b) The results of the analytical experiments are shown in Table 3.

The results of the carbon-13 and proton NMR examinations, elemental analyses, and physicochemical constants are shown in Table 1.

CONCLUSIONS

1. Radical telomerization of vinyltrimethylsilane with 5,5-dimethyl-1,3-dioxane leads in the main to retention of the dioxane ring of the telogen and its substitution in positions 2 and 4.

2. When 4-methyl-1,3-dioxane is used in the telomerization of vinyltrimethylsilane, the course of the reaction is changed; the dioxane ring of the telogen is generally opened with regioselective breaking of a bond at the most-substituted carbon atom.

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ACETYLDEMETALLATION OF BENZYLTRIMETHYLSTANNANE

IN THE PRESENCE OF ALUMINUM BROMIDE

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A characteristic property of organometallic benzyl compounds in reactions with electrophiles is the possibility of concurrent attacks at the α -C atom (electrophilic substitution, SE) and at the o- or p-position of the benzene ring to form intermediate semiquinone structures (electrophilic fragmentation, FE):



We have previously expressed the supposition that the reaction with attack on the benzene ring, when benzyl derivatives of Hg react with CH_3COC1 in the presence of $AlBr_3$ [1], can be considered as heterolytic fragmentation (FE) [2]. The present work studies the possibility of analogous reactions for the Sn analog PhCH₂SnMe₃. The latter does not react with a tenfold excess of MeCOC1 either in CH_2Cl_2 (42°C, 2-4 days) or in a sealed ampul (60°C, 1.5 days). But, in the presence of $AlBr_3$ (cf. [3]) in an argon atmosphere this reaction goes smoothly even at reduced temperature:*

*It is impossible to ignore the possibility of acetyldestannation of PhCH₂SnMe₃ via scission of the Me-Sn bond. Indeed, at -20° the reaction forms 5% acetone. Therefore, subsequently

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 $PhCH_{2}SnMe_{3} \frac{MeCOCI/A1Br_{3}(1:1)}{CH_{2}Cl_{2}; -50^{\circ}; 5min} p-MeCOC_{6}H_{4}CH_{2}COMe + p-MeC_{8}H_{4}COMe + PhMe}{(60-65\%) (25-30\%) (0-3\%)}$

The yield of products was determined by GLC analysis of the reaction mixture. Then the reaction mixture was treated with 2,4-dinitrophenylhydrazine sulfate solution and the resulting mixture of mono- and diketone 2,4-dinitrophenylhydrazones (DNPH) was separated by chromatography on aluminum oxide. DNPH structure was confirmed by elemental analysis and comparison of melting point and Rf in systems of various polarities with authentic samples [4, 5]. The ketone yields found by GLC were confirmed by gravimetric determination of the respective DNPH.

It should be noted that the results of acetyldestannation of PhCH₂SnMe₃ by reaction with MeCOC1/AlBr3, both in nature of products (in both cases there was para-attack of the benzene ring) and in product distribution, were practically the same as in the analogous acetyldemercuration of PhCH₂HgCl [1].

This observation leads to the presumption that in both reactions the same intermediate is responsible for the final product composition; e.g., a benzyl-type organoaluminum compound. It is known that AlBr₃ efficiently catalyzes the most varied demetallations of organometallic derivatives of groups II-IV; this is usually attributed to its ability as a Lewis acid to increase the electrophilic activity of a reagent [6] (route A). But, in theory we can propose other ways to catalyze such reactions. These ways are related to the ability of Al³⁺ salts to take part in concomitant (route B) or successive-parallel (route C) processes of alkyl exchange or one-electron oxidation to form organoaluminum intermediates. The latter are able to react more efficiently than the initial organometallic compound with the demetallating reagent [7] (cf. [8-10]) (see scheme).

