Acyl Iodides in Organic Synthesis: X.* Reactions with Triorganylsilanes and Triphenylgermane

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Abstract—Reaction of acyl iodides RCOI (R = Me, Ph) with triorganylsilanes $R'_2R''SiH$ in toluene gives 50–60% of the corresponding triorganyliodosilanes $R'_2R''SiI$. Triethylsilane reacts with the same acyl iodides under solvent-free conditions to afford the corresponding aldehyde and triethyliodosilane as primary products. Triethyliodosilane undergoes subsequent transformations into hexaethyldisiloxane and triethyl(acyloxy)silane $Et_3SiOCOR$ (R = Me, Ph). Reactions of acyl iodides RCOI (R = Me, Ph) with triphenylgermane in the absence of a solvent lead to formation of iodo(triphenyl)germane in more than 90% yield.

Methods have been reported previously for the synthesis of trialkyliodosilanes via reactions of hexaalkyldisiloxanes with AlI_3 [2] or with iodine and aluminum [3], as well as by iodination of trialkylsilanes with iodine or hydrogen iodide [4] and iodobenzene in the presence of nickel colloid generated *in situ* [5]. With a view to reveal general relations holding in reactions of triorganylsilanes with the above iodinating agents and acyl iodides, we examined reactions of acetyl and benzoyl iodide with organosilicon and organogermanium hydrides, Et_3SiH (**I**), Ph_3SiH (**II**), Me_2PhSiH (**III**), and Ph_3GeH (**IV**).
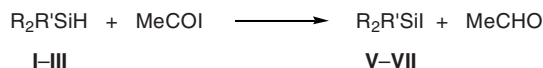
It is known that aliphatic and aromatic carboxylic acid chlorides react with triorganylsilanes to give triorganylchlorosilanes and the corresponding aldehydes and esters and that these reactions require the presence of a catalyst, such as $AlCl_3$ [6, 7], palladium [8, 9] or rhodium complexes [10], or Cr, Mo, Fe, Ni, or Co acetylacetonate [11–13]. Unlike acyl chlorides, acetyl iodide and benzoyl iodide were found to readily react with triorganylsilanes R_3SiH in the absence of a catalyst. The reactions of acetyl iodide with silanes **I**–**III** in toluene at 100°C in 6 h gave the corresponding

triorganyliodosilanes Et_3SiI (**V**), Me_2PhSiI (**VI**), and Ph_3SiI (**VII**) in 55–65% yield (Scheme 1).
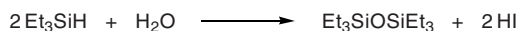
When the reaction of acetyl iodide with triethylsilane (**I**) was performed under solvent-free conditions at 50–60°C (reaction time 14 h), we obtained a mixture of acetaldehyde, triethylsilyl acetate, and hexaethyldisiloxane. The formation of acetaldehyde indicates that the reaction shown in Scheme 1 occurs in the first stage. However, in this case we failed to isolate triethyliodosilane (**V**). Its trace amount was detected in the reaction mixture by ^{1}H NMR spectroscopy [δ, ppm: 1.00 s (3H, CH_3CH_2SiI)]. The major part of Et_3SiI is converted into hexaethyldisiloxane via reaction with water which is usually adsorbed on glass walls of the reaction vessel (Scheme 2). The formation of hexaalkyldisiloxanes from trialkyliodosilanes in glass vessels in the absence of moisture was observed previously by us [14] and other authors [15]. Hydrogen iodide liberated as a result of hydrolysis was identified using an aqueous solution of $AgNO_3$ (as AgI).

Hexaethyldisiloxane then reacts with initial acetyl iodide to give triethylsilyl acetate and triethyliodosilane, as we reported previously [1] (Scheme 3).

Scheme 1.

$$R_2R'SiH \; + \; MeCOI \longrightarrow R_2R'SiI \; + \; MeCHO$$
$$\textbf{I–III} \qquad\qquad\qquad\qquad \textbf{V–VII}$$

Scheme 2.

$$2\,Et_3SiH \; + \; H_2O \longrightarrow Et_3SiOSiEt_3 \; + \; 2\,HI$$

Scheme 3.

