Reaction of α-(trialkylstannyl)acetylenes with metallic sodium

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α-Trialkylstannylacetylenes react under mild conditions with metallic sodium at the Sn—C(sp) bond to give hexaalkyldistannanes and sodium acetylalkynides in *ca.* 65—85 % yields.

Key words: α-(trialkylstannyl)acetylenes, reaction with sodium; hexaalkyldistannanes; sodium acetylenides; trialkylstannyl(trimethylsilyl)acetylenes; bis(trialkylstannyl)acetylenes.

The Sn—C(sp) bond in tin alkynides is polarized and sensitive to the action of different reagents. Due to this, α-organostannylacetylenes can be used for preparing different organic and organometallic compounds.

Previously[1—4] we found that α-acetylenic organotin compounds can react at the Sn—C(sp) bond with C—H-acids, stannum organohalides, organolithium compounds, etc. However, their reaction with metallic sodium, which is the subject of this study, is poorly known.[5]

We have found that trialkylstannylacetylenes (**1**) react readily with metallic sodium at the Sn—C(sp) bond to give hexaalkyldistannanes (**2**) and sodium alkynides (**3**) according to the following equation:

$$2R_3SnC{\equiv}CR' + 2Na \longrightarrow R_3Sn{-}SnR_3 + 2R'C{\equiv}CNa,$$

where R, R′ = Me, Bu; Me, Ph; Me, Me_3Si; Et, Vin; Et, Ph; Et, Me_3Si; Bu, Bu; Bu, Ph; Bu, and Me_3Si.

The reaction of **1** with Na proceeds under mild conditions in aprotic solvents such as ether, benzene, hexane, *etc.* The reactivity of compounds **1** at the Sn—C(sp) bond decreases as the size of the organic radical increases. For example, the reaction of sodium with trimethyl(phenylethynyl)stannane in ether at 35—36 °C is virtually complete in 3 h, whereas the reaction with tributyl(phenylethynyl)stannane under the same conditions takes 20—25 h. The yields of compounds **2** and **3** are 70—80 % and up to 90 %, respectively. The rate of the reaction substantially depends on the dispersity of sodium.

Apparently, at the first stage, the electron is transferred from the sodium atom to the Sn—C(sp) bond. The radical anion formed decomposes to give the alkynide anion and the $R_3Sn^{\cdot}$ radical. Then the latter either dimerizes to give **2** or reacts with metallic sodium to give R_3SnNa which is able to react with compound **1** at the Sn—C(sp) bond.

$$R_3SnC{\equiv}CR' \xrightarrow{Na} [R_3SnC{\equiv}CR']^{\dot{-}}\,Na^{+} \longrightarrow [R_3Sn^{\cdot}] + NaC{\equiv}CR'$$

$$R_3Sn{-}SnR_3 \longleftarrow [R_3Sn^{\cdot}] \xrightarrow{Na} R_3SnNa \xrightarrow{R_3SnC\equiv CR'}$$

$$\longrightarrow R_3Sn{-}SnR_3 + NaC{\equiv}CR'$$

The proposed chemism of the process is confirmed by the reactions of the intermediate and final products with trimethylchlorosilane and acetone and by the reaction of **1** with Na in the presence of trimethylchlorosilane, which results in the synthesis of trimethylsilyltrialkylstannanes and trimethylsilylacetylenes.

$$Me_3SiC{\equiv}CR' \xleftarrow{Me_3SiCl} R'C{\equiv}CNa \xrightarrow{MeCOMe} R'C{\equiv}C(OH)Me_2$$

$$R_3SnC{\equiv}CR' + 2Na + 2Me_3SiCl \longrightarrow R_3SnSiMe_3 + Me_3SiC{\equiv}CR',$$

where R, R' = Bu, Ph; Et, and Me_3Si.

Under similar conditions trialkylstannyl(trimethylsilyl)acetylenes react with sodium to give organosilyltrialkylstannanes without participation of the Sn—C(sp) bond.

$$R_3SnC{\equiv}CSiMe_3 + 2Na + 2Me_3SiCl \longrightarrow$$

$$\longrightarrow R_3SnSiMe_3 + Me_3SiC{\equiv}CSiMe_3$$

However, bis(trialkylstannyl)acetylenes react with sodium very slowly and yield a complex mixture of compounds. In this case, an alternative chemism of the process is possible, which will be the subject of our further investigations.

