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SHORT COMMUNICATIONS

Reactions of Phosphines with Aluminum Carbenoids

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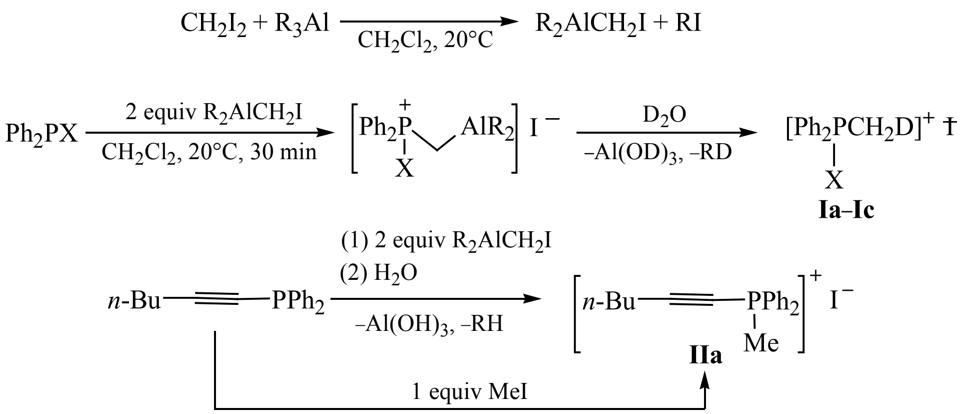
Metal carbenoids are known as highly reactive compounds that are often used as intermediates in the organic synthesis [1, 2]. We formerly studied the reactions with acetylenes of various structures of aluminum carbenoids obtained *in situ* from CH_2I_2 and trialkylalanes [3–5]. It was established that the structure of compounds obtained and the mechanism of their formation essentially depended on the nature of the substituent at the acetylene bond. In order to elucidate the role of the nature of the substituent at the acetylene bond we studied the transformation of organophosphorus acetylenes under the action of the aluminum carbenoids.

The reaction of hex-1-yn-1-yl(diphenyl)phosphine with the obtained in situ diethyl(iodomethyl)aluminum Et_2AlCH_2I [6] after treating the mixture with deuterium oxide afforded 1-hexynyl-(deuteromethyl) diphenylphosphonium iodide (**Ia**) in a quantitative yield.

The structure of the compound obtained was confirmed by an authentic synthesis of hex-1-yn-1-yl(diphenyl) phosphonium iodide (**IIa**) by the reaction of hex-1-yn-1-yl(diphenyl)phosphine with 1 equiv of MeI without solvent The ^{13}C and ^{1}H NMR spectra of thus prepared phosphonium salt and the hydrolysis product of the reaction mixture were identical.

In the ^{13}C NMR spectrum of compound **Ia** a doublet of triplets was observed at δ 14.00 ppm due to the coupling of carbon atom with phosphorus and deuterium nuclei.

Thus it was established that the reaction of (hex-1-yn-1-yl)diphenylphosphine with aluminum carbenoid Et_2AlCH_2I led to the formation of a phosphonium salt, and the acetylene bond was not involved into the reaction. In this case the C–I bond in the aluminum carbenoid was more reactive than the metal–carbon bond. Besides the



X = hex-1-yn-1-yl (**a**), Ph (**b**), *n*-Bu (**c**); R = Et, *i*-Bu.

phosphonium substituent evidently reduced the reactivity of the acetylene bond by decreasing its nucleophilicity.

Inasmuch as the reaction with the aluminum carbenoids proceeded exclusively at the phosphine center we studied the behavior in this reaction of a series of phosphines like Ph_3P, Ph_2PBu-*n*. In all events phosphonium salts formed in the reaction with large yields independent of the nature of the trialkylalane [Et_3Al, $(i\text{-}Bu)_3Al$] used for the generation of the aluminum carbenoid.

