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Acyl Iodides in Organic Synthesis: VII. Reactions with Trialkyl(alkynyl)silanes, -germanes, and -stannanes

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Abstract—Reactions of acyl iodides R^1COI (R^1 = Me, Ph) with trialkyl(alkynyl)silanes, -germanes, and stannanes ($R^2C{\equiv}CMR^3_3$; M = Si, Ge, Sn) were studied. Acyl iodides reacted with the germanium and tin derivatives with cleavage of the M–C_{sp} bond and formation of the corresponding trialkyl(iodo)germanes and -stannanes R^3_3MI (M = Ge, Sn) and alkynyl ketones $R^1C(O)C{\equiv}CR^2$ and $R^1C(O)C{\equiv}CC(O)R^1$. By contrast, the reaction of acetyl iodide with ethynyl(trimethyl)silane gave only a small amount of 1,2-diiodovinyl(trimethyl) silane as a result of iodine addition at the triple bond. Bis(trimethylsilyl)ethyne failed to react with acetyl iodide.

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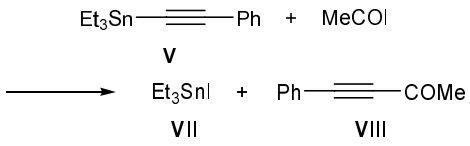
Readily accessible acyl chlorides usually react with aprotic compounds only under severe conditions or in the presence of a catalyst (Lewis acid) [1, 2]. By contrast, acyl iodides RCOI (R = Me, Ph) are highly reactive iodinating, deoxygenating, and acylating agents [3]. We showed that acyl iodides readily react with alcohols and phenols [4, 5], acyclic and cyclic ethers [6], alkyl vinyl ethers [7], carboxylic acids [8], and esters [9] under mild conditions without a catalyst.

In continuation of these studies, we set ourselves the goal of estimating the synthetic potential of acyl iodides in organometallic chemistry. The present communication reports the results of our study on reactions of acyl iodides RCOI (R = Me, Ph) with acetylenic derivatives of Group IV elements (Si, Ge, Sn), which possess two reaction centers, M–C and C≡C bonds. As substrates we used ethynyl(trimethyl)silane (**I**), bis(triethylsilyl)ethyne (**II**), triethyl(ethynyl)germane (**III**), bis(triethylgermyl)ethyne (**IV**), triethyl(phenylethynyl) stannane (**V**), and bis(triethylstannyl)ethyne (**VI**).

It is known that the Sn–C_{sp} bond in triethyl(phenylethynyl)stannane (**V**) is cleaved by the action of acetyl chloride only at 120°C and that benzoyl chloride does not react with **V** under these conditions [10]. Unlike acyl chlorides, acetyl iodide readily reacted with triethyl(phenylethynyl)stannane (**V**) even at room temperature. The reaction was accompanied by heat evolution, and the products were triethyl(iodo)stannane (**VII**) and 4-phenyl-3-butyn-2-one (**VIII**) (Scheme 1) formed as a result of cleavage of the Sn–C_{sp} bond.

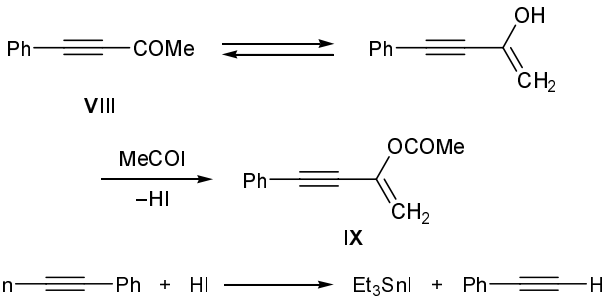
Scheme 1.



Likewise, the Sn–C_{sp} bond in triethyl(phenylethynyl)stannane was readily cleaved by the action of benzoyl iodide. However, in this case only triethyl(iodo)stannane (**VII**) was isolated from the reaction mixture in a high yield (84%). The corresponding acetylenic ketone PhCOC≡CPh underwent polymerization during the process.

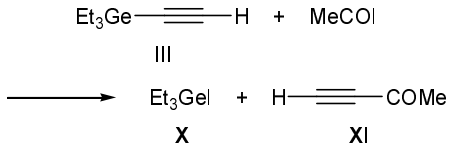
The reaction of triethyl(phenylethynyl)stannane (**V**) with acetyl iodide, as well as with acetyl chloride [10], was accompanied by formation of phenylacetylene in addition to compounds **VII** and **VIII**. Phenylacetylene is likely to be formed following a mechanism analogous to that described in [10] for the reaction with acetyl chloride (Scheme 2); therefore, the yield of ketone **VIII** is low (~24%), while the yield of triethyl(iodo)stannane reaches ~67%. Acylation of the enol form of **VIII** gives 2-acetoxy-4-phenyl-1-buten-3-yne (**IX**) which undergoes polymerization.

