ISSN 1070-3632, Russian Journal of General Chemistry, 2006, Vol. 76, No. 3, pp. 488–489. © Pleiades Publishing, Inc., 2006.
Original Russian Text © E.N. Varaksina, V.F. Mironov, S.A. Mezentsev, R.Z. Musin, A.I. Konovalov, 2006, published in Zhurnal Obshchei Khimii, 2006, Vol. 76, No. 3, pp. 513–514.

LETTERS TO THE EDITOR

Regio- and Stereoselective Chlorination of 2,6-Dichloro-4-phenyl-3,4,5,6-tetrahydro-2*H*-1,2λ^5-benzoxaphosphinin-2-one: Addition of Two Equivalents of Chlorine with Aromaticity Disturbance

E. N. Varaksina, V. F. Mironov, S. A. Mezentsev, R. Z. Musin, and A. I. Konovalov

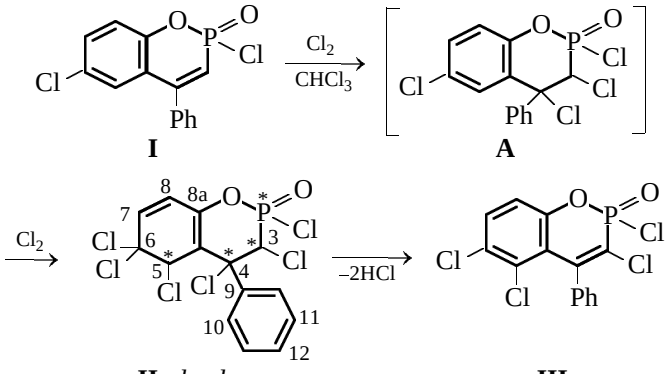
Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center, Russian Academy of Sciences, ul. Arbuzova 8, Kazan, Tatarstan, 420088 Russia

Received August 10, 2005

DOI: 10.1134/S1070363206030212

Recently we showed that the reaction of 2,2,2-trichloro-1,3,2λ^5-benzodioxaphosphole with phenylacetylene gives rise to 2,6-dichloro-4-phenyl-3,4,5,6-tetrahydro-2*H*-1,2λ^5-benzoxaphosphinin-2-one (**I**) that is a phosphorus analog of natural coumarins and α-chromenes [1]. Chemical properties of 1,2-benzoxaphosphinine derivatives have not been investigated. In the present work we found that compound **I** can be chlorinated under mild conditions to form a 1:2 adduct in nearly quantitative yield. The ^{31}P NMR spectrum of the reaction mixture no longer shows the signal of starting compound **I** (δ_P 17.4 ppm, d, $^2J_{PCH}$ 24.6 Hz) and contains signals at δ_P 22.4 (d, $^2J_{PCH}$ 11.8 Hz) (d_1) and 17.9 ppm (d, $^2J_{PCH}$ 8.3 Hz) (d_2) with the intensity ratio 2:3. The ^{1}H NMR spectrum contains the corresponding doublets of the H^3 proton at δ 5.30 ($^2J_{PCH^3}$ 11.9 Hz) and 5.26 ppm ($^2J_{PCH^3}$ 8.6 Hz). Detailed inspection of the ^{13}C and ^{13}C–{^{1}H} NMR spectra (see below) shows that, together with the chlorination of the C^3=C^4 bond, regioselective addition of a chlorine molecule by one of the double bonds of the benzene ring takes place, which disturbs aromaticity of the phenylene system. The spectral data also point to formation of two isomeric compounds. This effect distinguishes benzophosphinines from coumarines where such processes are unknown. It is necessary to note that such an easy loss of aromaticity is energetically compensated for by the formation of two new C–Cl bonds, because the possible elimination of HCl to form a benzo fragment does not take place even under fairly strong heating (100–120°C, 30 min).

Taking into account the chemical shifts and multiplicity of signals in the ^{13}C and ^{13}C–{^{1}H} NMR spectra, we assigned to the obtained isomers structure



I **A** **II**, d_1, d_2 **III**

II. In spite of the presence of four chiral atoms, a mixture of two diastereomers (d_1 and d_2) is formed. It is interesting to note that the electron impact mass spectrum lacks the molecular ion of compound **II** but contains the molecular ion of compound **III** that results from the elimination of two HCl molecules at high temperatures.

The reaction evidently begins with chlorination of the more reactive C^3=C^4 bond to give tetrahydrophosphinine **A** which is further chlorinated to compound **II**. There have been a few works on the halogenation of organic compounds, involving aromaticity disturbance. The authors of these works explain this process in terms of the radical mechanism (for review, see [2]). Nevertheless, the majority of such reactions require rigid conditions to occur and provide complex mixtures of diastereomers. The unusually high regio- and stereoselectivity of the chlorination of phosphinine **I** is evidently connected with the presence of an annelated heterocycle which significantly alters the electron density distribution in the benzo fragment. This reaction can be regarded as a promising synthetic approach to new phosphorus-containing cyclodienes.

Chlorination of phosphinine I. To a solution of 4.4 g of phosphinine **I** in 10 ml of CH_2Cl_2, a solution of 2.0 g of chlorine in 20 ml of CH_2Cl_2 was added dropwise with stirring at –40°C. The reaction mixture was kept for 6 h until it warmed up to 20°C and then for 2 days at this temperature. The solvent and excess chlorine were removed in a vacuum, and the residue was dried in a vacuum (0.1 mm Hg) at 80°C.

