ISSN 1070-3632, Russian Journal of General Chemistry, 2006, Vol. 76, No. 8, pp. 1324–1326. © Pleiades Publishing, Inc., 2006.
Original Russian Text © G.B. Bagdasaryan, P.S. Pogosyan, G.A. Panosyan, G.V. Asratyan, M.G. Indzhikyan, 2006, published in Zhurnal Obshchei Khimii, 2006, Vol. 76, No. 8, pp. 1380–1382.

Nucleophilic Addition of Azoles to Triphenyl-(phenylethynyl)phosphonium Bromide and Base Hydrolysis of the Addition Products

G. B. Bagdasaryan[a], P. S. Pogosyan[a], G. A. Panosyan[b], G. V. Asratyan[a], and M. G. Indzhikyan[a]

[a] *Institute of Organic Chemistry, National Academy of Sciences of Armenia, ul. Z. Kanakertsi 167A, Yerevan, 375091 Armeniya*

[b] *Molecular Structure Research Center, National Academy of Sciences of Armenia, Yerevan, Armenia*

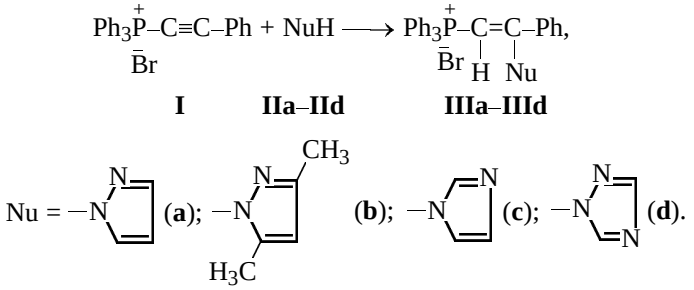
Received December 30, 2005

Abstract — Reactions of pyrazole, 3,5-dimethylpyrazole, imidazole, and 1,2,4-triazole with triphenyl(phenylethynyl)phosphonium bromide gave the corresponding 2-azolyl-2-phenylethenyl(triphenyl)phosphonium salts. Base hydrolysis of the addition products led to the formation of 2-azolyl-1,2-diphenylethyl(diphenyl)phosphine oxides.

DOI: 10.1134/S1070363206080299

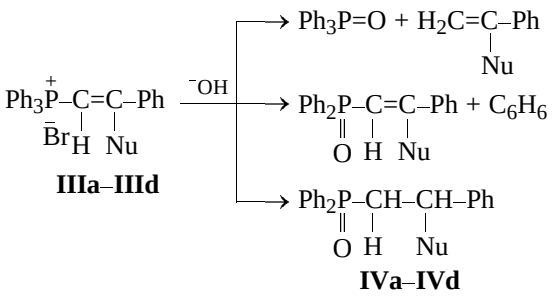
There are numerous published data on nucleophilic addition to phosphonium salts containing a triple carbon–carbon bond in the α- or β-position [1–4]. We previously reported on the reactions of triphenyl-(phenylethynyl)phosphonium bromide (**I**) with phenylhydrazine and hydroxylamine [5, 6]. In this study we examined the reaction of phosphonium salt **I** with azoles. The latter were selected taking into account their extracting ability. It is known that some organophosphorus compounds, especially tertiary phosphine oxides, are highly selective extractants for noble and transition metals and that tertiary phosphine oxides can be obtained by base hydrolysis of quaternary phosphonium salts. Combination of phosphine oxide and azole fragments in a single molecule could give rise to new efficient extractants.

We have found that pyrazole at 80°C adds to salt **I** to give triphenyl[2-phenyl-2-(1*H*-pyrazol-1-yl)ethenyl]phosphonium bromide. However, we succeeded in isolating the latter only as a mixture with the initial salt at a ratio of 60 : 40 (according to the ^{1}H NMR data). Our attempts to separate this mixture by recrystallization were unsuccessful. Analogous patterns were observed in the reactions of salt **I** with 3,5-dimethylpyrazole, imidazole, and 1,2,4-triazole; the ratios of addition products **IIIb**–**IIId** and initial salt **I** were 90 : 10, 75 : 25, and 80 : 20, respectively.



