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Bromination Regiochemistry of 4-Phenyl-2,7-dichloro-2*H*-chryseno-[6,5-*e*][1,2]phosphinine 2-Oxide

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Abstract—Regioselective bromination of 4-phenyl-2,7-dichloro-2*H*-chryseno[6,5-*e*][1,2]phosphinine 2-oxide proceeded in the position *3* with the formation of 3-bromo-4-phenyl-2,7-dichloro-2*H*-chryseno[6,5-*e*][1,2] phosphinine 2-oxide; the structure of its 2-*tert*-butylamino derivative was established by XRD analysis and correlation spectroscopy.

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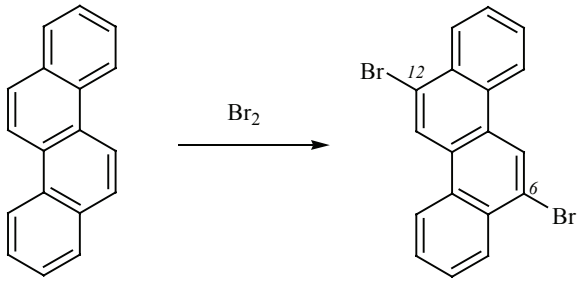
Halogenation of aromatic compounds, including the polyfused arenes, is widely used in the organic synthesis. Haloarenes are successfully utilized in versatile research, particularly in cross-coupling reactions, as show the numerous publications concerning this topic. However the problem of the halogenation regioselectivity still remains urgent, and it is especially complex for polycyclic systems like chrysene and its derivatives whose properties [1–7] and biological activity [8–11] are subjected to intense investigation.

Nowadays several publications concern the chrysene bromination; the commonly used reagents are *N*-bromosuccinimide [12] or bromine [13–21]. The application to the synthesis of dibromo derivatives of a system aluminum oxide–$CuBr_2$ was also described [22]. All these data indicate two possible reaction paths: monohalogenation into position *6* or at once into positions *6* and *12*. This fact may be explained if the chrysene would be represented as two fused naphthalene fragments with two activated *peri*-positions (Scheme 1).

The regioselectivity of chrysene bromination depends both on tthe solvent and on the reaction conditions: The reaction of chrysene with bromine in nitrobenzene at room temperature leads to the formation of 6-bromochrysene in 84% yield and of trace amounts of the dibromo derivative [21]; the replacement of the solvent for more polar carbon disulfide and heating at 40°C excludes the formation of the dibromination product at a slight reduction of the monobrominated compound yield [13–15]. At the same time the use of the two-fold or greater excess of bromine in *sym*-tetrachloroethane [16], acetic acid [17], carbon disulfide [18], or nitrobenzene [19, 20] at the boiling temperature of the solvent made it possible to obtain 6,12-dibromochrysene in a pure state.

We studied the bromination of 4-phenyl-2,7-dichloro-2*H*-chryseno[6,5-*e*][1,2]phosphinine 2-oxide **(II)**, the product of the cascade reaction of chrysenequinone (**I**) with phosphorus trichloride in the presence of phenylacetylene [23]. Compound **II** contains a chrysene fragment fused to oxaphosphinine heterocycle; its reaction with a slight excess of bromine in chloroform at room temperature afforded solely product **III** of the regioselective bromination in the position *3* of the heterocycle

Scheme 1.

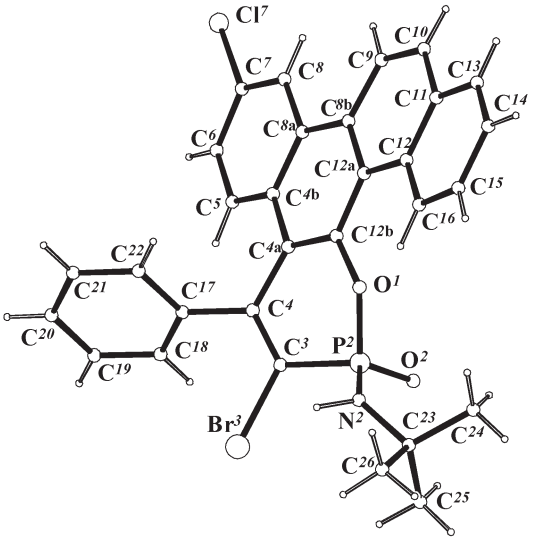


(Scheme 2). As a result of this conversion the signal of the phosphorus atom in the ^{31}P NMR spectrum of the initial heterocycle **II** (δ, 16.4 ppm, $^{2}J_{PCH}$ 28.0 Hz) transforms into a singlet (11.4 ppm). The arylene fragment does not undergo the halogenation**.**

3-Bromo-4-phenyl-2,7-dichloro-2*H*-chryseno[6,5-*e*][1,2]phosphinine 2-oxide (**III**) by reaction with *tert*-butylamine was converted into the corresponding cyclic amide **IV** that after keeping in air in dioxane solution suffered a partial hydrolysis at the P–N bond retaining the heterocycle and forming salt **V** (Scheme 3).