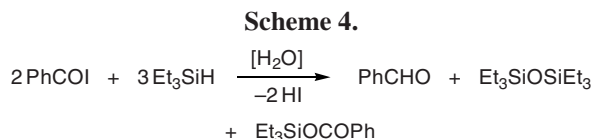$$Et_3SiOSiEt_3 \; + \; MeCOI \longrightarrow Et_3SiOCOMe \; + \; Et_3SiI$$
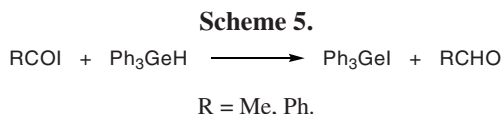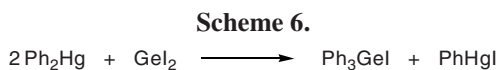
* For communication IX, see [1].

Benzoyl iodide reacted with triethylsilane (**I**) in the absence of a solvent in a similar way but under more severe conditions (220°C, 3 h). The products were benzaldehyde, hexaethyldisiloxane, and triethylsilyl benzoate (Scheme 4).

Scheme 4.

$$2\,PhCOI \;+\; 3\,Et_3SiH \;\xrightarrow[-2\,HI]{[H_2O]}\; PhCHO \;+\; Et_3SiOSiEt_3$$
$$+\; Et_3SiOCOPh$$

By contrast, reactions of acyl iodides RCOI (R = Me, Ph) with triphenylgermane (**IV**) in the absence of a solvent at 100°C (R = Me) or 200–220°C (R = Ph) afforded only iodotriphenylgermane (yield 91–98%) and the corresponding aldehyde (Scheme 5).

Scheme 5.

$$RCOI \;+\; Ph_3GeH \;\longrightarrow\; Ph_3GeI \;+\; RCHO$$
$$R = Me,\ Ph.$$

As with silicon hydrides, acetyl iodide reacted with Ph₃GeH more readily than did benzoyl iodide due to positive inductive effect of the methyl group. This reaction underlies a simple and convenient procedure for the synthesis of iodo(triphenyl)germane. The only previously known method for the preparation of this compound was based on the reaction of germanium diiodide with diphenylmercury [16] (Scheme 6).

Scheme 6.

$$2\,Ph_2Hg \;+\; GeI_2 \;\longrightarrow\; Ph_3GeI \;+\; PhHgI$$

The product structure was determined on the basis of their elemental analyses and ^{1}H, ^{13}C, and ^{29}Si NMR and IR spectra.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer from thin films. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra were measured on a Bruker DPX-400 spectrometer (400 MHz) from solutions in chloroform-*d* using tetramethylsilane or hexamethyldisiloxane as internal reference. Initial acyl iodides were prepared by reaction of the corresponding acyl chlorides with anhydrous sodium iodide [17].

Reaction of acetyl iodide with triethylsilane. *a.* Acetyl iodide, 11.8 g (0.07 mol), was added under stirring to a solution of 8.08 g (0.07 mol) of triethylsilane in 10 ml of toluene, and the mixture was heated for 6 h at 100°C. Vacuum distillation gave 9.6 g (58%)

of triethyliodosilane, bp 85°C (22 mm), $n_D^{20} = 1.4948$; published data [3]: bp 191°C, $n_D^{20} = 1.4948$. ^{1}H NMR spectrum: δ 0.99 ppm, s (3H, **CH₃**CH₂Si). ^{29}Si NMR spectrum: δ_{Si} 29.47 ppm.

b. A mixture of 3.6 g (0.02 mol) of acetyl iodide and 2.5 g (0.02 mol) of triethylsilane was placed in an ampule, the ampule was evacuated to a residual pressure of 10–12 mm, and the mixture was heated for 14 h at 50–60°C. According to the ^{1}H, ^{13}C, and ^{29}Si NMR and IR spectra, the mixture contained acetaldehyde, triethylsilyl acetate, and hexaethyldisiloxane. IR spectrum, ν, cm⁻¹: 1745 (CHO), 1710 (CH₃CO), 1050 (SiOSi). ^{1}H NMR spectrum, δ, ppm: 0.51 q (2H, CH₂Si), 0.75 q (2H, CH₂Si), 0.92 s (3H, **CH₃**CH₂Si), 1.0 s (3H, **CH₃**CH₂Si), 2.05 s (3H, CH₃CO), 6.7 d (1H, CHO). ^{13}C NMR spectrum, δ_C, ppm: 4.2 (**CH₃**CH₂Si), 6.1 (CH₃**CH₂**Si), 6.2 (**CH₃**CH₂Si), 7.1 (CH₃**CH₂**Si). ^{29}Si NMR spectrum, δ_{Si}, ppm: 8.99 (Et₃SiOSiEt₃), 25.36 (Et₃SiOCOCH₃).