Hence, the replacement of an organic radical R′ in the system $R_3SnC{\equiv}CR'$ with a trimethylsilyl group has no essential effect on the reactivity of the Sn—C(sp) bond with respect to sodium, whereas the replacement

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Table 1. Reactions of organostannylacetylenes with sodium

$R_3SnC{\equiv}CR'$		Reaction conditions	Compounds prepared (yield (%))
R	R'		
Me	Bu	Ether, 30—35 °C, 5 h	$Me_3Sn{-}SnMe_3$ (85), $NaC{\equiv}CBu$ (80)
Me	Me_3Si	Ether, 30—35 °C, 7 h	$Me_3Sn{-}SnMe_3$ (72), $NaC{\equiv}CSiMe_3$ (66)
Et	Ph	Ether, 35 °C, 12 h	$Et_3Sn{-}SnEt_3$ (64), $NaC{\equiv}CPh$ (60)
Et	Bu	Hexane, 50 °C, 10 h	$Et_3Sn{-}SnEt_3$ (84), $NaC{\equiv}CBu$ (45)
Et	Me_3Si	Hexane, 50 °C, 15 h	$Et_3Sn{-}SnEt_3$ (78), $NaC{\equiv}CSiMe_3$ (53)
Bu	Ph	Ether, 35 °C, 25 h	$Bu_3Sn{-}SnBu_3$ (46), $NaC{\equiv}CPh$ (39)
Bu	Bu	Benzene, 80 °C, 20 h	$Bu_3Sn{-}SnBu_3$ (67), $NaC{\equiv}CBu$ (52)
Bu	Me_3Si	Benzene, 80 °C, 18 h	$Bu_3Sn{-}SnBu_3$ (59), $NaC{\equiv}CSiMe_3$ (40)

of R′ by a trialkylstannyl group results in substantial deactivation of this bond in the reaction under study.

Experimental

The reaction of trimethyl(phenylethynyl)stannane with sodium. Trimethyl(phenylethynyl)stannane (3.98 g, 0.015 mol) in 40 mL of ether was added dropwise with stirring to a suspension of finely dispersed sodium (0.35 g, 0.015 mol) in 30—40 mL of absolute Et_2O. The reaction mixture was stirred with light boiling of ether, until the sodium was completely consumed to give the acetylenide (2—3 h). The content of the flask was filtered under a nitrogen atmosphere, and 3.53 g (72 %) of hexamethylstannane with b.p. 51—52 °C (8 Torr) and m.p. 23 °C was separated from the filtrate by distillation.

The residue of sodium phenylacetylenide was transferred to an apparatus for synthesis, suspended in 40 mL of absolute ether, and treated with 1.58 g (0.015 mol) of trimethylchlorosilane. The reaction mixture was stirred at 35 °C for 3 h, the residue was separated, and the filtrate was evaporated. Trimethyl(phenylethynyl)silane (1.53 g, 58.6 %, in terms of initial **1**) was obtained by distillation of the residue, b.p. 56—57 °C (2 Torr), n_D^{20} 1.5282.

The reaction of triethyl(vinylethynyl)stannane with sodium. The reaction was carried out in the same manner as described above. 3.76 g (73 %) of hexaethyldistannane with b.p. 114—115 °C (2 Torr), n_D^{20} 1.5770 was prepared from 6.32 g (0.025 mol) of triethyl(vinylethynyl)stannane and 0.575 g (0.025 mol) of sodium in 50 mL of ether.

The obtained residue of sodium vinylacetylenide reacts with 1.45 g (0.025 mol) of acetone in 50 mL of ether to give 1.32 g (48 %) of dimethylvinylethynylcarbinol with b.p. 36 °C (5 Torr), n_D^{20} 1.4778.

The reactions of the other trialkylstannylacetylenes with sodium were carried out in a similar manner. The reaction conditions are given in Table 1.

The reaction of triethylstannyl(trimethylsilyl)acetylene with sodium in the presence of trimethylchlorosilane. Triethylstannyl(trimethylsilyl)acetylene (6.06 g, 0.02 mol) was added dropwise with stirring to a mixture (0.92 g, 0.04 mol) of finely dispersed sodium and trimethylchlorosilane (4.32 g, 0.04 mol) in 30 mL of absolute ether. The reaction mixture was stirred for 3 h at room temperature and for 1 h at 35 °C. The solid precipitate was filtered off, the filtrate was evaporated, and the residue was distilled. The yield of bis(trimethylsilyl)acetylene, b.p. 32—34 °C (10 Torr), n_D^{20} 1.4245, was 2.28 g (45 %); the yield of trimethylsilyltriethylstannane, b.p. 80—81 °C (10 Torr, n_D^{20} 1.4551, was 4.05 g (75 %).

The reaction of bis(triethylstannyl)acetylene with sodium. 10 g (0.023 mol) of bis(triethylstannyl)acetylene and 0.5 g (0.022 mol) of sodium were placed in an apparatus for synthesis, and the mixture was heated at 35—50 °C for 100 h with stirring under a nitrogen atmosphere. The obtained jelly-like material was treated with 2.6 g (0.024 mol) of trimethylchlorosilane in 20 mL of ether, and the precipitate was separated by filtration. The distillation of the filtrate afforded 3.8 g (57 %) of trimethylsilyltriethylstannane, b.p. 105—107 °C (8 Torr), n_D^{20} 1.4548, and 2.1 g of starting bis(triethylstannyl)acetylene, b.p. 140—142 °C (8 Torr), n_D^{20} 1.5085.

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