The structure of compound **IV** was established from ^{1}H and ^{31}P NMR spectra and also by XRD analysis of a single crystal obtained by slow evaporation of the solvent from the dioxane solution of substance **IV** (see the figure). The conformation of the heterocycle is a distorted *boat*, fragments $O^{1}C^{12b}C^{4a}C^{4}$ and $P^{2}C^{3}C^{4}C^{4a}$ are coplanar in the limits of 0.052(4), 0.001(3), 0.023(4) Å, atoms C^{3}, P^{2} and O^{1}, C^{12b} deviate from the plane to the same side, but to different distances. The dihedral angle between the planes is 17.9(2)°. The phosphoryl group is situated in the axial position, the amino group, the equatorial. The phenyl substituent at the atom C^{4} is inclined to the double $C^{3}=C^{4}$ bond by an angle 60.8(5)°. The chrysene fragment is slightly twisted, the dihedral angle between flat benzo fragments and flat naphtho fragment is 7.3(2)°. The presence of the bromine atom in the position *3* does not affect the torsion of the chrysene part which practically does not differ from that found in the structure **II** [23].

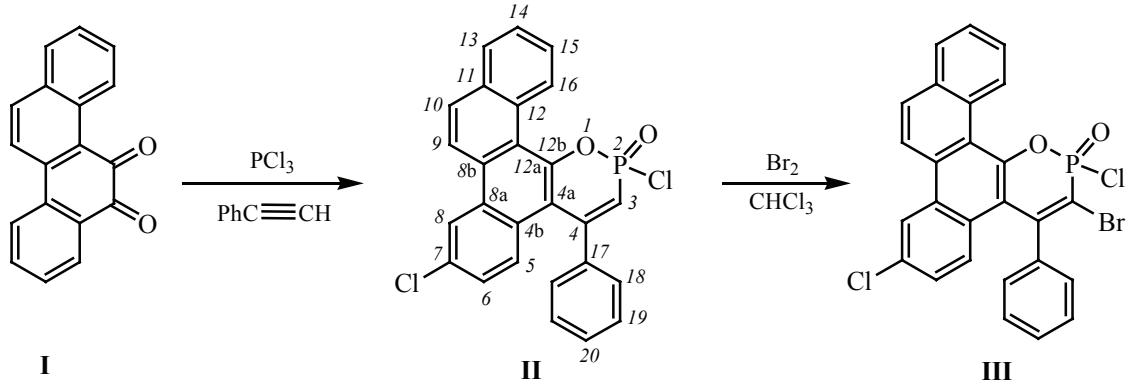
The structure of the product of hydrolysis of cyclic amide **IV**, ammonium salt **V**, was established from ^{1}H, ^{13}C, $^{13}C–\{^{1}H\}$ NMR spectra. The parameters of the carbon spectra are listed in the table. The application of the methods of the correlation spectroscopy $^{1}H–^{13}C$ HSQC and $^{1}H–^{13}C$ HMBC made it possible to perform the complete interpretation of the carbon spectra.