By vacuum distillation we isolated hexaethyldisiloxane {bp 80–82°C (4 mm), $n_D^{20} = 1.4340$; published data [18]: bp 236.3°C (760 mm), $n_D^{20} = 1.4340$. Found, %: C 58.24; H 12.59; Si 22.53. $C_{12}H_{30}Si_2O$. Calculated, %: C 58.46; H 12.27; Si 22.78} and triethylsilyl acetate {bp 180–183°C, $n_D^{20} = 1.4180$; published data [19]: bp 173.4°C, $n_D^{20} = 1.4190$}.

Reaction of benzoyl iodide with triethylsilane. A mixture of 6.0 g (0.03 mol) of benzoyl iodide and 3.0 g (0.03 mol) of triethylsilane was heated for 3 h at 220°C. According to the ^{1}H, ^{13}C, and ^{29}Si NMR spectra, the mixture contained benzaldehyde, hexaethyldisiloxane, and triethylsilyl benzoate. ^{1}H NMR spectrum, δ, ppm: 0.52 (2H, CH₂Si), 0.93 s (3H, **CH₃**CH₂), 7.33–7.88 m (5H, C₆H₅), 8.23 q (1H, CHO). ^{13}C NMR spectrum, δ_C, ppm: 5.58 (**CH₃**CH₂), 6.74 (CH₂Si), 128.73–135.51 (C_{arom}). ^{29}Si NMR spectrum, δ_{Si}, ppm: 8.90 (Et₃SiOSiEt₃), 29.82 (Et₃SiOCO). Distillation gave hexaethyldisiloxane and triethylsilyl benzoate with bp 133–134°C (9 mm), $n_D^{20} = 1.4910$; published data [19]: bp 133°C (8 mm), $n_D^{20} = 1.4930$.

Reaction of acetyl iodide with dimethyl(phenyl)silane. A solution of 11.3 g (0.07 mol) of acetyl iodide and 9.1 g (0.07 mol) of dimethyl(phenyl)silane in 10 ml of toluene was heated for 4 h at 90°C. The solvent was distilled off, and the residue was distilled under reduced pressure to isolate 5.09 g (56%) of iodo(dimethyl)(phenyl)silane, bp 65°C (3 mm), $n_D^{20} = 1.5656$; published data [20]: bp 65°C (3 mm), $n_D^{20} = 1.5660$. ^{1}H NMR spectrum, δ, ppm: 0.99 s (3H,

CH$_3$), 7.33–7.60 m (5H, C$_6$H$_5$). ^{29}Si NMR spectrum: δ$_{Si}$ 0.214 ppm.

Reaction of acetyl iodide with triphenylsilane. A solution of 3.9 g (0.02 mol) of acetyl iodide and 4.0 g (0.02 mol) of triphenylsilane in 5 ml of toluene was heated for 6 h at 100°C. The solvent was distilled off, the residue was recrystallized from anhydrous hexane, and the product was evacuated at a residual pressure of 2 mm. Yield of iodo(triphenyl)silane 3.6 g (63%), mp 154–156°C; published data [21]: mp 154–156°C. ^{29}Si NMR spectrum, δ$_{Si}$ 8.78 ppm.

Reaction of acetyl iodide with triphenylgermane. A mixture of 3.4 g (0.02 mol) of acetyl iodide and 6.1 g (0.02 mol) of triphenylgermane was heated for 4 h at 100–105°C. The precipitate was filtered off and recrystallized from heptane. Yield of iodo(triphenyl)germane 8.4 g (98%), mp 156–157°C; published data [16]: mp 157°C. Found, %: C 50.51; H 3.63; Ge 17.09; I 29.00. C$_{18}$H$_{15}$GeI. Calculated, %: C 50.18; H 3.51; Ge 16.85; I 29.46.

Reaction of benzoyl iodide with triphenylgermane. A mixture of 2.3 g (0.01 mol) of benzoyl iodide and 3.0 g (0.01 mol) of triphenylgermane was heated for 6 h at 220°C. From the reaction mixture we isolated 3.9 g (91%) of iodotriphenylgermane and 0.8 g (76%) of benzaldehyde with bp 177–178°C, n_D^{20} = 1.5455.

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