 $R-M \xrightarrow{E-N} \begin{bmatrix} (A) \\ (B) \\ (B)$

In order to study this problem, we carried out the acetyldestannation of $\rm PhCH_2SnMe_3$ with "reverse" order of reagent addition. A mixture of PhCH₂SnMe₃ and AlBr₃ was held for 5 min at -50° and then treated with MeCOC1:



The result of this experiment differs from that described above with the "normal" order of reagent addition. Here the yield of mono- and diketone decreases, traces (up to 1%) of product of α -attack on benzyl methyl ketone appear, and most important, the toluene yield increases sharply, from 0-3 to 20%. Toluene formation can be attributed to hydrolysis of unreacted organoaluminum intermediate when the reaction mixture is treated with water. To confirm this assumption, a mixture of $PhCH_2SnMe_3$ and $AlBr_3$ in CH_2Cl_2 was held at -50° for 5 min, then treated with 3% aqueous HC1. (Previously, special experiments had shown that under such conditions PhCH₂SnMe₃ does not hydrolyze.) Now the only product was toluene in 90% yield (the reaction with PhCH₂SnMe₃ is quantitative): †

all reactions were carried out at -50°, where no scission of the Me-Sn bond was observed. Special experiments showed that under those conditions there was no acetylation of the benzene ring of benzyl methyl ketone or appreciable acetylation of toluene; i.e., formation of mono- and diketones is not a result of secondary reactions.

⁺GLC demonstrated the absence of the possible by-products PCH2Br, PhCH2OH, PhCH0, and (PhCH₂),.

{PhCH₂SnMe₃ + AlBr₃} $\xrightarrow{\text{HCl/H_2O}}$ PhMe ((0%) -50°C; 5 min

In order to prove that toluene forms specifically at the hydrolysis step, a mixture of $PhCH_2SnMe_3$ and $AlBr_3$ in CH_2Cl_2 was held at -50° for 5 min, then treated with 3% DCl in D_2O . Toluene was separated by preparative GLC; by deuteroanalysis and IR and mass spectra it contained 0.75 D/mole, and D was distributed among the α -, o-, and p-positions of the ring:



Although our data are clear evidence for a reaction between $PhCH_2SnMe_3$ and $AlBr_3$, to make an unequivocal choice between the alternate structures of the intermediate compound that they form is still quite difficult. It is known that $AlBr_3$ can take part in alkyl exchange of organometallic compounds [11]; therefore, $PhCH_2AlBr_2$ can be proposed as the intermediate. AlBr_3 can also be a one-electron oxidant of aromatic hydrocarbons [12]; in such a case the reaction may include intermediate formation of the radical ion pair $(PhCH_2SnMe_3)^+$. $AlBr_3^-$ or the products of their subsequent conversions. It is also impossible to exclude the possibility that the intermediate contains not one, but several Al atoms, because, in the deuterolysis of the reaction mixture with DCl and D_2O trideuterotoluene forms. Finally, if we consider that the hydrolysis of the reaction mixture takes place at the H_2O-HCl-CH_2Cl_2 interace, we cannot exclude the formation of unstable complex acids such as H⁺AlX₄⁻ at the moment of hydrolysis; these may also determine product composition, especially when we take account of the polydeuterated toluenes in the deuterolysis products (cf. [13, 14].

EXPERIMENTAL

IR spectra of deuterotoluenes were obtained on a UR-10 instrument in cyclohexane. Mass spectrometric analysis was carried out on a MI-1305 instrument at 60 eV. Solvents were purified by the usual methods and were distilled from P_2O_5 in an argon atmosphere before use. Acetyl chloride was boiled for 10 h to remove traces of HCl and was distilled from N,N-dimethylaniline before use. AlBr₃, c.p. grade, was placed in a retort (in a dry chamber) connected to a reaction flask filled with argon. The flask was evacuated for 10 min, then refilled with argon. Reactions were carried out in an argon atmosphere.

Composition of products of acetyldemetallation was determined by GLC on a model 1-64 Tsvet-2 instrument. Stationary phase was 15% PEG-1500 on Celite 545; glass column 2.3 m long, inside diameter 3 mm, carrier gas (N_2) pressure 0.4 kg/cm². Column temperature preset at 60-160°C by program, detector temperature 200°. It was shown in advance with standard mixtures that these conditions insure good separation of all products. Internal standards for quantitative GLC were ethylbenzene and acetophenone. Calibration showed that the calculation factors for toluene with respect to ethylbenzene, and benzyl methyl ketone and p-methyl-acetophenone with respect to acetophenone were close to unity, and were thereafter taken as l.