The geometry of the molecule of compound **IV** in the crystal and numeration of atoms (one of the two independent molecules is shown). Selected bond lengths, bond and torsion angles are as follows: $Br^{3}–C^{3}$ 1.890(3), $P^{2}–O^{2}$ 1.455(3), $P^{2}–O^{1}$ 1.607(2), $P^{2}–N^{2}$ 1.614(3), $P^{2}–C^{3}$ 1.776(4), $Cl^{7}–C^{7}$ 1.735(4), $O^{1}–C^{12b}$ 1.371(4), $N^{2}–C^{23}$ 1.486(4), $C^{4a}–C^{12b}$ 1.377(5), $C^{4a}–C^{4b}$ 1.443(5), $C^{4a}–C^{4}$ 1.491(5), $C^{8b}–C^{12a}$ 1.407(5), $C^{8b}–C^{9}$ 1.430(5), $C^{8a}–C^{8b}$ 1.450(5), $C^{12a}–C^{12b}$ 1.434(5), $C^{8a}–C^{4b}$ 1.414(5), $C^{8a}–C^{8}$ 1.427(5), $C^{8}–C^{7}$ 1.362(5), $C^{12a}–C^{12}$ 1.466(5), $C^{4b}–C^{5}$ 1.409(5) Å; $O^{2}P^{2}O^{1}$ 115.2(1), $O^{2}P^{2}N^{2}$ 115.6(2), $O^{1}P^{2}N^{2}$ 101.3(2), $O^{2}P^{2}C^{3}$ 115.2(2), $O^{1}P^{2}C^{3}$ 97.8(2), $N^{2}P^{2}C^{3}$ 109.6(2), $O^{2}P^{2}N^{2}C^{23}$ 6.7(4), $O^{1}P^{2}C^{3}Br^{3}$ –148.1(2), $O^{1}P^{2}C^{3}C^{4}$ 28.0(3), $O^{2}P^{2}C^{3}Br^{3}$ 89.2(2), $O^{2}P^{2}C^{3}C^{4}$ –94.7(3), $C^{3}C^{4}C^{4a}C^{4b}$ 158.4(3) deg.

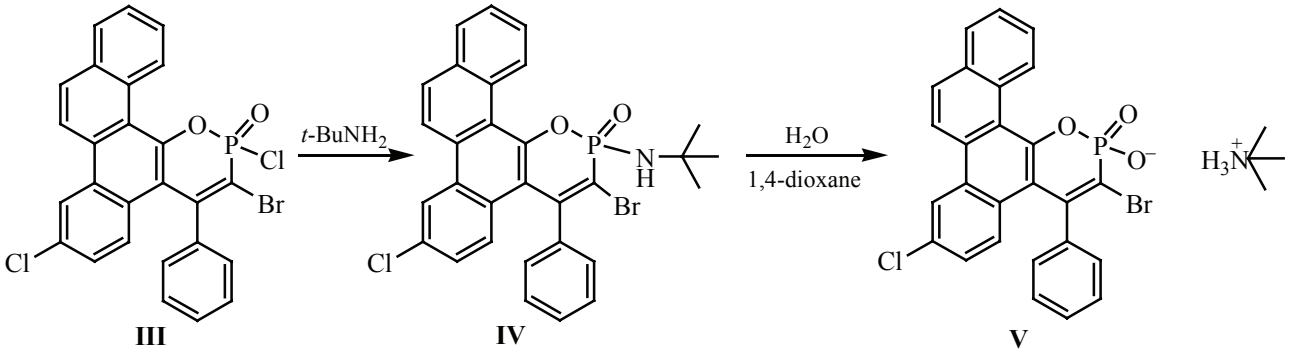
Hence the bromination of a complex polycyclic phosphorus heterocycle, 4-phenyl-2,7-dichloro-2*H*-chryseno[6,5-*e*][1,2]phosphinine 2-oxide, proceeds regioselectively in the position *3* of the heterocycle though

Scheme 2.



I **II** **III**

Scheme 3.



III **IV** **V**

in the arylene fragment activated positions *6* and *12* are present.

EXPERIMENTAL

IR spectra were recorded on a spectrometer Bruker Vector-22 from mulls of compounds in mineral oil. ^{1}H and ^{13}C NMR spectra were registered on a spectrometer Bruker Avance-400 [400 (^{1}H), 100.6 MHz (^{13}C)], ^{31}P NMR spectra, on a spectrometer Bruker CXP-100 (36.48 MHz) in DMSO-d_6. The chemical shifts are reported with respect to the residual signals of the deuterated solvent. The solvents before use were purified an dried by standard procedures. Melting points were measured on an instrument SMP10 Stuart, elemental analysis was carried out on an analyzer CHNS-3. Chrysene quinone (**I**) was obtained by method [24].

