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Tertiary Phosphine Oxides in Reaction with Benzaldehyde

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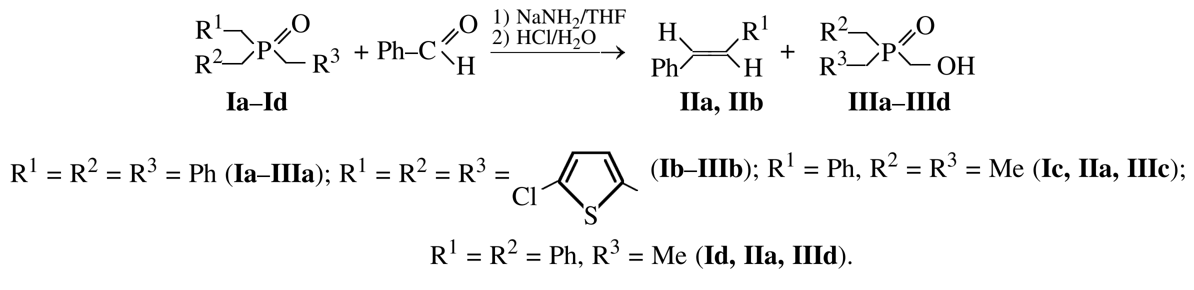
Abstract—Symmetrical and unsymmetrical tertiary phosphine oxides containing benzyl and 5-chloro-2-thienyl radicals stereoselectively react with benzaldehyde in the sodium amide–THF system to form the *E* isomers of 1-organyl-2-phenylethene and diorganylphosphinic acids in high yields. Triethyl, tris(2-phenylethyl)-, and tris[(4-methoxyphenyl)methyl]phosphine oxides under the above-mentioned conditions do not react with benzaldehyde.

Recently we reported [1–3] that symmetrical tribenzylphosphine oxide **Ia** under conditions of the Wittig–Horner reaction have opened fresh opportunities for stereoselective synthesis of 1,2-disubstituted alkenes, including functionally substituted alkenes and their hetero analogs, which are promising optical switches and photochemical sensors [4, 5], intermediate products for production of dyes, optical bleachers, complex-forming agents and clusters [6], drugs [7, 8], and natural antioxidants and chelating agents like pinosylvin and resveratrol [8, 9].

In the present work, with the purpose of extending the preparative potential of the Wittig–Horner reaction, we have explored the reactivity of new available (prepared from elemental phosphorus and organyl halides or styrene) symmetrical and unsymmetrical tertiary phosphine oxides [10–12] toward benzaldehyde.

It was found that in the reaction studied, along with tribenzylphosphine oxide (**Ia**), its hetero analog, tris[(5-chloro-2-thienyl)methyl]phosphine oxide (**Ib**), as well as unsymmetrical benzyldiethyl- and dibenzylethylphosphine oxides (**Ic, Id**) can be successfully used. Successive treatment of phosphine oxides **Ia**–**Id** with $NaNH_2$–THF, benzaldehyde (at 58–60°C), and aqueous HCl (at room temperature) gives the *E* isomers of 1,2-diphenylethene (**IIa**) (with phosphine oxides **Ia, Ic, Id**) and 1-thienyl-2-phenylethene (**IIb**) (with phosphine oxide **Ib**). In this way we also prepared previously unknown or hardly available dibenzyl, bis[(5-chloro-2-thienyl)methyl]-, diethyl-, and benzylethylphosphinic acids **IIIa**–**IIId** in yields of up to 65%.



(1)

The electron-acceptor phenyl and thienyl radicals in the methylenephosphoryl group in phosphine oxides **Ia**–**Id** favor reaction (1) by stabilizing intermediate carbanion **A**. At the same time, tris[(4-methoxyphenyl)methyl]phosphine oxide under the above conditions fails to react with benzaldehyde, which can be explained by destabilization of the carbanion by the electron-donor methoxy group (p–π conjugation).

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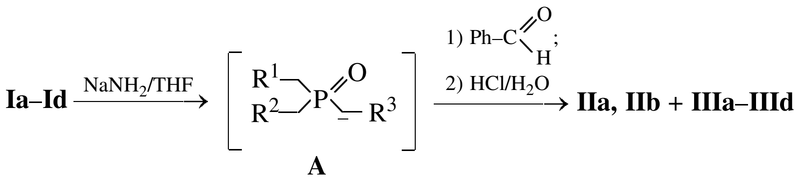

(2)

An even stronger anion-destabilizing effect is characteristic by alkyl and phenylalkyl radicals, because of which we could involve triethyl- and tris(2-phenylethyl)phosphine oxides in reaction (1).

These results complement the known data [13] concerning the determining role of the nature of substituents in triorganylphosphine oxides in their deprotonation under conditions of the Wittig–Horner reaction. The synthetic material presented in this work considerably extends the range of application of the Wittig–Horner reaction for stereoselective synthesis of substituted stylbenes and suggest that this strategy can be succssfully extended to hetero analogs of benzyl halides having substituents in the heteroring.

