ISSN 1070-3632, Russian Journal of General Chemistry, 2008, Vol. 78, No. 6, pp. 1287–1289. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © D.A. Tatarinov, V.F. Mironov, E.N. Varaksina, A.I. Konovalov, 2008, published in Zhurnal Obshchei Khimii, 2008, Vol. 78, No. 6, pp. 1049–1050.

LETTERS TO THE EDITOR

Reaction of 4-Aryl-2,6-dichlorobenzo[*e*][1,2]oxaphosphinine 2-Oxides with Organomagnesium Compounds as a Convenient Synthetic Approach to (*Z*)-Dialkyl(aryl)[2-(2-hydroxyaryl)-2-arylethenyl]phosphine Oxides

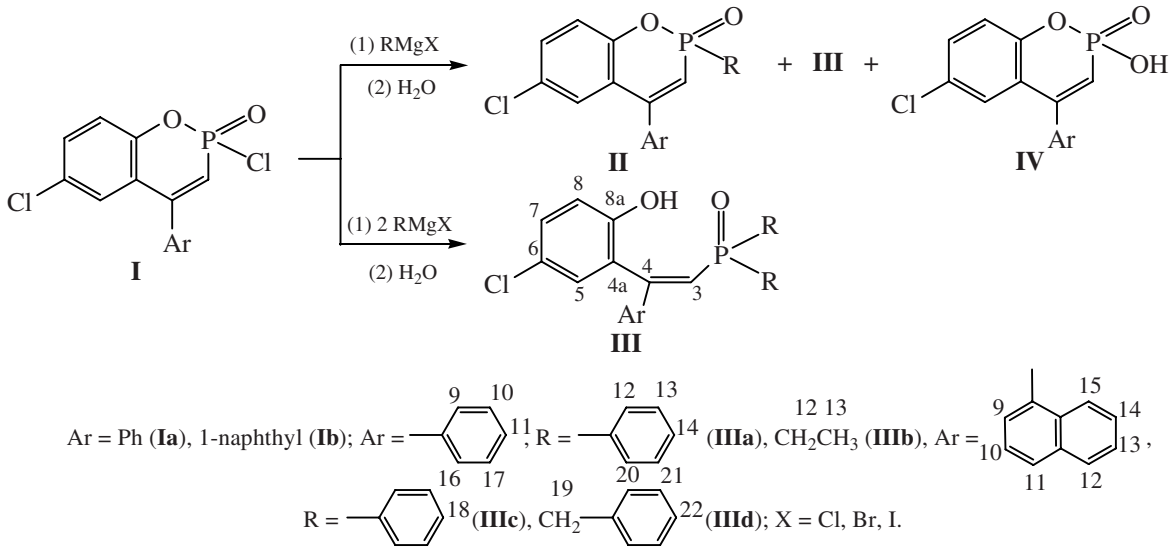
D. A. Tatarinov, V. F. Mironov, E. N. Varaksina, and A. I. Konovalov

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

Received June 27, 2007

DOI: 10.1134/S1070363208060340

We recently prepared benzo[*e*][1,2]oxaphosphinine 2-oxides [1, 2], phosphorus analogs of coumarins which are widespread in nature and possess diverse biological activity [3]. The chemical behavior of this class of compounds is comparatively poorly studied. Thus it was shown that they fairly readily chlorinated [4] and brominated [5] into the heterocyclic fragment to form finally 3-halo derivatives. In the present work we investigated for the first time reactions of 4-aryl-2,6-dichlorobenzo[*e*][1,2]oxaphosphinine 2-oxides **I** with organomagnesium reagents (Grignard reagents). Taking into account the data summarized in the monograph [6], we expected that the reactions would lead to 2-alkyl(aryl)-4-aryl-6-chlorobenzo[*e*][1,2]oxaphosphinine 2-oxides **II** which attract some interest as complexing agents for rare metals. However, phosphinines **I** were found to react unambiguously with a double excess of Grignard reagents to give functionally substituted phosphine oxides **III** in quantitative yields. At an equimolar ratio of the starting reagents, mixtures of phosphinines **II**, phosphine oxides **III**, and 2-hydroxy-4-aryl-6-chlorobenzo[*e*][1,2]-oxaphosphinine 2-oxides **IV** formed. It is obvious that Grignard reagents almost equally reactive toward



exocyclic P–Cl and endocyclic P–O bonds, which makes impossible, when using both arylmagnesium halides and primary alkylmagnesium halides, to direct the process exclusively to substitution of the chlorine atom to form compounds **II**.

The structure of (*Z*)-dialkyl(aryl)[2-(2-hydroxyaryl)-2-arylethenyl]phosphine oxides **III** was confirmed by means of ^{1}H, ^{31}P and ^{13}C NMR and IR spectroscopy. Phosphine oxides **III** contain a hydroxy group in the δ position to the phosphoryl group and, therefore, they can find application as starting compounds for synthesis of chelating phosphines and neutral chelating ligands for extraction of rare and nonferrous metals.