***tert*-Butylammonium 3-bromo-4-phenyl-2,7-dichloro-2*H*-chryseno[6,5-*e*][1,2]phosphinin-2-olate 2-oxide (V)**. To a slurry of 0.63 g (1.40 mmol) of compound **II** in 15 mL of dry chloroform at 25°C was added dropwise in an atmosphere of dry argon 0.08 mL (1.50 mmol) of bromine; hydrogen bromide liberated, the precipitate dissolved. On the completion of bromine addition the reaction mixture was left standing at room temperature for 8 h. Through the solution argon was bubbled for 30 min to remove the residue of hydrogen bromide, 0.44 mL (4.20 mmol) of *tert*-butylamine was added, and the reaction mixture was heated at boiling for 2 h. On cooling the separated *tert*-butylammonium chloride was filtered off, the filtrate was evaporated in a vacuum (12 mm Hg). The white powder was treated with 5 mL of dioxane, the precipitate was filtered off and dried in a vacuum (12 mm Hg). Yield 0.3 g (40%), light brown powder, mp 243–245°C. IR spectrum, ν, cm^{-1}: 3177 (N–H), 1600 (C=C), 1228 (P=O). ^{1}H NMR spectrum, δ, ppm (*J,* Hz): 1.23 s (9H, CH_3), 7.15 d.d (1H, H*6*, $^3J_{HCCH}$ 9.2, $^4J_{HCCCH}$ 1.9), 7.19–7.21 m (2H, H*18*), 7.31–7.34 m (3H, H*19*, H*20*), 7.39 d (1H, H*5*, $^3J_{HCCH}$ 9.2), 7.70–7.77 m (2H, H*14*, H*15*), 8.08 br.s (3H, N^+H_3), 8.13–8.15 m (1H, H*13*), 8.19 d (1H, H*10*, $^3J_{HCCH}$ 9.2), 8.85 d (1H, H*9*, $^3J_{HCCH}$ 9.2), 8.86 d (1H, H*8*, $^4J_{HCCCH}$ 2.2), 9.97 m (1H, H*16*). ^{31}P NMR spectrum, δ, ppm: –7.7 (s). Found, %: C 60.49; H 4.30; N 2.25. $C_{30}H_{26}BrClNO_3P$. Calculated, %: C 60.57; H 4.41; N 2.35.

***N*-*tert*-Butyl-3-bromo-4-phenyl-2,7-dichloro-2*H*-chryseno[6,5-*e*][1,2]phosphinin-2-amine 2-oxide (IV)** was obtained as light-yellow crystals after keeping for two days the filtrate after the separation of compound **V**. Yield 0.46 g (55%), mp 287–290°C. IR spectrum, ν, cm^{-1}: 2923–3200 (N–H), 1614 (C=C), 1231 (P=O). ^{1}H NMR spectrum, δ, ppm (*J,* Hz): 1.28 s (3H, CH_3), 5.97 d (1H, NH, $^2J_{PNH}$ 12.2), 7.21 d.d (1H, $^3J_{HCCH}$ 9.5, $^4J_{HCCCH}$ 2.2), 7.26 m (2H), 7.41 m (4H), 7.77–7.81 m (2H), 8.20 d.d (1H, $^3J_{HCCH}$ 9.5, $^4J_{HCCCH}$ 2.3), 8.28 d (1H, $^3J_{HCCH}$ 9.0), 8.92 d (1H, $^3J_{HCCH}$ 9.5), 8.93 s (1H), 9.80 d (1H, $^3J_{HCCH}$ 8.1). ^{13}C NMR spectrum was not recorded because of the low solubility of compound **IV** in organic solvents. ^{31}P NMR spectrum, δ, ppm: 5.1 d ($^2J_{PNH}$ 12.2 Hz). Found, %: C 62.30; H 4.09; N 2.38. $C_{30}H_{24}BrClNO_2P$. Calculated, %: C 62.46; H 4.19; N 2.43.

XRD analysis was carried out on a diffractometer Smart Apex II CCD (λMoK_α 0.71073 Å). The structure was solved by the direct method using SIR program [25] and was refined first in isotropic and then in anisotropic approximation along software SHELXL97 [26] and WinGX [27].

Compound **IV**. $C_{30}H_{24}BrClNO_2P$. *M* 576.82. Crystals triclinic, space group *P*-1, *a* 12.7470(13), *b* 12.8340(13),

Parameters of ^{13}C NMR spectra[a] of *tert*-butylammonium 3-bromo-4-phenyl-2,7-dichloro-2*H*-chryseno[6,5-*e*]-[1,2]phosphinin-2-olate 2-oxide (**V**) in DMSO-d_6

