ELECTROCHEMICAL SYNTHESIS OF DIFLUOROPHOSPHORANES

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We have studied the electrochemical oxidation of tertiary phosphines, R_3P, on a platinum electrode in acetonitrile in the presence of nonhygroscopic n-amylammonium fluoride, $C_5H_{11}NH_3F$. The electrolysis was carried out with a Teflon partition in a galvanostatic mode and a current density from 3.3 to 6.7 mA/cm^2. The base electrolyte was Et_4NBF_4. The reaction proceeds with the transfer of two electrons per tertiary phosphine molecule. A trialkyl- or triaryldifluorophosphorane, R_3PF_2, is formed in all cases. Apparently, the anodic oxidation may be represented by the following equation: $R_3P - 2e + 2C_5H_{11}NH_3F \rightarrow R_3PF_2 + 2C_5H_{11}NH_3$.

Triethyldifluorophosphorane was obtained in 80% yield, bp 53°C, n_D^{20} 1.4062. ^{31}P NMR spectrum (δ, ppm): −13 (J_{P-F} = 570 Hz). ^{19}F NMR spectrum (δ, ppm): 44.

Tripropyldifluorophosphorane was obtained in 82% yield, bp 76°C (9 mm), n_D^{20} 1.4249. ^{31}P NMR spectrum: δ −15 (J_{P-F} = 580 Hz). ^{19}F NMR spectrum: δ 42.

Tributyldifluorophosphorane was obtained in 85% yield, bp 72°C (1 mm), n_D^{20} 1.4332. ^{31}P NMR spectrum: δ −15 (J_{P-F} = 580 Hz). ^{19}F NMR spectrum: δ 43.

Tri-n-amyldifluorophosphorane was obtained in 78% yield, bp 129-130°C (3 mm), n_D^{20} 1.4420. ^{31}P NMR spectrum: δ −15 (J_{P-F} = 580 Hz). ^{19}F NMR spectrum: δ 41.

Phenyldiethyldifluorophosphorane was obtained in 69% yield, bp 62°C (2 mm), n_D^{20} 1.4688. ^{31}P NMR spectrum: δ 38 (J_{P-F} = 620 Hz). ^{19}F NMR spectrum: δ 40.

Triphenyldifluorophosphorane was obtained in 71% yield, mp 142°C. ^{31}P NMR spectrum: δ 58 (J_{P-F} = 680 Hz). ^{19}F NMR spectrum: δ 39.

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