tion with 1 or 2% nickel or 1% palladium possess a considerable dehydrogenation activity, and at 200 and 250 °C, the yield of acetone obtained from isopropyl alcohol reaches at least 80% of the equilibrium value.[4] The initial activity of these catalysts almost does not decrease within 6—9 h, and they are characterized by a high selectivity (77—90%).

No phase of crystalline rhenium was observed in the active reduced 2% Re + 2% Ni sample by X-ray phase analysis. This sample can be assumed to exist in the highly dispersed state.

Thus, the developed sibunite-supported bimetallic catalysts containing 1—2% Re in combination with 1—2% Ni or 1% Pd are active and selective in the dehydrogenation of isopropyl alcohol.

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Synthesis and transformations of acyloxy(chloromethyl)phosphonates and acyloxy(chloromethyl)phosphinates

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The reactions of *O*-phenyl chloromethylphosphonochloridate and bis(chloromethyl)phosphinous chloride with sodium acetate afford the corresponding acyloxyphosphonates and acyloxyphosphinates, which are readily transformed due to disproportionation into pyrophosphonates and pyrophosphinates.

Key words: chloromethylphosphonates, bis(chloromethyl)phosphinates, reaction, disproportionation, pyrophosphonates, pyrophosphinates.

Many of the dialkylacyl phosphates (phosphonates and phosphinates) known at present time obtained by the reactions of the corresponding P^{IV} acid chlorides with silver or lead salts of carboxylic acids.[1] The use of sodium or potassium acetates in these reactions gives no positive results. At the same time, we established[2] that chloromethylphosphonochloridates and bis(chloromethyl)phosphinous chlorides exhibit a substantially greater electrophilic activity in nucleophilic substitution reactions than dialkyl chlorophosphates, alkyl(aryl) phosphonochloridates, and dialkyl(aryl) phosphinous chlorides. This suggested success in reactions of chloromethylphosphonates and -phosphinates with sodium acetate. In fact, the reaction of AcONa with *O*-phenyl chloromethylphosphonochloridate (**1**) in MeCN at room temperature results in the almost quantitative formation of *O*-acetyl *O*-phenylchloromethylphosphonate (**2**) (δ_P 14.82), whose structure was confirmed by the data of IR and ^1H and ^{31}P NMR spectroscopy, and the composition was established by elemental analysis.

$$\underset{\mathbf{1}}{\mathrm{PhO(ClCH_2)P(O)Cl}} + \mathrm{AcONa} \xrightarrow[-\mathrm{NaCl}]{} \underset{\mathbf{2}}{\mathrm{PhO(ClCH_2)P(O)OC(O)Me}}$$

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It is known[1] that under drastic conditions during vacuum distillation, dialkylacyl phosphates disproportionate to the corresponding pyrophosphates and acyl chlorides. It turned out that the introduction of the withdrawing chloromethyl group to the phosphorus atom facilitates this process: upon heating at 60 °C for 2 h, phosphonate **2** is transformed completely into pyrophosphonate **3** and acetic anhydride.

$$2\ \mathbf{2} \longrightarrow \underset{\mathbf{3}}{PhO(ClCH_2)P(O){-}O{-}P(O)(CH_2Cl)OPh} + Ac_2O$$

The reaction of bis(chloromethyl)phosphinous chloride **4** with AcONa results immediately in the formation of pyrophosphinate **5**. The reaction course was monitored by ^{31}P NMR spectroscopy, which showed that after mixing of the reagents, the spectrum of the reaction mixture contained signals of the starting phosphinous chloride **4**, pyrophosphinate 5 (δ_P 38.03), and a minor quantity of intermediate *O*-acetyl bis(chloromethylphosphinate (**6**) (δ_P 35.86). After 1 day, the spectrum of the reaction mixture contained a single signal of the final product 5.

$$\underset{\mathbf{4}}{(ClCH_2)_2P(O)Cl} + \mathbf{1} \xrightarrow[-NaCl]{} \underset{\mathbf{6}}{(ClCH_2)P(O)OC(O)Me} \longrightarrow$$

$$\longrightarrow \underset{\mathbf{5}}{(ClCH_2)_2P(O){-}O{-}P(O)(CH_2Cl)_2} + Ac_2O$$

Thus, the presence of chloromethyl groups in chlorides of acids of tetracoordinated phosphorus makes it possible to obtain acyloxyphosphonates and acyloxyphosphinates in high yields by the reactions with sodium acetate and facilitates their disproportionation to anhydrides of carboxylic and phosphonic or phosphinic acids.

Experimental

^{31}P NMR spectra were obtained on a Bruker MSL-400 NMR spectrometer with a working frequency of 161.97 MHz using a 85% solution of H_3PO_4 as the external standard. ^1H NMR spectra were recorded on a Varian T-60 spectrometer with a working frequency of 60 MHz using TMS as the internal standard. IR spectra of compounds as thin films or suspensions in Nujol were obtained on an UR-20 spectrometer in the 400—3600 cm^{-1} frequency range.

***O*-Acetyl *O*-phenylchloromethylphosphonate (2).** Acid chloride **1** (6.75 g, 0.03 mol) was added dropwise to a solution of AcONa (2.46 g, 0.03 mol) in anhydrous MeCN (30 mL). After 24 h, NaCl was filtered off, and the filtrate was concentrated in a vacuum of an oil pump. Phosphonate **2** was obtained (6.75 g, 90.5%) as a viscous transparent mass with n_D^{20} 1.5242. Found (%): Cl, 15.03; P, 12.85. $C_9H_{10}ClO_4P$. Calculated (%): Cl, 14.26; P, 12.46. ^1H NMR (CCl_4), δ: 2.00 (s, 3 H, CH_3); 3.50 (d, 2 H, CH_2P, J = 10 Hz); 7.13 (m, 5 H, Ph). ^{31}P NMR, δ: 14.82. IR, ν/cm^{-1}: 1075 (P—O—Ph); 1210 (P=O); 1590 (Ph); 1705 (C=O).

Bis(*O*-phenyl chloromethyl)pyrophosphonate (3). Phosphonate **2** (2.95 g, 0.012 mol) was heated at 60 °C for 2 h. Acetic anhydride (1.0 g, 80.6%) with n_D^{20} 1.3923 [3] was distilled off (oil pump) and condensed in a trap with liquid nitrogen. Compound 3 with m.p. 34—35 °C and b.p. 115 °C (0.05 Torr) was obtained as the residue (2.87 g, 87.6%). Found (%): Cl, 17.70; P, 15.17. $C_{14}H_{14}C_{12}O_5P_2$. Calculated (%): Cl, 17.94; P, 15.68. ^1H NMR (CCl_4), δ: 3.47 (d, 2 H, CH_2P, J = 10 Hz); 7.10 (m, 5 H, Ph). ^{31}P NMR, δ: 13.84. IR, ν/cm^{-1}: 1080 (P—O—Ph); 1210 (P=O); 1590 (Ph).

Tetrakis(chloromethyl)pyrophosphinate (5). Acid chloride **4** (3.6 g, 0.02 mol) was added dropwise with stirring to a solution of AcONa (1.6 g, 0.02 mol) in anhydrous MeCN (20 mL). After 24 h, NaCl was filtered off, and the filtrate was evaporated in a vacuum of a water aspirator. The residue was recrystallized from anhydrous CH_2C_{12} to obtain compound 8 (3 g, 98%) with m.p. 70—71 °C.[4] ^1H NMR (CCl_4), δ: 3.86 (d, 8 H, CH_2P, J = 9 Hz). ^{31}P NMR, δ: 38.03.

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