2,3,4,5,6,6-Hexachloro-4-phenyl-3,4,5,6-tetrahydro-2*H*-1,2λ^5-benzoxaphosphinin-2-one (II) was obtained as a light brown glassy substance. ^{1}H NMR spectrum (600 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 5.26 d (PCH, $^2J_{PCH}$ 8.6); 5.30 d (PCH, $^2J_{PCH}$ 11.9 Hz); 6.77 br.d (H^5, $^3J_{H^4CCH^5}$ 1.0), 7.03 d (H^5, $^3J_{H^4CCH^5}$ 1.8), 7.10 and 7.15 two d (H^8, $^3J_{HH}$ 8.6 and $^3J_{HH}$ 8.5); 8.34 br.d (H^7, $^3J_{HH}$ 8.5–8.6), 7.39–7.48 m (C_6H_5). ^{13}C NMR spectrum (150.9 MHz, $CDCl_3$), δ_C, ppm (*J*, Hz) (the multiplicity of signal in ^{13}C–{^{1}H} NMR spectrum is given in brackets): 64.04 d.d (d) (C^3, $^1J_{HC^3}$ 153.3, $^1J_{PC^3}$ 122.0); 60.49 d.d (d) (C^3, $^1J_{HC^3}$ 150.1, $^1J_{PC^3}$ 118.8), 74.34 br.s (s) (C^4), 73.61 br.s (d) (C^4, $^1J_{PC^3C^4}$ 2.5); 131.23 d.d.d (d) (C^{4a}, $^3J_{POC^{4a}}$ 5.0, $^3J_{HCCC^{4a}}$ 4.0, $^3J_{HCCC^{4a}}$ 4,0); 130.75 d.d (d) (C^{4a}, $^3J_{HCCC^{4a}}$ 6.6); 77.72 br.d (s) (C^5, $^1J_{HC^5}$ 181.9); 79.54 br.d (s) (C^5, $^1J_{HC^5}$ 210.7); 93.74 br.m (br.s) (C^6); 131.85 d.d (s) (C^7, $^1J_{HC^7}$ 169.4, $^3J_{HC^5CC^7}$ 6.3); 132.02 d.d (s) (C^7, $^1J_{HC^7}$ 168.7, $^3J_{HC^5CC^7}$ 6.3); 121.53 d.d (d) (C^8, $^1J_{HC^8}$ 167.3 $^3J_{POCC^8}$ 8.4); 121.63 d.d (d) (C^8, $^1J_{HC^8}$ 8.6); 146.92 m (d) (C^{8a}, $^2J_{POC^{8a}}$ 8.6), 146.77 m (d) (C^{8a}, $^2J_{POC^{8a}}$ 8.3), 138.08 m (d) (C^9, $^3J_{PCCC^9}$ 8.5, $^3J_{HC^{11}CC^9}$ 7.5), 135.95 br.m (br.d) (C^9, $^3J_{PCCC^9}$ 10.0), 127.92 d.d.d (s) (C^{10}, $^1J_{HC^{10}}$ 159.6, $^3J_{HC^{10'}CC^{10}}$ 6.8), 129.76 d.d.d (s) (C^{10}, $^1J_{HC^{10}}$ 162.3, $^3J_{HC^{10'}CC^{10}}$ 6.6, $^3J_{HC^{12}CC^{10}}$ 6.6), 128.95 d.d (s) (C^{11}, $^1J_{HC^{11}}$ 161.3, $^3J_{HC^{11'}CC^{11}}$ 8.0), 129.07 d.d (s) (C^{11}, $^1J_{HC^{11}}$ 162.8, $^3J_{HC^{11'}CC^{11}}$ 7.3), 130.74 d.t (s) (C^{12}, $^1J_{HC^{12}}$ 158.0, $^3J_{HC^{10}CC^{12}}$ 7.1), 129.79 d.t(s) (C^{12}, $^1J_{HC^{12}}$ 159.0, $^3J_{HC^{10}C^{12}}$ 7.2). Mass spectrum, *m/z* (ions containing the most abundant isotopes are given): 386, 384, 382, 380, 378 [$C_{14}H_7ClO_4P$] [$M^{+\cdot}$] (**III**), 343, 345, 347, 349, 351 [$M^{+\cdot}$ – Cl], 307, 309, 311, 313, 315 [$M^{+\cdot}$ – HCl – Cl]. Found, %: Cl 47.79. $C_{14}H_9Cl_6O_2P$. Calculated, %: Cl 47.02.

The NMR spectra were measured on Bruker Avance-600 (600 MHz, ^{1}H; 150.9 MHz, ^{13}C) and Bruker CXP-100 (36.48 MHz) spectrometers against internal HMDS or external H_3PO_4. The mass spectra were obtained on a Finnigan MAT TRACE–MS instrument, ionizing energy 70 eV, ion source temperature 200°C. Direct sample injection into the ion source was applied. The injector ampule was heated from 35 to 150°C at a step of 35 deg min^{-1}. The mass spectra were treated using the Xcalibur program.

ACKNOWLEDGMENTS

The work was financially supported by the Russian Foundation for Basic Research (project no. 03-03-32 542).

REFERENCES

1. Mironov, V.F., Konovalov, A.I., Litvinov, I.A., Gubaidullin, A.T., Petrov, R.R., Shtyrlina, A.A., Zyablikova, T.A., Musin, R.Z., Azancheev, N.M., and Il'yasov, A.V., *Zh. Obshch. Khim.*, 1998, vol. 68, no. 9, p. 1482.
2. *Halogen Verbindungen. Fluorverbindungen. Herstellung, Reactivitat und Umwahdlung. Chlorverbindungen. Herstellung. Metoden der organischen Chemie (Houben-Weyl)*, Stuttgart: Thieme, 1962, vol. 4/3.