After GLC analysis, all low-boiling materials were distilled out of the reaction mixture, and the residue was dissolved in 95% EtOH and poured into an alcoholic solution of 2,4-dinitrophenylhydrazine sulfate solution that was prepared according to [4]. The precipitated hydrazone mixture (2,4-DNPH) was filtered off, washed on the filter with 50% EtOH, dried in a vacuum desiccator, and separated on aluminum oxide (II activity) (column 40 cm, inside diameter 22 mm, height of adsorbent layer ~25 cm). In advance, using standard mixtures of the expected 2,4-DNPH (synthesized according to [3, 5]), conditions for quantitative separation were chosen. 2,4-DNPH of PhCH₂COMe and MeC₆H₄CH₂COMe were eluted with benzene; 2,4-DNPH of p-MeCOC₆H₄CH₂COMe, with 9:1 benzene-ethyl acetate. <u>Acetyldemetallation of PhCh₂SnMe₃ with Acetyl Chloride in Presence of AlBr₃</u>. Into a four-necked flask provided with a retort containing 0.67 g (2.5 mmole) of AlBr₃ catalyst were placed 0.20 g (2.5 mmole) of MeCOCl and 10 ml of CH_2Cl_2 . The solution was held for 10 min at -50°C, and then AlBr₃ was dropped from the retort into the reaction mixture. When the AlBr₃ had dissolved, a precooled solution of 0.26 g (1 mmole) of PhCH₂SnMe₃ in 5 ml of CH_2Cl_2 was poured into the flask. After 5 min stirring the reaction mixture was poured into a cooled 3% solution of HCl in H₂O. The organic layer was separated, washed with water, dried over MgSO₄, and analyzed.

<u>Test of Possible Acetyldemetallation of PhCH₂SnMe₃ without AlBr₃.</u> A mixture of 0.1 g (0.4 mmole) of PhCH₂SnMe₃ and 0.31 g (4 mmole) of MeCOC1 in a sealed ampul was kept in a 60°C thermostat for 40 h. Then the mixture was treated with 3% HCl, and the organic layer was washed with water, dried over MgSO₄, and analyzed. Carbonyl products were absent.

<u>Test of Possible Reaction between PhCh₂SnMe₃ and AlBr₃</u>. A solution of 0.26 g (1 mmole) of PhCH₂SnMe₃ and 0.67 g (2.5 mmole) of AlBr₃ was stirred for 5 min at -50°C, then decomposed with 3% HCl. The organic layer was separated, washed with water, and dried over MgSO₄. GLC analysis showed that the reaction product was 90% toluene. The initial stannane was not present.

<u>Deuterolysis of Reaction Mixture Obtained in Reaction of PhCH₂SnMe₃ with AlBr₃.</u> A solution of 1.2 g (4.7 mmole) of PhCH₂SnMe₃ and 3.2 g (12 mmole) of AlBr₃ was stirred for 5 min at -50°C, and then decomposed with 5% DCl in D₂O. The organic layer was separated, washed with water until neutral, and dried over MgSO₄. CH₂Cl₂ was distilled from the solution through a column filled with glass rings. From the residue there was obtained in an Aerograph Autoprep-705 preparative chromatograph 0.2 ml of chromatographically pure toluene.

Test of Possible Protolysis of $PhCH_2SnMe_3$ during Decomposition of Reaction Mixture by Dilute HC1. A solution of 0.26 g (1 mmole) of $PhCH_2SnMe_3$ in 15 ml of CH_2Cl_2 was treated with 3% HC1. The organic layer was washed twice with water and dried over $MgSO_4$. GLC analysis showed that toluene was absent, and that the initial amount of stannane was retained.

