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LETTERS TO THE EDITOR

New Type of Phosphorus-Containing Aldehydes

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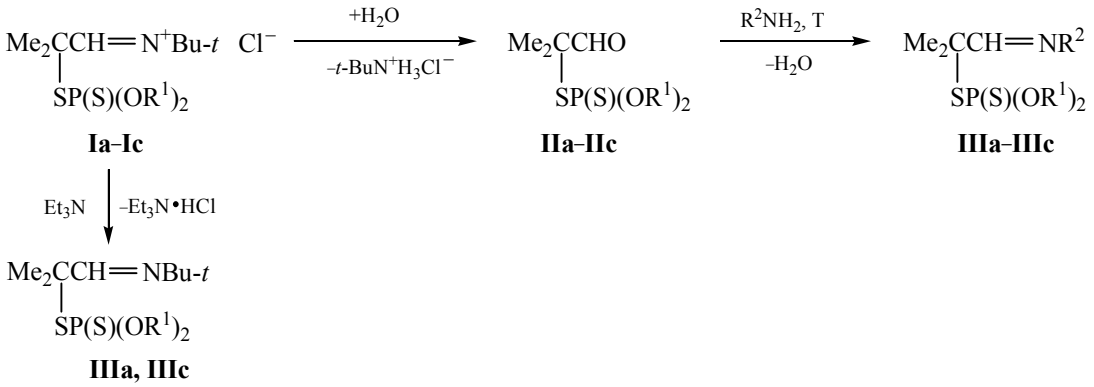
Phosphorylated aldehydes are commonly used in synthetic organic and hetero-organic chemistry [1, 2]. They can be conventionally divided into two groups: compounds with P(IV)–C bond and those with P(IV)–X bond. Compounds of the first type with the phosphoryl group separated from the aldehyde moiety by *n*-membered carbon chain, $R^1R^2P(O)(CR^3R^4)_nCHO$ (n = 0–16), have been described in detail in [1]. Aldehydes of the second type $R^1{}_2P(O)XCR^2R^3CHO$ [X = N, O, S] have been reported in [2]. Aldehydes with the $R^1{}_2P(O)$–N fragment have been obtained earlier [3] via reaction of hydrophosphoryl compounds with 3-(ethylamino)aldehyde under the Todd–Atherton reaction conditions. Phosphorus-containing aldehydes with a thiol moiety synthesized via hydrolysis of the corresponding acetals have been known [4]. However, data on their dithiophosphoric analogs has not been found in the literature.

We herein demonstrate that hydrolysis of the corresponding immonium salts **I** (obtained via reaction of *O*,*O*-dialkyldithiophosphoric acids with *N*-alkyl-2-chloraldimines [5]) results in the formation of 2-methyl-2-(*O*,*O*-dialkyl)dithiophosphatopropanals or *O*,*O*-di-alkyl *S*-(1,1-dimethyl-2-oxoethyl)dithiophosphates **IIa**–**IIc**.

The aldehydes **IIa**–**IIc** were prepared for the first time; they are promising synthons for synthesis of polyfunctional P,S- and N,P,S-containing organic compounds potentially having a wide spectrum of biological activity and complexing properties. For example, their interaction with primary amines gave the corresponding imines **IIIa**–**IIIc**. The latter could be obtained as well via authentic synthesis (treating the salts **Ia**–**Ic** with triethylamine) (Scheme 1).

Scheme 1.



I, II, R^1 = *i*-Pr (**a**), Et (**b**), *n*-Bu (**c**); **III**, R^1 = *i*-Pr, R^2 = *t*-Bu (**a**), *i*-Pr (**b**); R^1 = Bu, R^2 = Bu-*t* (**c**).

Composition and structure of the prepared compounds were confirmed by elemental analysis, ^{1}H and ^{31}P NMR spectroscopy.

