The first quantitative preparation of bis(trimethylsilyl)acylphosphane by action of acyl halide on tris(trimethylsilyl)phosphane

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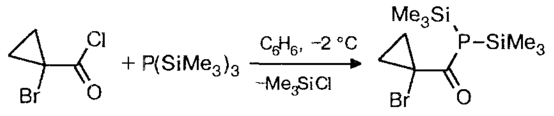
Previously, we showed that the reaction between various cyclobutane- and cyclopropanecarboxylic acid chlorides and tris(trimethylsilyl)phospane, leading to phosphoalkanes with small cycles, proceeds *via* the corresponding intermediate cyclobutyl- and cyclopropylcarbonyl-bis(trimethylsilyl)phosphanes. The presence of the latter in the reaction mixture can be revealed by NMR methods at temperatures ranging from −3 to ~20 °C. However, due to their low thermostability, even in such conditions they exists as mixtures with the starting reagents and the corresponding phosphaalkenes. Thus, to date no acyl-bis(trimethylsilyl)phosphane is known to have been isolated or identified in the individual state.

In the present work we describe the first example of preparation of a solution of acyl-bis(trimethylsilyl)phosphane in the pure state, by interaction between tris(trimethylsilyl)phosphane (**2**) and 1-bromocyclopropane carboxylic acid chloride. Thus, the addition of an equimolar amount of acyl chloride (**1**) in benzene or toluene to the phosphane (**2**) at temperatures below −2 °C under argon leads to the formation of the only (1-bromo-1-cyclopropylcarbonyl)-bis-(trimethylsilyl)phosphane (**3**) in quantitative yields (according to the data of ^{1}H, ^{13}C,and ^{31}P NMR). The solution contains neither the starting reagents, nor the corresponding phosphaalkene even in minor amounts.



1 **2** **3**, ~100 %

The thermal lability of acylphosphane (**3**) does not allow its isolation in individual state; however, the solution of **3** in toluene at a temperature below −2 °C in an inert atmosphere is distinguished by high stability and can be used in further chemical transformations.

The NMR spectra for compound **3** are in a good agreement with the reported data for comparable acylphosphanes[1–4].

^{1}H NMR -(toluene-d$_8$, −10 °C, δ,ppm, *J*/Hz): 0.26 (d, 18 H, 2 SiMe$_3$, $^3J_{PH}$ = 4.6); 1.09 (m, 2 H, CH$_2$); 1.53 (m, 2 H, CH$_2$). ^{13}C{^{1}H} NMR spectra (toluene-d$_8$, −10 °C, δ,ppm, *J*/Hz): 1.89 (d, 2 SiMe$_3$, $^2J_{PC}$ = 10.1); 21.5 (s, CH$_2$); 21.6 (s, CH$_2$); 40.8 (d, C—Br, $^2J_{PC}$ = 47.1); 219.1 (d, C=O, $^1J_{PC}$ = 49.2). ^{31}P NMR spectra (toluene-d$_8$, −10 °C, δ,ppm): −81.7.

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