Russian Journal of General Chemistry, Vol. 74, No. 9, 2004, pp. 1456–1458. Translated from Zhurnal Obshchei Khimii, Vol. 74, No. 9, 2004, pp. 1568–1570.

LETTERS TO THE EDITOR

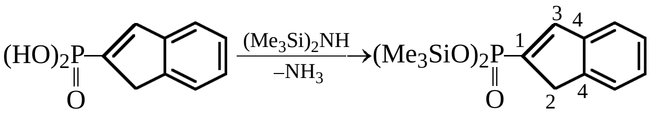
Reaction of Bis(trimethylsilyl) Inden-2-ylphosphonate with Azomethines

A. A. Prishchenko, M. V. Livantsov, O. P. Novikova, L. I. Livantsova, Ya. N. Koval', and D. P. Krut'ko

Lomonosov Moscow State University, Moscow, Russia

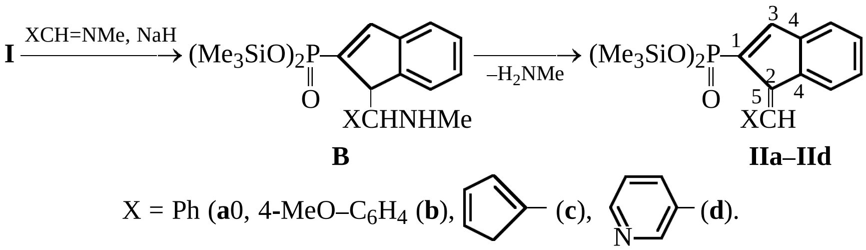
Received February 5, 2004

Recently we developed convenient methods for preparing 2-phosphorus-substituted derivatives of indane and indane-1-carboxylic acid containing various functional groups and heterocyclic fragments, which present interest as promising ligands and biologically active compounds [1]. In the present work we studied the reaction of bis(trimethylsilyl) inden-2-ylphosphonate (**I**) with azomethines, leading novel 2-phosphorus-substituted indene derivatives **II**. Starting phosphonate **I** was obtained in high yield by the reaction of bis(trimethylsilyl)amine with inden-2-ylphosphonic acid (**A**). The synthesis of the latter compound was described previously [2].



A **I**

The reaction of phosphonate **I** with azometines in diethyl ether with stirring in the presence of a sodium hydride initiator involves liberation of methylamine and formation of phosphonates **II** in high yields. According to the reaction scheme, intermediate adduct **B** is formed by a base-catalyzed addition of the indene as a CH acid by the double bond of the azomethine followed by methylamine liberation.



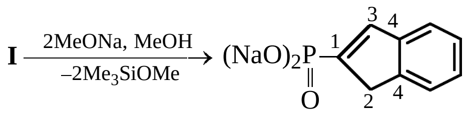
B **IIa–IId**

X = Ph (**a**0, 4-MeO–C_6H_4 (**b**), (**c**), (**d**).

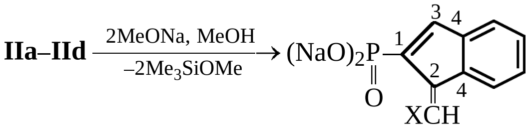
Treatment of phosphonates **I** and **II** with dilute methanolic sodium methylate gives water-soluble disodium salts **III** and **IV**. These salts are hygroscopic white (**III**) or lemon yellow crystals (**IV**).

The NMR spectra of compounds **I**–**IV** contain characteristic signals of substituted indene, aromatic, and heterocyclic fragments. The spectral parameters of these signals are listed below. In the ^{1}H NMR

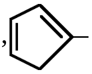
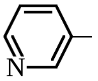
1070-3632/04/7409-1456 ©2004 MAIK "Nauka/Interperiodica"



III



IVa–IVd

X = Ph (**a**), 4-MeO–C_6H_4 (**b**),  (**c**),  (**d**).

spectra, the signals of these fragments partially or completely overlap in the range 6.5–8.00 ppm.

Bis(trimehylsilyl) inden-2-ylphosphonate (I). A mixture of 100 g of bis(trimethylsilyl)amine and 43 g of inden-2-ylphosphonic acid prepared according to [2] was refluxed until ammonia no longer evolved and then distilled in a vacuum to give 66.4 g of ester **I**, yield 89%, bp 149°C (1 mm), mp 52°C. ^{1}H NMR spectrum, δ, ppm: 3.50 s (C^2H_2), 7.1–7.4 m (5CH, C_9H_7), 0.21 d (Me_6Si_2, $^4J_{PH}$ 4.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 137.31 d (C^1, $^1J_{PC}$ 208.2 Hz), 39.57 d (C^2, $^2J_{PC}$ 15.2 Hz), 141.86 d (C^3, $^2J_{PC}$ 14.7 Hz), 142.54 d (C^4, $^3J_{PC}$ 21.3 Hz) and 144.6 d (C^4, $^3J_{PC}$ 12.3 Hz), 0.60 s (CSi). ^{31}P NMR spectrum, δ_P, ppm: –1.11 s.