***O*,*O*-Diethyl *S*-(1,1-dimethyl-2-oxoethyl)dithiophosphate (IIb).** 7.08 g of (0.038 mol) of *O*,*O*-diethyldithiophosphoric acid was added dropwise at 0–5°C to a solution of 6.20 g (0.038 mol) of *N*-*tert*-butyl-2-methyl-2-chloropropaneimine in 50 mL of anhydrous CCl_4. The mixture was stirred at room temperature for 6 h. Then 2–3 drops of conc. hydrochloric acid in 10 mL (0.56 mol) of water were added to the obtained immonium salt **Ib** at 10–15°C. The reaction mixture was stirred at room temperature for 1 h. The organic layer was separated, dried over magnesium sulfate, and evaporated. The residue was distilled under vacuum. Yield 7.31 g (75%), bp 84–85°C (0.08 mmHg), n_D^{20} 1.5109. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.43 t (6H, $\underline{CH_3}CH_2$, $^3J_{HH}$ 7.0 Hz), 1.54 d (6H, CMe_2, $^4J_{PH}$ 1.0 Hz), 4.2 m (4H, $Me\underline{CH_2}$), 9.44 s (1H, CHO). ^{31}P NMR spectrum (CCl_4): δ_P 86.80 ppm. Found, %: C 37.61; H 6.51; P 12.16; S 24.89. $C_8H_{17}O_3PS_2$. Calculated, %: C 37.49; H 6.69; P 12.09; S 25.01.

***O*,*O*-Diisopropyl *S*-(1,1-dimethyl-2-oxoethyl)dithiophosphate (IIa)** was prepared similarly from 5.65 g (0.035 mol) of *N*-*tert*-butyl-2-methyl-2-chloropropaneimine, 7.50 g (0.035 mol) of *O*,*O*-diisopropyldithiophosphoric acid, and 50 mL of carbon tetrachloride. Yield 7.03 g (74%), bp 88–89°C (0.1 mmHg), n_D^{20} 1.4971. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.42 d and 1.45 d (12H, $CH\underline{Me_2}$, $^3J_{HH}$ 6.0 Hz), 1.58 d (6H, CMe_2, $^4J_{PH}$ 1.0 Hz), 4.90 d. septets (2H, POCH, $^3J_{HH}$ 6.0, $^3J_{PH}$ 12.1 Hz), 9.54 s (1H, CHO). ^{31}P NMR spectrum (CCl_4): δ_P 84.08 ppm. Found, %: C 42.37; H 7.52; P 11.02. $C_{10}H_{21}O_3PS_2$. Calculated, %: C 42.24; H 7.44; P 10.89.

***O*,*O*-Dibutyl *S*-(1,1-dimethyl-2-oxoethyl)dithiophosphate (IIc)** was prepared similarly from 3.38 g (0.021 mol) *N*-*tert*-butyl-2-methyl-2-chloropropaneimine, 5.09 g (0.021 mol) of *O*,*O*-dibutyldithiophosphoric acid, and 30 mL of carbon tetrachloride. Yield 4.72 g (72%), bp 103–105°C (0.07 mmHg), n_D^{20} 1.5011. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.06 t (6H, $\underline{Me}CH_2$, $^3J_{HH}$ 7.0 Hz), 1.58 d (6H, Me_2CH, $^4J_{PH}$ 1.1 Hz), 1.33–2.05 m (8H, CH_2CH_2), 4.15 m (4H, $POCH_2$), 9.15 s (1H, CHO). ^{31}P NMR spectrum (CCl_4): δ_P 87.40 ppm. Found, %: C 49.91; H 9.18; P 7.92. $C_{12}H_{25}O_3PS_2$. Calculated, %: C 49.72; H 9.13; P 8.01.

***O*,*O*-Diisopropyl *S*-[1,1-dimethyl-2-(*N*-*tert*-butylimino)ethyl]dithiophosphate (IIIa).** *a*. A mixture of 3 g (0.01 mol) of aldehyde **IIa** and 0.73 g (0.01 mol) of *tert*-butylamine in 30 mL of benzene was refluxed during 6 h. Then benzene was removed, and the residue was distilled. Yield 2.7 g (79.6%), bp 93–94°C (0.05 mmHg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.31 s (9H, CMe_3), 1.46 d and 1.48 d (12H, $\underline{Me_2}CHO$, $^3J_{PH}$ 6.1 Hz), 1.68 d (6H, CMe_2, $^4J_{PH}$ 1.4 Hz), 4.96 d. septets (2H, $O\underline{CH}Me_2$, $^3J_{HH}$ 6.1, $^3J_{PH}$ 11.2 Hz), 7.95 s (1H, CH=N). ^{31}P NMR spectrum (CCl_4): δ_P 86.70 ppm. Found, %: C 49.63; H 8.99; P 8.97; S 18.69. $C_{14}H_{30}NO_2PS_2$. Calculated, %: C 49.54; H 8.91; P 9.12; S 18.87.