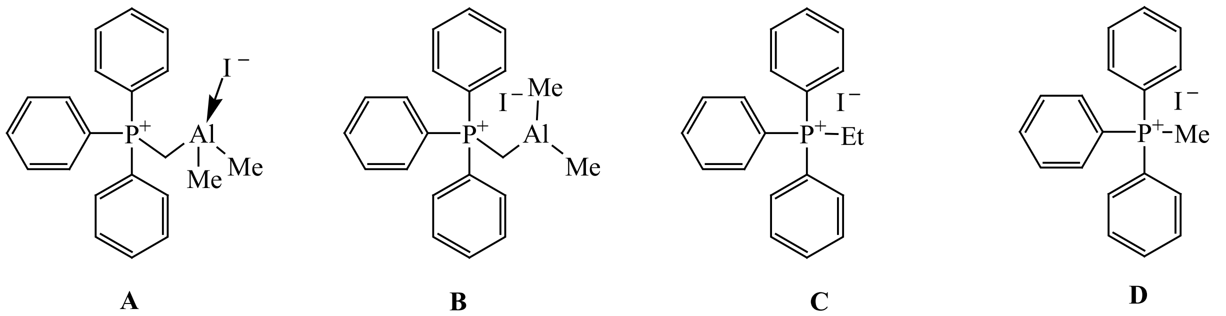
Notwithstanding the presence in the reaction mixture of iodoethane forming in the reaction of CH_2I_2 with R_3Al (R = Et, *i*-Bu) the phosphine reacted exclusively with the aluminum carbenoid R_2AlCH_2I. We believe that it results from the greater stabilization of the iodide anion in structure **A** that we assume to form as a result of the reaction (Fig. 1). Actually, the quantum-chemical calculations of structures **A**–**D** (to simplify the calculations methyl groups were used as alkyl substituents at the aluminum) in the basis 3-21+G* showed the energetical preference of the iodide anion coordination at the aluminum atom.

Thus we established that organophosphorus disubstituted acetylenes in contrast to their organosilicon analogs under the action of the aluminum carbenoids were not converted into compounds of cyclopropane series, but formed phosphonium salts.

Reaction of phosphines with aluminum carbenoids. General procedure. Into a reactor cooled to 0°C under the atmosphere of dry argon was charged 5 ml of CH_2Cl_2, 2 mmol of trialkylalane [Et_3Al or $(i\text{-}Bu)_3Al$], and 0.16 ml (2 mmol) of CH_2I_2, and the mixture was stirred for 1 h at 20°C. To the formed solution of the aluminum carbenoid 2 mmol of an appropriate phosphine was added, the reaction mixture was stirred for 30 min, then it was hydrolyzed with 5 ml of water, and filtered. The water layer was extracted with ethyl ether, the extract was combined with the organic layer, dried with $CaCl_2$, the solvents were distilled off in a vacuum. Phosphonium salt **Ia** was isolated by column chromatography on silica gel, eluent ethyl acetate–ethanol, 2:1 v/v. Compounds **Ib, Ic** were recrystallized from ethanol.

Hex-1-yn-1-yl(deuteromethyl)diphenylphosphonium iodide (Ia). Yield 94%. Viscous oily yellow fluid, R_f 0.4 (eluent ethyl acetate–ethanol, 4 : 1 v/v). ^1H NMR spectrum, δ, ppm (Fig. 2): 0.84 t (3H, CH_3, *J* 7.2 Hz), 1.3–1.4 m (2H, $C^{10}H_2$), 1.55–1.65 m (2H, C^9H_2), 2.6–2.7 m (2H, C^8H_2), 2.89 d (2H, $C\underline{H}_2DP$, *J* 14.0 Hz), 7.5–8.2 m (10H, Ph). ^{13}C NMR spectrum, δ, ppm: 13.40 (C^{11}), 14.00 d.t (C^1, *J* 20.5, *J* 62.4 Hz), 20.64 (C^8), 22.05 (C^{10}), 28.94 (C^9), 61.70 d (C^6, $^1J_{CP}$ 182.3 Hz), 119.40 d (C^2, $^1J_{CP}$ 98.5 Hz), 123.65 d (C^7, $^1J_{CP}$ 30.6 Hz), 130.40 d (C^4, $^1J_{CP}$ 14.2 Hz), 132.24 d (C^3, $^1J_{CP}$ 12.6 Hz), 135.26 d (C^5, $^1J_{CP}$ 2.4 Hz). Found, %: C 55.43; I 29.11. $C_{19}H_{21}DIP$. Calculated, %: C 55.76; I 31.01.

(Deuteromethyl)triphenylphosphonium iodide



$\Delta(\Delta_r^{298}G^o)$ 0 38.7 42.4 40.9 kcal mol^{-1}

Fig. 1. Calculated relative free Gibbs energy of the reaction of Ph_3P with Me_2AlCH_2I, EtI, and MeI (3-21+G*).

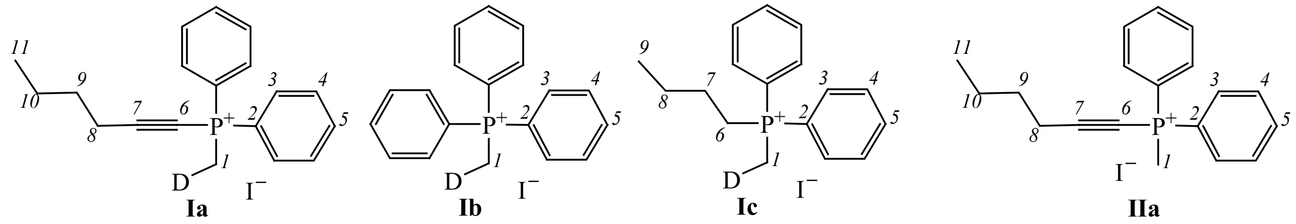


Fig. 2. Numeration of atoms in the ^1H and ^{13}C NMR spectra.