Scheme 2.



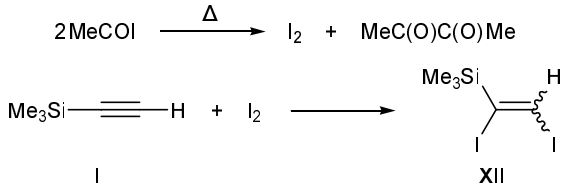
Cleavage of the Ge–C_{sp} bond in triethyl(ethynyl)germane (**III**) with acetyl iodide occurs at 80°C (reaction time 1 h), and triethyl(iodo)germane (**X**) and 3-butyn-2-one (**XI**) are formed in 70 and 72% yield, respectively (Scheme 3).

Scheme 3.



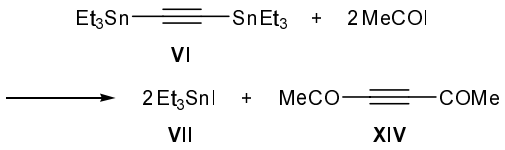
No cleavage of the Si–C_{sp} bond was observed in the reaction of acetyl iodide with ethynyl(trimethyl)silane (**I**). In this case, only a small amount (~10%) of 1,2-diiodovinyl(trimethyl)silane (**XII**) was formed. We failed to raise the yield of **XII** by UV irradiation; by contrast, it decreased to 3–5%. These data indicate heterolytic mechanism of iodination with participation of molecular iodine which is liberated via homolytic dissociation of acetyl iodide. The occurrence of the latter process follows from formation of biacetyl (**XIII**) (Scheme 4).

Scheme 4.

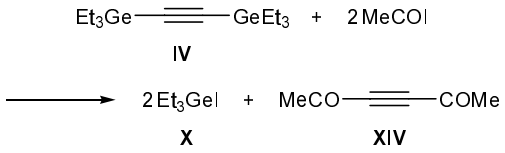


Acetyl iodide reacted with bis(triethylstannyl)ethyne (**VI**) even at room temperature with heat evolution (as with compound **V**). The reaction involved cleavage of both Sn–C_{sp} bonds to afford triethyl(iodo)stannane (**VII**) and 3-hexyne-2,5-dione (**XIV**) in 79 and 71% yield, respectively (Scheme 5). An analogous pattern was observed in the reaction of acetyl iodide with bis(triethylgermyl)ethyne (**IV**), but in this case heating to 80°C was necessary (Scheme 6). Bis(trimethylsilyl)ethyne (**II**) failed to react with acetyl iodide.

Scheme 5.



Scheme 6.



We can conclude that the reactivity of M–C_{sp} bond decreases in parallel with the atom number of M, i.e., in the series Sn > Ge ≫ Si. This is the result of both reduction in the M–C_{sp} bond polarity and enhancement of resonance interaction between the ethynyl group and heteroatom M [11].

EXPERIMENTAL

Acetyl iodide was synthesized by reaction of acetyl chloride with anhydrous sodium iodide according to the procedure described in [12]. Triethyl(phenylethynyl)stannane [13], bis(triethylstannyl)ethyne [14], bis(triethylgermyl)ethyne [15], triethyl(ethynyl)germane [16], ethynyl(trimethyl)silane [17], and bis(triethylsilyl)ethyne [18] were prepared by known methods. The IR spectra were recorded on a UR 20 spectrometer from samples prepared as thin films. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker DPX-400 spectrometer (400 MHz for ^{1}H) using chloroform-*d* as solvent and HMDS as internal reference. Chromatographic analyses were performed on an LKhM-8M instrument equipped with a thermal conductivity detector (carrier gas helium, 2-m×4-mm column, oven temperature programming).

Reaction of acetyl iodide with triethyl(phenylethynyl)stannane. Triethyl(phenylethynyl)stannane, 9.5 g (0.031 mol), was mixed with acetyl iodide, 5.31 g (0.031 mol), and the mixture spontaneously warmed up to 40°C. By distillation we isolated 0.68 g (21%) of phenylacetylene, bp 49–50°C (20 mm) (identified by GLC), and 6.91 g (66.6%) of triethyl(iodo)stannane (**VII**), bp 110°C (20 mm), n_D^{20} = 1.5642 [published data [19]: bp 105–106°C (16 mm), n_D^{18} =

1.5653]. Found, %: C 22.15; H 4.50; I 30.13; Sn 35.98. $C_6H_{15}ISn$. Calculated, %: C 21.65; H 4.51; I 35.6; Sn 35.6. Also, 0.98 g (23.8%) of 4-phenyl-3-butyn-2-one (**VIII**) was isolated, bp 135°C (20 mm), n_D^{23} = 1.5730; published data [20]: bp 86–88°C (1 mm), n_D^{20} = 1.5740.