Bis(trimethylsilyl) (1-benzylideneinden-2-yl)-phosphonate (IIa). To a solution of 4.5 g of phosphonate **I** in 10 ml of diethyl ether, 1.6 g of *N*-benzylidene-*N*-methylamine and 0.1 g of sodium hydride was added with stirring. After 2 h, the solvent was removed, and the residue was distilled in a vacuum to give 4.3 g of phosphonate **IIa**, yield 75%, bp 212°C (2 mm Hg), mp 74°C. ^{13}C NMR spectrum, δ_C, ppm: 135.93 d (C^1, $^1J_{PC}$ 208.3 Hz), 136.25 d (C^2, $^2J_{PC}$ 14.9 Hz), 141.94 d (C^3, $^2J_{PC}$ 12.3 Hz), 139.14 d (C^4, $^3J_{PC}$ 16.0 Hz) and 141.71 d (C^4, $^3J_{PC}$ 18.4 Hz), 136.83 d (C^4, $^3J_{PC}$ 6,1 Hz). ^{31}P NMR spectrum, δ_P, ppm: –2.87 s.

Phosphonates **IIb**–**IId** were prepared in a similar way.

Bis(trimethylsilyl) (4-methoxybenzylidene-inden-2-yl)phosphonate (IIb). Yield 78%, bp 210°C (1.5 mm Hg), mp 89°C. ^{1}H NMR spectrum, δ, ppm: 3.84 s (CH_3O). ^{13}C NMR spectrum. δ_C, ppm: 135.28 d (C^1, $^1J_{PC}$ 206.2 Hz), 136.14 d (C^2, $^2J_{PC}$ 14.8 Hz), 140.92 d (C^3, $^2J_{PC}$ 11.9 Hz), 138.92 d (C^4, $^3J_{PC}$ 17.0 Hz), and 141.61 d (C^4, $^2J_{PC}$ 12.1 Hz), 137.08 s (C^5), 159.96 s (=CO), 55.18 s (CH_3O). ^{31}P NMR spectrum, δ_P, ppm: –2.55 s.

Bis(trimethylsilyl) (1-furfurylideneinden-2-yl)-phosphonate (IIc). Yield 74%, bp 210°C (2 mm Hg), mp 61°C. ^{13}C NMR spectrum, δ_C, ppm: 133.82 d (C^1, $^1J_{PC}$ 205.6 Hz), 135.51 d (C^2, $^2J_{PC}$ 15.6 Hz), 140.60 d (C^3, $^2J_{PC}$ 12.3 Hz), 134.93 d (C^4, $^3J_{PC}$ 16.4 Hz) and 141.40 d (C^4, $^3J_{PC}$ 21.7 Hz), 127.84 s (C^5), 144.88 s (=CHO), 151.69 s (=CO). ^{31}P NMR spectrum, δ_P, ppm: –2.22 s.

Bis(trimethylsilyl) [1-(pyridin-3-ylmethylene)-inden-2-yl]phosphonate (IId). Yield 72%, bp 200°C (1 mm Hg), mp 65°C. ^{13}C NMR spectrum, δ_C, ppm: 133.33 d (C^1, $^1J_{PC}$ 208.2 Hz), 135.85 d (C^2, $^2J_{PC}$ 12.3 Hz), 142.70 d (C^3, $^2J_{PC}$ 12.5 Hz), 141.25 d (C^4, $^3J_{PC}$ 15.9 Hz) and 141,93 d (C^4, $^3J_{PC}$ 20.9 Hz), 136.75 s (C^5), 149.10 s (C=N) and 149.53 s (C=N). ^{31}P NMR spectrum, δ_P, ppm: –3.3 s.

Disodium inden-2-ylphosphonate (III). To a solution of 1.1 g of sodium methylate in 30 ml of methanol, a solution of 3.4 g of phosphonate **I** in 5 ml of diethyl ether was added with stirring and cooling to 10°C. The resulting mixture was heated to boiling, the solvent was distilled off, and the residue was kept in a vacuum (1 mm Hg) for 1 h to give 2.3 g (96%) of salt **III**. ^{1}H NMR spectrum, δ, ppm: 3.65 s (C^2H_2), 7.2–7.6 m (5 CH, C_9H_7). ^{13}C NMR spectrum, δ_C, ppm: 147.11 d (C^1, $^1J_{PC}$ 176.2 Hz), 40.68 d (C^2, $^2J_{PC}$ 11.9 Hz), 135.91 d (C^3, $^2J_{PC}$ 10.7 Hz), 144.64 d (C^4, $^3J_{PC}$ 18.9 Hz) and 145.62 d (C^4, $^3J_{PC}$ 10.7 Hz). ^{31}P NMR spectrum, δ_P, ppm: 10.70 s. Found, %: C 44.91; H 3.03. $C_9H_7Na_2O_3P$. Calculated, %: C 45.02; H 2.94.