EXPERIMENTAL

The ^1H and ^{31}P NMR spectra were recorded on a Bruker DPX-400 spectrometer in $CDCl_3$ against internal HMDS and external 85% phosporic acid, respectively. The IR spectra were recorded on a Specord 75-IR spectrometer.

Synthesis of 1-organyl-2-phenylethenes IIa, IIb and diorganylphosphinic acids IIIa–IIId (*general procedure*. Sodium amide, 6.6 mmol, was added to a solution of 2.2 mmol of triorganylphosphine oxide in 40 ml of THF heated to 58–60°C. The resulting mixture was stirred for 1 h at 58–60°C and, after 2.2 mmol of benzaldehyde had been added, refluxed for 1 h, cooled, diluted with 35 ml of water, and extracted with ether (3 × 10 ml). The ethereal extract was washed with water (2 × 8 ml), dried over potassium carbonate, the ether was removed, and the residue was dried in a vacuum to obtain (*E*)-1-organyl-2-phenylethene **IIa, IIb**. The aqueous layers were combined and acidified with 2 N HCl to pH 2–3. The precipitate that formed was successively washed with water, ethanol, ether, and dried in a vacuum to obtain diorganylphosphinic acid **IIIa, IIIb**. In the case of formation of water-soluble acids, the aqueous fraction was acidified and extracted with chloroform to obtain acid **IIIc, IIId**. Acid **IIId** was not isolated pure, and is probably present in the aqueous fraction among four organophosphorus compounds (δ_P 49.48, 46.20, 45.36, and 38.09 ppm, integral intensity ratio the ^{31}P NMR signals 20 : 48 : 10 : 22).

***E*-1,2-Diphenylethene (IIa)**, yield 88, 70, and 62% from phosphine oxides **Ia, Ic**, and **Id**, respectively. The constants and spectral data of ethene **IIa** agree with those reported in [1, 14].

***E*-1-(5-Chloro-2-thienyl)-2-phenylethene (IIb),** yield 71%, mp 66-68°C. ^1H NMR spectrum, δ, ppm: 6.79 s, 6.80 s (2H, H^3, H^4), 6.78 d (1H, H^α, $^3J_{HH}$ 15.8 Hz), 7.06 d (1H, H^β, $^3J_{HH}$ 15.8 Hz), 7.24 t (1H, H_p), 7.33 t (2H, H_m), 7.43 d (2H, H_o). The H^α and H^β signals were assigned on the basis of the ^1H–^1H NOEZSY spectrum which showed a cross peak corresponding to H^β–H_o coupling. Since the signals of H^3 and H^4 protons and one of the components of the H^α doublet in the ^1H NMR spectrum overlap, the H,C-correlation (HMQC) experiment was performed for signal assignment. ^{13}C NMR spectrum, δ_C, ppm: 124.03 (C^β), 128.02 (cross peak with the proton at 6.80, C^3, or C^4), 129.02 (C_o), 129.40 (cross peak with the proton at 6.79, C^3, or C^4), 130.54 (C_p), 131.22 (C^α), 131.43 (C_m). Found, %: C 64.83; H 4.08; Cl 16.11; S 14.39. $C_{12}H_9ClS$. Calculated, %: C 65.30; H 4.11; Cl 16.06; S 14.53.

Dibenzylphosphinic acid (IIIa), yield 65%, mp 189–190°C (from ethanol) (published data [15]: mp 191°C). ^1H NMR spectrum, δ, ppm: 2.85 d (4H, CH_2, $^2J_{PH}$ 16.9 Hz), 7.21 m (10H, C_6H_5), 9.02 s (1H, OH). ^{31}P NMR spectrum, δ_P, ppm: 49.48. Found, %: C 67.92; H 6.13; P 12.71. $C_{14}H_{15}O_2P$. Calculated, %: C 68.29; H 6.14; P 12.58.

Bis[(5-chloro-2-thienyl)methyl]phosphinic acid (IIIb), yield 39%, mp 168–170°C (from ethanol). ^1H NMR spectrum, δ, ppm: 3.16 d (4H, CH_2P, $^2J_{PH}$ 16.3 Hz), 6.77 t (2H, H^3), 6.99 d (2H, H^4, $^3J_{HH}$ 4.0 Hz). ^{31}P NMR spectrum, δ_P, ppm: 46.6. Found, %: C 36.83; H 2.73; Cl 21.68; P 9.56; S 19.43. $C_{10}H_9Cl_2O_2PS_2$. Calculated, %: C 36.71; H 2.77; Cl 21.67; P 9.47; S 19.60.

Diethylphosphinic acid (IIIc), yield 48%, bp 194–195°C (21 mm) [16]. ^1H NMR spectrum, δ, ppm: 1.05 t (6H, CH_3), 1.81 m (4H, CH_2), 9.08 s (1H, OH). ^{31}P NMR spectrum, δ_P, ppm: 51.8. Found, %: C 39.87; H 9.23; P 25.66. $C_4H_{11}O_2P$. Calculated, %: C 39.35, H 9.08, P 25.37.

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