Reaction of benzoyl iodide with triethyl(phenylethynyl)stannane (V). Benzoyl iodide, 5 g (0.004 mol), was mixed with triethyl(phenylethynyl)stannane (**V**), 6.59 g (0.004 mol), and the mixture spontaneously warmed up to 40°C. Distillation of the mixture gave 6.02 g (84%) of triethyl(iodo)stannane (**VII**). The residue was a bright yellow powder which did not melt and was insoluble in common solvents. Found, %: C 35.44; H 4.53; I 28.34; Sn 28.16. $C_{12}H_{20}IOSn$. Calculated, %: C 33.8; H 4.69; I 29.81; Sn 27.93.

Reaction of acetyl iodide with triethyl(ethynyl)germane (III). A mixture of 4.15 g (0.02 mol) of acetyl iodide and 4.5 g (0.02 mol) of trimethyl(ethynyl)germane (**III**) was heated for 1 h at 80°C. Distillation of the mixture gave 4.87 g (69.7%) of triethyl(iodo)germane (**X**), bp 90°C (20 mm), n_D^{22} = 1.519; published data [21]: bp 80°C (13 mm), n_D^{20} = 1.5262. Found, %: C 25.51; H 5.65; Ge 25.28; I 36.36. $C_6H_{15}GeI$. Calculated, %: C 25.13; H 5.23; Ge 25.2; I 44.32. Also, 1.21 g (72.9%) of 3-butyn-2-one (**XI**) was isolated, bp 82–83°C, n_D^{23} = 1.4050; published data [22]: bp 83.5–84.5°C, n_D^{20} = 1.4070.

Reactions of acetyl iodide with ethynyl(trimethyl)silane (I) and bis(triethylsilyl)ethyne (II). A mixture of 5.31 g (0.031 mol) of acetyl iodide and 3.06 g (0.031 mol) of ethynyl(trimethyl)silane (**I**) was heated for 8 h at 50–60°C. Distillation of the mixture gave 0.25 g (9.3%) of biacetyl (**XIII**) (which was identified by GLC using an authentic sample) and 1.1 g (10%) of 1,2-diiodovinyl(trimethyl)silane (**XII**), bp 70–75°C (1 mm), n_D^{23} = 1.6140; published data [23]: bp 70–72°C (1 mm), n_D^{20} = 1.6195. Found, %: C 16.63; H 4.31; I 71.25; Si 8.35. $C_5H_{10}I_2Si$. Calculated, %: C 16.75; H 4.47; I 70.94; Si 7.82.

A mixture of 5.31 g (0.031 mol) of acetyl iodide and 3.97 g (0.0152 mol) of bis(triethylsilyl)ethyne (**II**) was heated for 20 h at the boiling point. The subsequent vacuum distillation gave unreacted initial compounds.

Reaction of acetyl iodide with bis(triethylstannyl)ethyne (VI). Bis(triethylstannyl)ethyne (**VI**), 3.75 g (0.017 mol), was mixed with acetyl iodide, 2.9 g (0.017 mol), and the mixture spontaneously warmed up to 40°C. Distillation of the mixture gave 4.55 g (79.4 %) of triethyl(iodo)stannane (**VII**) and 1.33 g (71%) of 3-hexyne-2,5-dione (**XIV**), bp 45°C (20 mm). ^{1}H NMR spectrum, δ, ppm: 2.21 (3H, CH_3CO). ^{13}C NMR spectrum, δ_C, ppm: 166.43 (C=O), 93.22 (C≡C), 22.19 (CH_3).

Reaction of acetyl iodide with bis(triethylgermyl)ethyne (IV). A mixture of 4.46 g (0.026 mol) of acetyl iodide and 4.5 g (0.026 mol) of bis(triethylgermyl)ethyne (**IV**) was heated for 1 h at 80°C. Distillation of the mixture gave 5.15 g (68.4%) of triethyl(iodo)germane (**X**) and 1.06 g (67.9%) of 3-hexyne-2,5-dione (**XIV**) whose ^{1}H and ^{13}C NMR spectra were the same as above.

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