The isolated salt mixtures were subjected to base hydrolysis in a 3.5% solution of sodium hydroxide. Theoretically, phosphonium salts **IIIa**–**IIId** could react with alkali along three pathways.

The first two pathways are referred to as "paraffin cleavage" of phosphonium salts, while the third pathway involves migration of phenyl group to the α-position, which is well known for vinylphosphonium salts.



IIIa–**IIId** **IVa**–**IVd**

We have found only one example of β-migration of the benzyl group in diphenylbenzylvinylphosphonium hydroxide [4].

In all cases, the reactions of salts **IIIa**–**IIId** (as mixtures with **I**) with alkali gave mainly products of α-migration of phenyl group (compounds **IVa**–**IVd**). Triphenylphosphine oxide was isolated as minor product. Compounds **IIIa** and **IIIb** were identified in the reaction mixtures by ^{1}H and ^{31}P NMR spectroscopy, and **IIIc** and **IIId**, by ^{31}P NMR spectroscopy. In the ^{1}H NMR spectra, the most characteristic was the presence of a doublet signal from the olefinic proton (due to coupling with the phosphorus atom). It should also be noted that compounds **III** were formed mainly as a single stereoisomer.

According to the ^{1}H, ^{13}C, and ^{31}P NMR data, compound **IVa** is formed as an equimolar mixture of two diastereoisomers; phosphine oxides **IVb**–**IVd** were isolated as a single diastereoisomer. The ^{1}H NMR signals were assigned to CH protons in the α- and β-positions on the basis of the two-dimensional ^{1}H–^{13}C correlation spectrum of compound **IVb** and the spin–spin coupling constant $^1J_{PC}$ = 68.2 Hz for the α-carbon atom in the ^{13}C NMR spectrum.

EXPERIMENTAL

The NMR spectra were recorded at 303 K on a Varian Mercury-300 spectrometer at 300.08, 121.75, and 75.46 MHz for ^{1}H, ^{31}P, and ^{13}C, respectively. The chemical shifts were measured relative to tetramethylsilane as internal reference for ^{1}H and ^{13}C and orthophosphoric acid as external reference for ^{31}P. The IR spectra were obtained on UR-20 and Specord IR-75 spectrometers. The mass spectra (electron impact, 70 eV) were recorded on an MKh-1321 instrument with direct sample inlet into the ion source.

Triphenyl(phenylethynyl)phosphonium bromide was synthesized by the procedure described in [7].

Triphenyl[2-phenyl-2-(1*H*-pyrazol-1-yl)ethenyl]-phosphonium bromide (IIIa). A mixture of 5.6 g of triphenyl(phenylethynyl)phosphonium bromide (**I**) and 1.0 g of pyrazole (**IIa**) in 30 ml of anhydrous acetonitrile was heated for 33 h at 80°C. After cooling, the solvent was removed under reduced pressure, and the residue was washed with three portions of anhydrous diethyl ether and dried. The product was 6.1 g of a mixture of salts **IIIa** and **I** at a ratio of 60 : 40. Yield of salt **IIIa** 57.2%. Attempts to separate the salt mixture by recrystallization were unsuccessful. IR spectrum, ν, cm^{-1}: 1590 (P$^+$–CH=C), 2200 (C≡C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 6.04 d (1H, PCH, $^2J_{PH}$ = 15.8), 6.21 d.d (1H, 4-H, pyrazole, ^3J = 2.7, 1.9), 6.95 d (1H, 3-H, pyrazole, ^3J = 1.9), 7.45 d (1H, 5-H, pyrazole, ^3J = 2.7), 7.58–7.77 m (20H, C_6H_5). ^{31}P NMR spectrum (DMSO-d_6/CCl_4, 2 : 3): δ_P 22.2 ppm.

[2-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-2-phenylethenyl]triphenylphosphonium bromide (IIIb). A mixture of 2.0 g of salt **I**, 0.52 g of 3,5-dimethyl-1*H*-pyrazole (**IIb**), and 19 ml of anhydrous acetonitrile was heated for 17.5 h at 80°C. After removal of the solvent, the residue was recrystallized from water to obtain 2.26 g of a mixture of salts **IIIb** and **I** at a ratio of 90 : 10. Yield of salt **IIIb** 83.8%. IR spectrum, ν, cm^{-1}: 1660 (C=C). ^{1}H NMR spectrum (DMSO-d_6/CCl_4, 1 : 9), δ, ppm (*J*, Hz): 1.64 s (3H, CH_3), 1.65 s (3H, CH_3), 5.51 s (1H, 4-H, pyrazole), 6.89 d (1H, PCH, $^2J_{PH}$ = 15.6), 7.55–7.82 m (20H, C_6H_5). ^{31}P NMR spectrum (DMSO-d_6/CCl_4, 1 : 9): δ_P 22.2 ppm.