b. 1.62 g (16 mmol) of triethylamine was added dropwise at –5–0°C to a solution of 6.2 g (0.016 mol) of compound **Ia** in 25 mL of diethyl ether. The mixture was stirred for 3 h at room temperature. Triethylamine hydrochloride was filtered off, and the solvent was removed. The residue was distilled. Yield 4.1 g (77%), bp 91–92°C (0.02 mmHg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.31 s (9H, $C\underline{Me_3}$), 1.46 d and 1.48 d (12H, $\underline{Me_2}CHO$, $^3J_{HH}$ 6.1 Hz), 1.68 d (6H, CMe_2, $^4J_{PH}$ 1.4 Hz), 4.96 d. septets (2H, $O\underline{CH}Me_2$, $^3J_{HH}$ 6.1, $^3J_{PH}$ 11.2 Hz), 7.95 s (1H, CH=N). ^{31}P NMR spectrum (CCl_4): δ_P 86.70 ppm. Found, %: C 49.63; H 8.99; P 8.97; S 18.69. $C_{14}H_{30}NO_2PS_2$. Calculated, %: C 49.54; H 8.91; P 9.12; S 18.87.

c. 15.0 g (0.07 mol) of *O*,*O*-diisopropyldithiophosphoric acid was added dropwise upon stirring at 0–5°C to a solution of 11.3 g (0.07 mol) of *N*-*tert*-butyl-2-methyl-2-chloropropaneimine **Ia** in 50 mL of diethyl ether. The mixture was allowed to stand at 25°C for 24 h. Then, the mixture was treated with 7.1 g (0.07 mol) of triethylamine at 0–5°C. After stirring for 3 h, triethylamine hydrochloride was filtered off, and the solvent was removed. The residue was distilled in vacuum. Yield 16.8 g (71%), bp 86–87°C (0.02 mmHg).

***O*,*O*-Diisopropyl *S*-[1,1-dimethyl-2-(*N*-isopropylimino)ethyl]dithiophosphate (IIIb)** was prepared similarly via the method *a* from 3 g (0.01 mol) of the aldehyde **IIa**, and 0.6 g (0.01 mol) of isopropylamine. Yield 2.6 g (80%), bp 95–96°C (0.07 mmHg), n_D^{20} 1.4942. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.08 d (6H, $NCH\underline{Me_2}$, $^3J_{HH}$ 6.3 Hz), 1.30 d and 1.27 d (12H, $\underline{Me_2}CHO$, $^3J_{HH}$ 6.2 Hz), 1.50 d (6H, CMe_2, $^4J_{PH}$ 1.6 Hz), 3.30 q and 3.29 q (1H, $N\underline{CH}Me_2$, $^3J_{HH}$ 6.3 Hz), 4.77 d. septets (2H, CHOP, $^3J_{HH}$ 6.2, $^3J_{PH}$ 12 Hz), 7.76 s (1H, CH=N). ^{31}P NMR spectrum (CCl_4): δ_P 88.10 ppm.

Found, %: C 47.72; H 8.77; P 9.68; N 4.47. $C_{13}H_{28}NO_2PS_2$. Calculated, %: C 47.98; H 8.67; P 9.52; N 4.30.

***O*,*O*-Dibutyl *S*-[1,1-dimethyl-2-(*N*-*tert*-butylimino)-ethyl]dithiophosphate (IIIc)** was prepared similarly via the method *b* from 5.8 g (0.014 mol) of the immonium salt **Ic** and 1.42 g (0.014 mol) of triethylamine. Yield 4.06 g (79%), bp 126–127°C (0.08 mmHg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.08 t (3H, MeCH_2, $^3J_{HH}$ 7.0 Hz), 1.28 s (9H, CMe_3), 1.48 d (6H, CMe_2, $^4J_{PH}$ 1.2 Hz), 1.35–2.01 m (8H, CH_2CH_2), 4.02–4.43 m (4H, $POCH_2$), 7.84 s (1H, CH=N). ^{31}P NMR spectrum (CCl_4): δ_P 90.22 ppm. Found, %: C 52.40; H 9.48; P 8.31; N 3.67. $C_{16}H_{34}NO_2PS_2$. Calculated, %: C 52.29; H 9.33; P 8.33; N 3.81.

^{1}H and ^{13}C NMR spectra were recorded with an AVANCE 400 WB spectrometer (400.13 and 100.61 MHz, respectively) in $CDCl_3$ relative to internal TMS. ^{31}P NMR spectra were registered with an AVANCE 400 WB (161.98 MHz) and BrukerMSL-400 (162 MHz) spectrometers relative to external 85% H_3PO_4.

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