A one-step oxidative synthesis of trimethylantimony(v) diacylates

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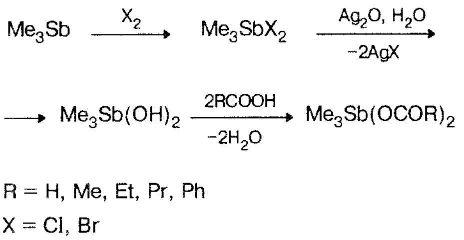
Trimethylantimony(v) diacylates $Me_3Sb(OCOR)_2$ (R = H, Me, Ph) have been obtained in 72—75 % yield by the interaction of trimethylantimony with *tert*-butylhydroperoxide and carboxylic acids at the ratio of 1 : 1 : 2 in benzene (20 °C, 20 h) in the presence of sodium sulfate.

Key words: trimethylantimony(v) diacylates; synthesis, trimethylantimony; oxidative acylation.

Until now, trimethylantimony diacylates have been obtained by a three-step method[1] that includes the oxidation of the starting trimethylantimony to the respective halide followed by its transformation to the hydroxide and then to the desired compound according to the general Scheme 1.

Scheme 1



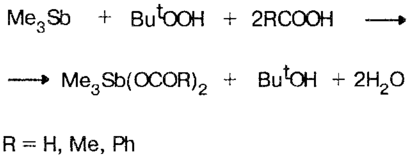
$$Me_3Sb \xrightarrow{X_2} Me_3SbX_2 \xrightarrow[-2AgX]{Ag_2O,\ H_2O} Me_3Sb(OH)_2 \xrightarrow[-2H_2O]{2RCOOH} Me_3Sb(OCOR)_2$$

R = H, Me, Et, Pr, Ph
X = Cl, Br

Trimethylantimony diacylates have been synthesized by the oxidation procedure[2] proposed by us for phenyl derivatives of antimony(v) and bismuth(v).[3–6]

The reaction of trimethylantimony with *tert*-butylhydroperoxide (TBHP) and carboxylic acids was performed in one stage in benzene at 20 °C using a stoichiometric ratio of the reagents according to Scheme 2.

Scheme 2



$$Me_3Sb + Bu^tOOH + 2RCOOH \longrightarrow Me_3Sb(OCOR)_2 + Bu^tOH + 2H_2O$$

R = H, Me, Ph

The yields of antimony(v) acylates after recrystallization were 72—75 %, and the yield of *tert*-butanol was 95—100 %. When the relative amounts of TBHP and the acid were increased 1.5—2 times, the yields of the target products approached 100 %.

It should be noted that the reaction by Scheme 2 was carried out in the presence of sodium sulfate as this additive increased the yield and purity of the products.

The antimony(v) compounds prepared are colorless and odorless crystalline compounds which sublime *in vacuo* without decomposition. They are easily soluble in benzene, chloroform, toluene, and THF, but poorly soluble in hexane. The IR spectra (ν/cm^{-1}): 550—565 (ν(Sb—C)), 1210—1305 (ν(C—O)), 1390—1410 ($\delta(CH_3)$), 1620—1625 (ν(C=O)), 2925—2930 ($\nu_s(CH_3)$), 3010—3020 ($\nu_{as}(CH_3)$) corroborate the structure of the compounds obtained.

Experimental

IR spectra in the 4000—400 cm^{-1} region were recorded in KBr pellets on a Specord spectrophotometer.

Synthesis of trimethylantimony diacylates. A mixture of trimethylantimony (5 mmol), TBHP (5 mmol), a carboxylic acid (10 mmol), and anhydrous Na_2SO_4 (1 g) was kept for 20 h at 20 °C in a sealed ampule. Then the ampule was opened, and the liquid phase was distilled off under reduced pressure. The condensate was analyzed by GLC to determine the content of *tert*-butanol. The solid residue was recrystallized from a benzene—hexane mixture. The yield of trimethylantimony diacylates was 72—75 %. Prior to recrystallization, trimethylantimony dibenzoate was purified from an admixture of benzoic acid by sublimation (120 °C, 0.5 Torr). The following compounds were obtained: trimethylantimony diformate (m.p. 81 °C; *cf.* Ref. 1: m.p. 81 °C), trimethylantimony diacetate (m.p. 81 °C; *cf.* Ref. 1: m.p. 81 °C), and trimethylantimony dibenzoate (m.p. 160 °C, *cf.* Ref. 1: m.p. 154 °C).

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ESR study of radicals obtained from vinylalkoxysilanes and their adducts with branched fluoroalkenes

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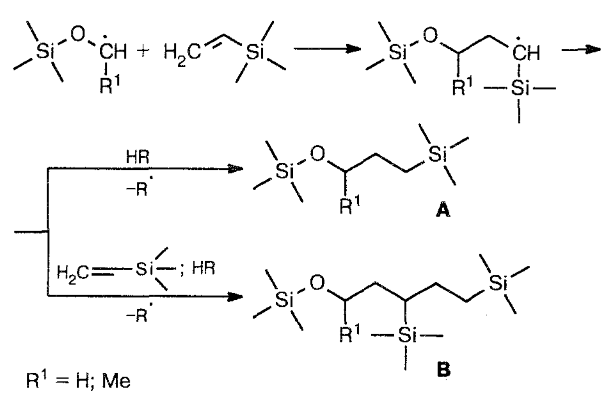
ESR spectra of radicals obtained by abstracting a hydrogen atom from methylvinyldimethoxysilane and methylvinyldiethoxysilane through the action of the *tert*-butoxy radical were studied. It was shown that the radicals appearing react with branched fluorinated olefins to give relatively stable radical adducts.

Key words: vinylalkoxysilanes; fluoroalkene; radical; ESR.

The structure of the polymers formed by the radical polymerization of vinylsilanes $CH_2{=}CH{-}Si{-}R^1R^2_2$ (R^1 = Me; R^2 = MeO, EtO, Pr^nO, Pr^iO) has been studied previously[1—3] by NMR spectroscopy. The data obtained on the structure of the fragments of the polymer chains (**A**, **B**) of polyvinylsilanes make it possible to assume that the reaction of vinylalkoxysilanes (VAS) with an initiating radical involves abstraction of a H atom from the alkoxy group of VAS resulting in a primary radical, the addition of which at the double bond of VAS produces a new radical. The secondary radical can either add to the double bond of the next VAS molecule or participate in chain transfer by the abstraction of H from the alkoxy group according to Scheme 1.

Scheme 1



In the present work the structure of primary radicals and the process of their addition to branched fluoroalkenes have been studied by ESR in order to establish the possibility of the radical copolymerization of VAS. The UV irradiation of 10 % solutions of methylvinyldi-

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