[2-(1*H*-Imidazol-1-yl)-2-phenylethenyl]triphenylphosphonium bromide (IIIc). A mixture of 4.0 g of salt **I**, 0.73 g of imidazole, and 26 ml of anhydrous acetonitrile was heated for 27.5 h under reflux. The solvent was removed, and the residue was washed with anhydrous diethyl ether, water, and alcohol–chloroform (3 : 2) and dried. Yield of salt **IIIc** 3.45 g (74.8%). ^{31}P NMR spectrum (DMSO-d_6/CCl_4, 1 : 3): δ_P 19.7 ppm.

Tpiphenyl[2-phenyl-2-(1*H*-1,2,4-triazol-1-yl)-ethenyl]phosphonium bromide (IIId). A mixture of 3.0 g of salt **I**, 0.56 g of 1*H*-1,2,4-triazole (**IId**), and 20 ml of anhydrous acetonitrile was heated for 50 h

under reflux. The solvent was removed, and the residue was washed with anhydrous diethyl ether, dissolved in water, and extracted with chloroform to isolate 3.35 g of a mixture of salts **IIId** and **I** at a ratio of 80 : 20. Yield of salt **IIId** 77.4%. Attempts to separate the salt mixture by recrystallization were unsuccessful. IR spectrum: ν(C=C) 1590 cm^{-1}. ^{31}P NMR spectrum ($CDCl_3$): δ_P 17.7 ppm.

[1,2-Diphenyl-2-(1*H*-pyrazol-1-yl)ethyl]diphenylphosphine oxide (IVa). A mixture of 2.0 g of **I/IIIa** salt mixture and 50 ml of 3.5% aqueous sodium hydroxide was heated for 13.5 h at the boiling point under stirring. The mixture was cooled and extracted with diethyl ether. The white solid separated at the diethyl ether–water phase boundary was washed with diethyl ether and dried. Yield of **IVa** 0.65 g (62%, calculated on **IIIa**), mp 280–282°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 4.93 d.d (0.5H, $^2J_{PH}$ = 5.6, ^3J = 11.3) and 5.09 d.d (0.5H, PCH, $^2J_{PH}$ = 4.8, ^3J = 11.0), 5.66 d.d (0.5H, ^3J = 2.5, 1.8) and 5.83 d.d (0.5H, 4-H, pyrazole, ^3J = 2.5, 1.8), 6.10 d.d (0.5H, ^3J = 11.3, $^3J_{PH}$ = 6.1) and 6.34 d.d (0.5H, NCH, ^3J = 11.0, $^3J_{PH}$ = 10.5), 6.83–7.76 m (22H, C_6H_5; 3-H and 5-H, pyrazole). ^{31}P NMR spectrum ($CDCl_3$): δ_P 29.4, 30.7 ppm. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*J*, Hz): 50.47 d ($^1J_{PC}$ = 64.2) and 51.64 d (PCH, $^1J_{PC}$ = 66.9), 65.60 d and 69.11 d (NCH, $^2J_{PC}$ = 4.3), 105.15 d (J_{PC} = 3.4) and 105.53 d (J_{PC} = 3.7, C^4, pyrazole), 127–139 (C_{arom}). Found: M^+ 448; calculated: *M* 448.

Removal of the solvent from the combined extracts gave 0.15 g (15%) of triphenylphosphine oxide with mp 152–154°C, which showed no depression of the melting point on mixing with an authentic sample.

Compounds **IVb**–**IVd** were obtained in a similar way.