CONCLUSIONS

1. Benzyltrimethylstannane reacts with MeCOCl in the presence of $AlBr_3$ by attack at the para position of the benzene ring (FE mechanism) to form a mixture of mono- and diketones (p-MeCOC₆H₄Me and p-MeCOC₆H₄CH₂COMe). The nature and relative amounts of products correspond to the reaction of PhCH₂HgCl under analogous conditions, and depends on the order of reagent addition.

2. A mixture of $PhCH_2SnMe_3$ and $AlBr_3$ after brief contact and hydrolysis gives toluene in high yield; this can be explained by the formation of reactive organoaluminum intermediates. Deuterolysis of the mixture gives mono-, di-, and trideuteritoluenes, with o-deuterotoluene predominant.

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ATTEMPT TO SYNTHESIZE SELENIUM AND TELLURIUM ANALOGS

OF 1,5-BIS(ARYL)-2,4-DIAZA-1,3,5-TRITHIA-2,3-PENTADIENES

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Acyclic azathienes have been thoroughly studied and have found wide use in organic synthesis. The study of acyclic azaselenes and azatellurenes has only begun [1]. The purpose of the present work was to attempt the synthesis of the Se and Te analogs of 1,5-bis(aryl)-2,4-diaza-1,3,5-trithia-2,3-pentadienes.

According to the data of [2], a convenient synthesis of 1,5-bis(aryl)-2,4-diaza-1,3,5trithia-2,3-pentadienes would be the reaction of aromatic sulfenyl chlorides with 1,3-bis-(trimethylsilyl)-1,3-diaza-2-thiaallene (I). Actually, compound (I) reacts readily with phenyl- and pentafluorophenylsulfenyl chlorides to form 1,5-bis(phenyl)- and 1,5-bis-(pentafluorophenyl)-2,4-diaza-1,3,5-trithia-2,3-pentadienes (II) and (III), which were previously synthesized by other methods [1]. But while (I) and phenylselenenyl chloride react under mild conditions to form 1,5-bis(phenyl)-2,4-diaza-3-thia-1,5-diselena-2,3-pentadiene (IV) in high yield, the only identifiable product of the reaction of (I) with pentafluorophenylselenenyl chloride is decafluorodiphenyl diselenide. The reaction of (I) with phenyltellurenyl bromide (the chloride is not described) gives a product of empirical formula $C_6H_5BrN_2S_2$. Te (V), probably with a heterocyclic structure.

A general approach to the synthesis of 1,5-bis(aryl)-2,4-diaza-1,3,5-trithia-2,3-pentadienes and their selenium and tellurium analogs might be the reaction of N-arylchalcogenylhexamethyldisilazanes with chalcogen tetrahalide. From lithium N,N-bis(trimethylsilyl)amide and arylchalcogenyl halides, N-phenylsulfenyl-, N-pentafluorophenylsulfenyl-, N-phenylselenenyl-, and N-pentafluorophenylselenenylhexamethyldisilazanes (VI)-(IX) were synthesized ((VI) and (VII) have been described previously [3-5]). N-Phenyltellurenyl hexamethyldisilazane could not be synthesized by this method. Nor was it possible to cleave the Te-Te bond of diphenyl ditelluride by the action of sodium N,N-bis(trimethylsilyl)amide in boiling benzene (in contrast to the S-S bond of diphenyl disulfide [3]).

The reaction of (VIII) with SeCl₄ gives two products: diphenyl diselenide and an unidentified material that decomposes explosively when separated from the reaction mixture. In this connection other reactions of (VI)-(IX) with selenium and tellurium tetrahalides were not carried out.

Compound (VII) does not react with SF_4 in THF at ~20°. According to [6], under similar conditions SF_4 can be replaced by SCl_2 or S_2Cl_2 . But the reactions of compounds (VII)-(IX) with SCl_2 give cyclotetraazathiene (SN)₄ and diaryl dichalcogenides.

From the UV spectra of (II) and (IV) it follows that replacement of S by Se at positions 1 and 5 of the azathiene chain of (II) increases the energy of transition to the first excited state; λ_{max} of the longwave band shifts from 460 to 392 nm. A similar hypsochromic shift takes place when H is replaced by F in (II); in the spectrum of (III) the long-wave absorption maximum appears at 402 nm.

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