Compound IIIa. A solution of 10 g (0.0321 mol) of oxaphosphinine **Ia** [1] in 10 ml of benzene was added dropwise with stirring in argon to phenylmagnesium bromide prepared from 1.7 g of Mg and 7.8 ml of bromobenzene in 50 ml of ether by a conventional procedure [7]. The reaction mixture was heated under reflux for 30 min and cooled, after which it was neutralized with a solution of 6 ml of conc. HCl in 35 ml of distilled water. The solution was stirred for 30 min to let it warm to room temperature; therewith, precipitate formation was observed. The precipitate was filtered off, washed with 10–15 ml of ether, and dried in air or in a vacuum (12 mm Hg) to obtain 12 g (87%) of compound **IIIa**, mp 185–186°C. Found, %: C 72.65, H 4.91, P 7.29. $C_{26}H_{20}ClO_2P$. Calculated, %: C 72.47, H 4.64, P 7.20. ^{31}P–{^{1}H} NMR spectrum (36.46 MHz, $CDCl_3$), δ_P, ppm: 22.6. ^{1}H NMR spectrum (600 MHz, DMSO-d_6, 45°C, d, ppm, *J,* Hz): 9.17 br.s (OH, 1H), 7.70 br.m (H^{12}, 4H), 7.49 br.m (H^{14}, 2H, $^{3}J_{HC^{13}CH^{14}}$ 7.1), 7.40 br.m (H^{13}, *4H*), 7.30–7.34 m (H^{7}, H^{8}, H$^{9-11}$, *7H*), 6.33 br.s (H^{5}, 1H), 7.03 d (H^{3}, 1H, $^{2}J_{PCH^3}$ 20.5).

Compound IIIb. Yield 94 %, mp 75–77°C. Found, %: C 64.29, H 6.12, P 9.41. $C_{18}H_{20}ClO_2P$. Calculated, %: C 64.57, H 5.98, P 9.27. ^{31}P–{^{1}H} NMR spectrum (36.46 MHz, $CDCl_3$), δ_P, ppm: 47.5. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, δ, ppm, *J,* Hz): 1.09 d.t (H^{13}, 6*H*, $^{3}J_{PCCH}$ 17.6, $^{3}J_{HCCH}$ 7.5), 1.64–1.70 m (H^{12}, 4*H*, *AB*-part of the spectrum *ABMX*$_3$, $^{3}J_{H(X)CCH(A)}$ 7.5, $^{3}J_{H(X)CCH(B)}$ 7.5), 6.32 d (PCH^{3}, $^{2}J_{PCH}$ 18.1), 6.92 d (H^{5}, $^{4}J_{HCCCH}$ 2.6), 7.05 d (H^{8}, $^{3}J_{HCCH}$ 8.7), 7.19 d.d (H^{7}, $^{3}J_{HCCH}$ 8.7, $^{4}J_{HCCCH}$ 2.6), 7.26 br.m (H^{9}, 2H, $^{3}J_{HCCH}$ 7.5–7.7), 7.31 br.m (H^{10}, 2H, $^{3}J_{HCCH}$ 7.5–7.7, $^{3}J_{HCCH}$ 7.1), 7.33 m (H^{11}, 1H, $^{3}J_{HCCH}$ 7.1), 8.57 br.s (OH, 1H).

Compound IIIc. Yield 97 %, mp 173–175°C. Found, %: C 75.11, H 4.77, P 6.23. $C_{30}H_{22}ClO_2P$. Calculated, %: C 74.92, H 4.58, P 6.45. ^{31}P–{^{1}H} NMR spectrum (162.0 MHz, DMSO-d_6), δ_P, ppm: 16.8. ^{1}H NMR spectrum (600 MHz, DMSO-d_6, 45°C, δ, ppm, *J,* Hz): 6.49 d (H^{8}, 1H, $^{3}J_{H^7CCH^8}$ 8.7), 6.70 d (H^{3}, 1H, $^{2}J_{PCH^3}$ 20.6), 6.96 d.d (H^{7}, 1H, $^{3}J_{H^8CCH^7}$ 8.7, $^{4}J_{H^5CCCH^7}$ 2.4), 7.20 d (H^{5}, 1H, $^{4}J_{H^7CCCH^5}$ 2.4), 7.38 d (H^{9}, 1H, $^{3}J_{HCCH}$ 7.0), 7.42–7.44 and 7.46–7.47 m (H^{10}, H^{13}, H^{14}, H^{17}, H^{18}, 9H), 7.75 d.d (H^{16}, 4H, $^{3}J_{HCCH}$ 11.4, $^{3}J_{HCCH}$ 7.6), 7.87 d (H^{15}, 1H, $^{3}J_{HCCH}$ 8.1), 7.91 d.d (H^{12}, 1H, $^{3}J_{HCCH}$ 6.2, $^{4}J_{HCCCH}$ 3.2), 8.17 d.d (H^{11}, 1H, $^{3}J_{HCCH}$ 6.1, $^{4}J_{HCCCH}$ 3.2), 9.71 s (OH, 1H).