[2-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-1,2-diphenylethyl]diphenylphosphine oxide (IVb) was synthesized from 0.9 g of salt mixture **I/IIIb** by heating for 7 h at the boiling point. The product was recrystallized from alcohol. Yield 0.3 g (42.2%). ^1H NMR spectrum (DMSO-d_6/CCl_4, 1:3), δ, ppm (*J*, Hz): 2.01 s (3H, CH_3), 2.08 s (3H, CH_3), 5.03 d.d (1H, PCH, $^2J_{PH}$ = 5.2, ^3J = 11.2), 5.30 s (1H, 4-H, pyrazole), 5.86 d.d (1H, NCH, ^3J = 11.2, $^3J_{PH}$ = 5.7), 6.77–6.98 m (6H), 7.04–7.19 m (6H) and 7.41–7.55 m (7H, C_6H_5). ^{31}P NMR spectrum ($CDCl_3$): δ_P 29.8 ppm. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*J*, Hz): 10.19 (CH_3), 13.17 (CH_3), 50.95 d (PCH, $^1J_{PC}$ = 68.2), 62.74 d (NCH, $^2J_{PC}$ = 5.0), 103.51 (C^4, pyrazole), 126–146 (C_{arom}).

[2-(1*H*-Imidazol-1-yl)-1,2-diphenylethyl]diphenylphosphine oxide (IVc) was synthesized from 2.3 g of salt **IIIc**. The product was recrystallized from anhydrous alcohol. Yield 0.7 g (34.7%). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 4.43 d.d (1H, PCH, $^2J_{PH}$ = 7.0, ^3J = 10.9); 6.18 d.d (1H, NCH, ^3J = 10.9, 8.2); 6.74 s (1H, CH, imidazole); 6.88 s (1H, CH, imidazole); 6.95–7.06 m (6H), 7.09–7.29 m (8H), 7.30–7.42 m (5H), and 7.47–7.55 m (2H, C_6H_5 and CH, imidazole). ^{31}P NMR spectrum ($CDCl_3$): δ_P 29.7 ppm.

Removal of the solvent from the combined extracts gave 0.2 g (17%) of triphenylphosphine oxide with mp 152–154°C, which showed no depression of the melting point on mixing with an authentic sample.

Diphenyl[1,2-diphenyl-2-(1*H*-1,2,4-triazol-1-yl)-ethyl]phosphine oxide (IVd) was obtained from 2.0 g of salt **IIId** (reaction time 17 h). Yield 0.35 g (25%). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 4.81 d.d (1H, PCH, $^2J_{PH}$ = 5.8, ^3J = 11.3); 6.25 d.d (1H, NCH, ^3J = 11.3, $^3J_{PH}$ = 6.3); 7.73 s (1H, CH, triazol); 7.73 s (1H, CH, triazole); 6.92–7.04 m (6H), 7.08–7.24 m (6H), 7.29–7.38 m (2H), 7.38–7.54 m (4H), and 7.59– 7.65 m (2H, C_6H_5). ^{31}P NMR spectrum ($CDCl_3$): δ_P 29.3 ppm.

Removal of the solvent from the combined extracts gave 0.15 g (14.7%) of triphenylphosphine oxide with mp 152–154°C, which showed no depression of the melting point on mixing with an authentic sample.

REFERENCES

1. Norobu, M., Dickstein, J.L., and Miller, S.J., *J. Chem. Soc., Perkin Trans. 1*, 1979, no. 9, p. 2103.

2. Schweiser, E.E. and De Voc Coff, S., *J. Org. Chem.*, 1978, vol. 43, no. 15, p. 2972.

3. Hoffmann, H. and Foerster, H., *Tetrahedron Lett.*, 1964, nos. 17–18, p. 983.

4. Shutt, J.R. and Trippett, S., *J. Chem. Soc. C*, 1969, no. 15, p. 2038.

5. Khachatryan, R.A., Zalinyan, S.A., Bagdasaryan, G.B., Sarkisova, E.A., and Indzhikyan, M.G., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2002, no. 1, p. 139.

6. Khachatryan, R.A., Khachikyan, R.Dzh., Zalinyan, S.A., Gevorkyan, G.A., Karamyan, N.V., and Indzhikyan, M.G., *Arm. Khim. Zh.*, 2001, vol. 54, nos. 3–4, p. 41.

7. Dickstein, J.L. and Miller, S.J., *J. Org. Chem.*, 1972, vol. 37, no. 13, p. 2168.