Salts **IVa**–**IVd** were prepared in a similar way.

Disodium (1-benzylideneinden-2-yl)phosphonate (IVa). Yield 97%. ^{13}C NMR spectrum, δ_C, ppm: 143.22 d (C^1, $^1J_{PC}$ 174,4 Hz), 136.09 d (C^2, $^2J_{PC}$ 8.4 Hz), 136.68 d (C^3, $^2J_{PC}$ 9.8 Hz), 139.98 d (C^4, $^3J_{PC}$ 12.09 Hz) and 143.64 d (C^4, $^3J_{PC}$ 20.4 Hz), 136.43 s (C^4). ^{31}P NMR spectrum, δ_P, ppm: 7.81 s. Found, %: C 58.43; H 3.41. $C_{16}H_{11}Na_2O_3P$. Calculated, %: C 58.55; H 3.38.

Disodium (4-methoxybenzylideneinden-2-yl)-phosphonate (IVb). Yield 97%. ^{1}H NMR spectrum, δ, ppm: 3.78 s (CH_3O). ^{13}C NMR spectrum, δ_C, ppm: 143.31 d (C^1, $^1J_{PC}$ 172.9 Hz), 135.97 d (C^2, $^2J_{PC}$

8.3 Hz), 135.65 d (C^3, $^2J_{PC}$ 9.5 Hz), 139.76 d (C^4, $^3J_{PC}$ 12.8 Hz) and 143.57 d (C^4, $^3J_{PC}$ 16.0 Hz), 137.08 s (C^5), 159.08 s (=CO), 55.54 s (CH_3O). ^{31}P NMR spectrum, δ_P, ppm: 8.11 s. Found, %: C 56.89; H 3.74. $C_{17}H_{13}Na_2O_4P$. Calculated, %: C 57.00; H 3.66.

Disodium (1-furfurylideneinden-2-yl)phosphonate (IVc). Yield 95%. ^{13}C NMR spectrum, δ_C, ppm: 143.86 d (C^1, $^1J_{PC}$ 173.3 Hz), 135.78 d (C^3, $^2J_{PC}$ 11.4 Hz), 136.49 d (C^4, $^3J_{PC}$ 12.1 Hz) and 143.52 d (C^4, $^3J_{PC}$ 17.4 Hz), 128.32 s (C^5), 145.45 s (=CHO), 152.18 s (=CO). ^{31}P NMR spectrum, δ_P, ppm: 8.32 s. Found, %: C 52.64; H 2.91. $C_{14}H_9Na_2O_4P$. Calculated, %: C 52.85; H 2.85.

Disodium [1-(pyridin-3-ylmethylene)inden-2-yl]phosphonate (IVd). Yield 98%. ^{13}C NMR spectrum, δ_C, ppm: 143.30 d (C^1, $^1J_{PC}$ 175.5 Hz), 135.97 d (C^2, $^2J_{PC}$ 7,2 Hz), 137.82 d (C^3, $^2J_{PC}$ 11.6 Hz), 142.91 d (C^4, $^3J_{PC}$ 11.8 Hz) and 144.08 d (C^4, $^3J_{PC}$ 16.8 Hz), 137.26 s (C^5), 149.68 s (C=N) and 150.04 s (C=N). ^{31}P NMR spectrum, δ_P, ppm: 7.26 s. Found, %: C 54.59; H 3.04. $C_{15}H_{10}NNa_2O_3P$. Calculated, %: C 54.73; H 3.06.

The NMR spectra were recorded on a Varian VXR-400 spectrometer in $CDCl_3$ or D_2O (**III, IV**) against TMS (^1H, ^{13}C) and 85% phosphoric acid in D_2O (^{31}P).

REFERENCES

1. Prishchenko, A.A., Livantsov, M.V., Novikova, O.P., Livantsova, L.I., Koval’, Ya.N., and Grigor’ev, E.V., *Zh. Obshch. Khim.*, 2003, vol. 73, no. 10. p. 1753; Prishchenko, A.A., Livantsov, M.V., Novikova, O.P., Livantsova, L.I., Koval’, Ya.N., and Grigor’ev, E.V., *Zh. Obshch. Khim.*, 2003, vol. 73, no. 11, p. 1930.
2. Bergmann, E. and Bondi, A., *Chem. Ber.*, 1930, vol. 63, no. 5, p. 1158.