(9)
C(2)	0.4637(1)	0.1382(2)	0.8458(1)	3.2(1)
C(3)	0.4783(2)	0.0915(2)	0.7900(1)	2.95(9)
C(4)	0.5867(2)	0.0582(2)	0.77342(9)	2.83(9)
C(5)	0.6814(1)	0.0640(2)	0.80914(9)	2.51(8)
C(6)	0.6626(1)	0.1091(2)	0.86431(9)	2.62(8)
C(7)	0.3793(2)	0.0773(2)	0.7483(1)	3.5(1)
C(8)	0.2675(2)	0.0745(4)	0.7777(1)	6.7(1)
C(9)	0.3799(2)	0.1955(4)	0.7062(1)	7.5(1)
C(10)	0.3880(3)	-0.0581(4)	0.7149(1)	7.7(1)
C(11)	0.7976(1)	0.0146(2)	0.79130(9)	2.73(9)
C(12)	0.8007(2)	-0.0274(3)	0.7287(1)	3.9(1)
C(13)	0.8859(2)	0.1281(3)	0.8008(1)	3.8(1)
C(14)	0.8289(2)	-0.1114(2)	0.8274(1)	4.3(1)
C(15)	0.6217(1)	0.2755(2)	1.03711(9)	2.98(9)
C(16)	0.5512(2)	0.1895(3)	1.0678(1)	3.9(1)
C(17)	0.5067(2)	0.2290(3)	1.1193(1)	4.4(1)
C(18)	0.5314(2)	0.3552(3)	1.1417(1)	4.6(1)
C(19)	0.5998(2)	0.4434(3)	1.1126(1)	4.6(1)
C(20)	0.6447(2)	0.4043(2)	1.0608(1)	3.8(1)
C(21)	0.7624(2)	0.0710(2)	1.01149(9)	3.06(9)
C(22)	0.8313(2)	0.1075(3)	1.0571(1)	4.1(1)
C(23)	0.8842(2)	0.0082(3)	1.0697(1)	5.0(1)
C(24)	0.8657(2)	-0.1288(3)	1.0789(1)	5.5(1)
C(25)	0.7967(2)	-0.1666(3)	1.0346(1)	5.5(1)
C(26)	0.7467(2)	-0.0676(3)	1.0001(1)	4.2(1)
C(27)	0.7696(2)	0.3524(2)	0.95127(9)	3.02(9)
C(28)	0.8861(2)	0.3502(3)	0.9517(1)	4.0(1)
C(29)	0.9452(2)	0.4657(3)	0.9351(1)	4.9(1)
C(30)	0.8891(2)	0.5828(3)	0.9179(1)	5.1(1)
C(31)	0.7737(2)	0.5856(3)	0.9166(1)	4.7(1)
C(32)	0.7146(2)	0.4709(2)	0.9329(1)	3.8(1)

Method b: 9,10-Phenanthrenequinone (**2c**) (0.52 g, 2.5 mmol), triphenylphosphane (0.66 g, 2.5 mmol), pyridine (5 ml), and liquid ammonia (5 ml) were placed in a cooled Carius tube under argon. It was heated at 80–90°C for 3 h. After cooling volatile components were removed in vacuo, and the residue was treated with ether and ethanol to yield pale yellow crystals of **3c**. Yield 0.64 g (55%).

5,7-Di-tert-butyl-2,3-dihydro-2,2,2-triphenyl-1,3,2λ⁵-benzoxazaphosphole (**3a**): According to method b starting from 2.5 mmol of 3,5-di-*tert*-butyl-*o*-benzoquinone (**2a**) and triphenylphosphane; yield 1.0 g (83%), m.p. 160–163°C (MeOH). – IR (KBr): ν = 3433 cm^{-1}, 3057, 2947, 2900, 2860, 1584, 1483, 1432, 1387, 1360, 1340, 1300, 1254, 1214, 1114, 1090, 1030, 994, 880, 854, 750, 720, 700, 680, 654, 567, 543, 514, 472. – MS (70 eV): *m/z* (%) 481 (M$^+$, 100), 466(50), 404(40), 296(12), 262(30), 108(17). – ^{1}H NMR (CD$_2$Cl$_2$, 80 MHz): δ = 0.97 (s), 1.26 (s), 1.40 (s), 7.1–7.7 (br). – ^{31}P-NMR (C$_6$D$_6$): δ = 7.8, −48.0; (CD$_2$Cl$_2$) 9.5, −46.3.

$C_{32}H_{36}NOP$ (481.6) Calcd. C 79.80 H 7.54 N 2.91
Found C 79.92 H 7.52 N 2.95

2,3-Dihydro-2,2,2-triphenylnaphtho[2,1-d]-1,3,2λ⁵-oxazaphosphole (**3b**): According to method b only a black residue could be obtained. All efforts to isolate **3b** failed.

CAS Registry Numbers

1c: 3942-85-6 / **2a**: 115420-84-3 / **2b**: 524-42-5 / **2c**: 84-11-7 / **3a**: 115509-24-5 / **3b**: 115420-83-2 / **3c**: 115420-82-1 / **4a**: 36050-67-6 / PPh$_3$: 603-35-0

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