(Ib). Yield 92%. White crystals, mp 183.5–184°C. ^{1}H NMR spectrum, δ, ppm (Fig. 2): 3.10 d (2H, CH_2DP, J 12.8 Hz), 7.60–7.85 m (15H, Ph). ^{13}C NMR spectrum, δ, ppm: 11.46 d.t (C^{1}, J 20.0, J 57.0 Hz), 118.79 d (C^{2}, $^1J_{CP}$ 88.0 Hz), 130.56 d (C^{4}, $^1J_{CP}$ 12.8 Hz), 133.29 d (C^{3}, $^1J_{CP}$ 10.6 Hz), 135.30 (C^{5}). Found, %: C 56.12; I 29.70. $C_{19}H_{17}DIP$. Calculated, %: C 56.31; I 31.32.

Butyl(deuteromethyl)diphenylphosphonium iodide (Ic). Yield 95%. White crystals, mp 157.5–158°C. ^{1}H NMR spectrum, δ, ppm (Fig. 2): 0.84 t (3H, $C^{9}H_3$, J 6.0 Hz), 1.4–1.6 m (4H, $C^{7,8}H_2$), 2.74 d (3H, CH_2DP, J 13.2 Hz), 3.1–3.25 m (2H, $C^{6}H_2$), 7.55–8.0) m (10H, Ph). ^{13}C NMR spectrum, δ, ppm: 8.74 d.t (C^{1}, J 20.6, J 55.0 Hz), 13.61 (C^{9}), 23.04 d (C^{6}, $^1J_{CP}$ 50.6 Hz), 23.55 d (C^{7}, $^1J_{CP}$ 16.7 Hz), 24.08 d (C^{8}, $^1J_{CP}$ 4.2 Hz), 119.21 d (C^{2}, $^1J_{CP}$ 84.5 Hz), 130.35 d (C^{4}, $^1J_{CP}$ 12.4 Hz), 132.59 d (C^{3}, $^1J_{CP}$ 10.0 Hz), 134.81 d (C^{5}, $^1J_{CP}$ 3.0 Hz). Found, %: C 53.43; I 30.24. $C_{17}H_{21}DIP$. Calculated, %: C 53.00; I 32.94.

Hex-1-yn-1-yl(methyl)diphenylphosphonium iodide (IIa) was obtained from 1 mmol of hex-1-yn-1-yl(diphenyl)-phosphine and 0.14 g (1 mmol) of MeI at 20°C. Yield 97%, mp 158–158.5°C (ethanol). ^{13}C NMR spectrum, δ, ppm (Fig. 2): 13.41 (C^{11}), 14.31 d (C^{1}, $^1J_{CP}$ 61.2 Hz), 20.69 (C^{8}), 22.03 (C^{10}), 28.91 (C^{9}), 61.81 d (C^{6}, $^1J_{CP}$ 182.3 Hz), 119.42 d (C^{2}, $^1J_{CP}$ 98.5 Hz), 123.68 d (C^{7}, $^1J_{CP}$ 30.6 Hz), 130.44 d (C^{4}, $^1J_{CP}$ 14.2 Hz), 132.25 d (C^{3}, $^1J_{CP}$ 12.6 Hz), 135.33 d (C^{5}, $^1J_{CP}$ 2.4 Hz). Found, %: C 55.84; H 5.32. $C_{19}H_{22}IP$. Calculated, %: C 55.90; H 5.43.

Initial phosphines were prepared by the reaction of Ph_2PCl with the appropriate organomagnesium compounds in THF. Dichloromethane before use was distilled over P_2O_5. The reaction products were subjected to liquid chromatography on a Hewlett Packard 1050 instrument (column Zorbax ODS, 250 × 4.6 mm, eluent MeCN, flow rate 1 ml/min, UV detection at wavelength 254 nm). Elemental analysis was performed on an analyzer Karlo Erba 1106. Iodine analysis was carried out by Schoeniger combustion [7]. ^{1}H and ^{13}C NMR spectra were registered on a spectrometer Bruker Avance 400 (operating frequencies 400 and 100 MHz respectively), internal references TMS and $CDCl_3$. TLC was carried out on Silufol UV-254 plates, eluent ethyl acetate–ethanol, 4:1 v/v. The quantum-chemical calculations were performed with complete geometry optimization by RHF method in the basis 3-21+G* using GAMESS software [8].

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