Atom	δ, ppm (*J*, Hz)[b]	Cross-peaks in spectrum HMBC	Cross-peaks in spectrum HSQC
C^{3}	121.89 d (d) ($^1J_{PC}$ 180.5)	–	–
C^{4}	142.69 br.d.t (d) ($^2J_{PCC}$ 8.4, $^2J_{HCCC}$ 3.6–4.0)	H^{18}	–
C^{4a}	119.30 d.d (d) ($^3J_{PCCC}$ 12.5, $^3J_{HCCC}$ 3.3)	H^{5}	–
C^{4b}	128.41 br.d.d (s) ($^3J_{HC^6CC}$ 7.2 , $^3J_{HC^8CC}$ 7.2)	H^{6}, H^{5}, H^{8}	–
C^{5}	128.99 d (s) ($^1J_{HC}$ 165.8)	H^{6}	H^{5}
C^{6}	126.16 d.d (s) ($^1J_{HC}$ 167.0, $^3J_{HCCC}$ 5.3)	H^{5}, H^{8}	H^{6}
C^{7}	130.35 d.d.d (s) ($^3J_{HC^5CC}$ 8.0, $^2J_{HCC}$ 2.7-3.1, $^2J_{HCC}$ 1.6–2.0)	H^{6}, H^{5}, H^{8}	–
C^{8}	123.51 d.d (s) ($^1J_{HC}$ 163.7, $^3J_{HCCC}$ 4.8)	H^{6}	H^{8}
C^{8a}	128.89 d.d (s) ($^3J_{HC^5CC}$ 7.2, $^3J_{HC^9CC}$ 3.3)	H^{5}, H^{9}	–
C^{8b}	129.83 m (s) (the signal overlapped with components of signals C^{18} and C^{16})	H^{10}, H^{8}	–
C^{9}	121.31 d (s) ($^1J_{HC}$ 162.2)	H^{10}	H^{9}
C^{10}	130.32 br.d.d (s) ($^1J_{HC}$ 161.9, $^3J_{HC^{13}CC}$ 5.6)	H^{13}, H^{9}	H^{10}
C^{11}	133.66 br.d.d.d (s) ($^3J_{HC^9CC}$ 7.3–7.5, $^3J_{HC^{14}CC}$ 7.3–7.5, $^3J_{HC^{16}CC}$ 6.0–6.3)	H^{14}, H^{13}, H^{10}, H^{9}, H^{16}	–
C^{12}	129.98 m (s)	H^{16}, H^{13}, H^{10}, H^{15}	–
C^{12a}	122.12 m (s) ($^3J_{POCC}$ 3.7)	H^{16}, H^{9}	–
C^{12b}	150.75 br.d (d) ($^2J_{POC}$ 8.4)	H^{9}	–
C^{13}	129.03 br.d.d (s) ($^1J_{HC}$ 161.0, $^3J_{HC^{15}CC}$ 7.2)	H^{10}, H^{15}, H^{14}	H^{13}
C^{14}	127.31 d.d (s) ($^1J_{HC}$ 161.6, $^3J_{HC^{16}CC}$ 8.7)	H^{16}, H^{13}	H^{14}
C^{15}	127.35 d.d (s) ($^1J_{HC}$ 160.6, $^3J_{HC^{13}CC}$ 9.0)	H^{16}, H^{13}	H^{15}
C^{16}	129.03 d.d (s) (the signal overlapped with components of signals C^{18} andC^{19})	H^{14}, H^{15}	H^{16}
C^{17}	140.88 d.t (d), ($^3J_{PCCC}$ 11.0, $^3J_{HC^{19}CC}$ 7.0–8.0)	H^{18}, H^{19}	H^{17}
C^{18}	130.18 d.d.d (s) ($^1J_{HC}$ 160.1, $^3J_{HCCC}$ 6.0–7.0, $^3J_{HCCC}$ 6.0–7.0)	H^{22}, H^{20}	H^{18}
C^{19}	128.62 br.d.d (s) ($^3J_{HCCC}$ 6.9)	H^{21}	H^{19}
C^{20}	128.23 d.t (s), ($^1J_{HC}$ 161.3, $^3J_{HCCC}$ 7.4)	H^{18}, H^{22}	H^{20}

[a] Of the anion part of the molecule. Cation fragment $[(CH_3)_3CNH_3]^+$: 27.54 q.sept (s) (CH_3, $^1J_{HC}$ 126.8, $^3J_{HCCC}$ 4.1 Hz), 51.41 m (s) [$\underline{C}(CH_3)_3$].
[b] The form of the signal in the $^{13}C-\{^1H\}$ NMR spectrum is given in parentheses.

c 17.6330(18) Å; α 104.216(1), β 109.921(1), γ 91.217(1)°; *V* 2611.5(5) Å^3, *Z* 4; 23(2)°C, *F*(000) 1176, $2\theta_{max}$ 54.000°, *wR*(F^2) 0.13426 (for 11268 reflections), *R* 0.0472 [for 6182 reflections with $I^2 \geq 2\sigma$ (*I*)]. Crystallographic data are deposited into the Cambridge Crystallographic Data Center, CCDC 801243.

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