Compound IIId. Yield 94%, mp 178–181°C. Found, %: C 75.34, H 5.47, P 6.29. $C_{32}H_{26}ClO_2P$. Calculated, %: C 75.52, H 5.11, P 6.10. ^{31}P–{^{1}H} NMR spectrum (162.0 MHz, DMSO-d_6), δ_P, ppm: 30.8. IR spectrum, cm^{-1}: 417, 454, 479, 504, 538, 582, 620, 640, 683, 699, 720, 745, 783, 798, 815, 842, 863, 883, 911, 930, 957, 1019, 1031, 1069, 1118, 1153, 1198, 1229, 1283, 1342, 1377, 1411, 1455, 1495, 1586, 1601, 1710, 1825, 1884, 1958, 2717, 2921, 3030, 3441. ^{1}H NMR spectrum (600 MHz, DMSO-d_6, 45°C, δ, ppm, *J,* Hz): 3.27 and 3.33 m (CH_2, 4H, $^{2}J_{H(A)CH(B)}$ 13.5–14.0, $^{2}J_{PCH(B)}$ 13.5–14.0, $^{2}J_{PCH(A)}$ 15.2), 6.12 d (H^{3}, 1H, $^{2}J_{PCH3}$ 22.8), 6.59 d (H^{5}, 1H, $^{4}J_{H7CCCH5}$ 2.7), 6.79 d (H^{8}, 1H, $^{3}J_{H7CCH8}$ 8.7), 7.12 d.d (H^{7}, 1H, $^{3}J_{H8CCH7}$ 8.7, $^{4}J_{H^5CCCH^7}$ 2.7), 7.17 d.d (H^{9}, 1H, $^{3}J_{HCCH}$ 7.1, $^{4}J_{HCCCH}$ 0.9), 7.30–7.35 m (H$^{16-18}$, 10H), 7.44 d.d (H^{10}, 1H, $^{3}J_{HCCH}$ 7.2, $^{3}J_{HCCH}$ 8.1), 7.46 and 7.50 m (H^{13} and H^{14}, 2H; $^{3}J_{HCCH}$ 8.2, $^{3}J_{HCCH}$ 6.8, $^{4}J_{HCCCH}$ 1.4; $^{3}J_{HCCH}$ 8.2, $^{3}J_{HCCH}$ 6.8, $^{4}J_{HCCCH}$ 1.2), 7.85 br.d (H^{15}, 1H, $^{3}J_{HCCH}$ 8.3), 7.91 and 7.93 br.d (H^{11} and H^{12}, 2H, $^{3}J_{HCCH}$ 7.3–8.7), 10.01 br.s (OH, 1H).

The spectra were measured under the conditions described in [2].

ACKNOWLEDGMENTS

The work was financially supported by the Russian Foundation for Basic Research (project nos. 07-03-000180 and MK-1434.2006.3).

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. Mironov, V.F., Shtyrlina, A.A., Varaksina, E.N., Gubaidullin, A.T., Azancheev, N.M., Dobrynin, A.B.,

Litvinov, I.A., Musin, R.Z., and Konovalov, A.I., *Zh. Obshch. Khim*., 2004, vol. 74, no. 12, p. 1953.

3. *Terpenoidy i kumariny* (Terpenoids and Coumarins), *Tr. Botanich. Inst. Imeni V.L.Komarova Akad. Nauk SSSR*, Pigulevskii, G.V., Ed., Moscow: Nauka, 1965, *Ser. V*: *Rastit. Syr'e*, no. 12.
4. Varaksina, E.N., Mironov, V.F., Mezentsev, S.A., Musin, R.Z., and Konovalov, A.I., *Zh. Obshch. Khim*., 2006, vol. 76, no. 3, p. 513.
5. Varaksina, E.N., Mezentsev, S.A., Mironov, V.F., and Konovalov, A.I., *Mendeleev Comm*., 2006, vol. 16, no. 2, p. 100.
6. *The Chemistry of Organophosphorus Compounds*, Hartley, F.R., Ed., New York: Wiley, 1992, vol. 2; Organic Phosphorus Compounds, Kosolapoff, G.M. and Maier, L., Eds., New York: Interscience, 1972, vol. III, p. 341.
7. *Preparativnaya organicheskaya khimiya* (Preparative Organic Chemistry), Vul'fson, N.S., Ed., Moscow: Khimiya, 1964.