Journal of Organometallic Chemistry, 74 (1974) 67—73

THERMAL DECOMPOSITION OF 4-TOSYLOXYBUTYLTRIMETHYLTIN: THREE PATHWAYS IN THE PROTONOLYSIS OF 3-BUTENYLTRIMETHYLTIN

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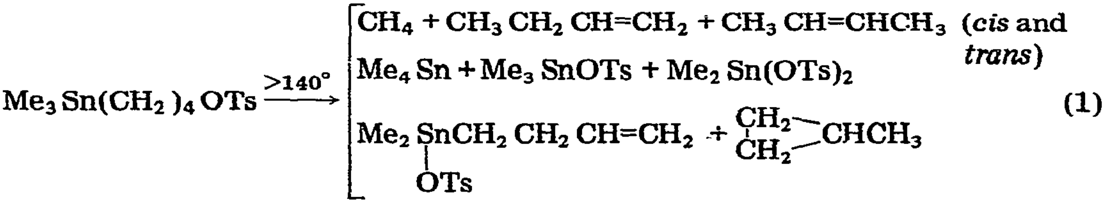
(Received January 29th, 1974)

Summary

The thermal decomposition of 4-tosyloxybutyltrimethyltin has been shown to occur by an initial dehydrotosylation to form toluenesulfonic acid and 3-butenyltrimethyltin. The reaction can be arrested at this stage if a base such as sodium carbonate or, better, 2,6-lutidine is present to neutralize the acid. In the absence of base the initial products react with each other to form methylcyclopropane, 1-butene, methane, trimethyltin tosylate and 3-butenyldimethyltin tosylate as secondary products. Further reactions lead to the additional products: Tetramethyltin, dimethyltin ditosylate, and *cis*- and *trans*-2-butenes.

A survey of the behavior of simple ω-tosyloxyalkyltrimethyltins has revealed a striking difference between the propyl and butyl analogs [1]. The former undergoes facile thermal decomposition to produce an essentially quantitative yield of cyclopropane. 4-Tosyloxybutyltrimethyltin, on the other hand, requires somewhat more drastic conditions for decomposition, and a complex mixture of products results. Those characterized to date are shown in eqn. 1.



$$\mathrm{Me_3Sn(CH_2)_4OTs} \xrightarrow{>140^\circ} \left[\begin{array}{l} \mathrm{CH_4 + CH_3CH_2CH{=}CH_2 + CH_3CH{=}CHCH_3}\ (\textit{cis}\ \text{and}\ \textit{trans}) \\ \mathrm{Me_4Sn + Me_3SnOTs + Me_2Sn(OTs)_2} \\ \mathrm{Me_2\underset{\displaystyle OTs}{\underset{|}{Sn}}CH_2CH_2CH{=}CH_2 + \overset{CH_2}{\underset{CH_2}{|}}{>}CHCH_3} \end{array}\right. \qquad (1)$$

This report is concerned with the general course of the decomposition and, in particular, the modes of formation of methylcyclopropane and the other four-carbon products.

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TABLE 1

COMPOSITION OF GAS EVOLVED IN THE DECOMPOSITION OF 4-TOSYLOXYBUTYLTRIMETHYLTIN

	140°	160°	180°	200°
$t_{1/2}$ (gas formation)	12 h	1 h	2 min.	<2 min.
methane, % of total	63	38.5	35.5	29.5
C_4, % of total	37	61.5	64.5	70.5
C_4 distribution (%)				
1-butene	52	53	56	57
cis-2-butene	10	8	6	6.5
trans-2-butene	9	9	7	5
methylcyclopropane	29	30	31	31.5

The results of an examination of the gaseous products of the decomposition of 4-tosyloxybutyltrimethyltin at three temperatures are given in Table 1. These reveal that decomposition occurs at a measurable rate above 140°, that the amount of methane formed decreases with temperature, and that the proportion of 1-butene (and, perhaps, methylcyclopropane) increases slightly with temperature at the expense of the 2-butenes. These proportions are not the result of thermodynamic control (see below); neither do the conditions of the experiments assure that they are the consequences of kinetic control alone. Cyclobutane was not found among the products.

When the decomposition was carried out in boiling (154°) dimethylformamide the half-life was 2 h, and 95% of the gas was methane; when boiling (153°) anisole was used as solvent, extremely slow decomposition occurred (5% after 5 h).

The only reasonable source of methane appeared to be protonolysis of the methyl—tin bond. When the decomposition was carried out in the presence of suspended sodium carbonate, carbon dioxide and small amounts of hydrocarbon were formed. If 2,6-lutidine was used as a solvent no gaseous hydrocarbons were evolved. About 12% of 3-butenyltrimethyltin was isolated after six hours at 143° with the added lutidine. Also, when 4-tosyloxybutyltrimethyltin was heated at 180° at 15 mm, 3-butenyltrimethyltin distilled and was isolated in 20% yield. These observations point to dehydrotosylation (eqn. 2), as a necessary prelude to formation of methane and the C_4 hydrocarbons.

$$\mathrm{Me_3SnCH_2CH_2CH_2CH_2OTs} \rightarrow \mathrm{Me_3SnCH_2CH_2CH{=}CH_2} + \mathrm{HOTs} \qquad (2)$$

To test this postulate, 3-butenyltrimethyltin and *p*-toluenesulfonic acid were heated at 80°. Gas evolution occurred with a half life of 30 minutes. Its composition was 55% methane and 45% C_4H_8 consisting of 47% 1-butene, 16.5% *trans*-2-butene, 13.5% *cis*-2-butene and 22% methylcyclopropane. Thus, all of the hydrocarbons formed in the decomposition of 4-tosyloxybutyltrimethyltin are also formed in the reaction of 3-butenyltrimethyltin with toluenesulfonic acid. The fact that the product distributions differ can be attributed in part to the difference in temperatures and in part to the fact that equilibration of the C_4 hydrocarbons occurs readily in the presence of the acid, as shown in Table 2.

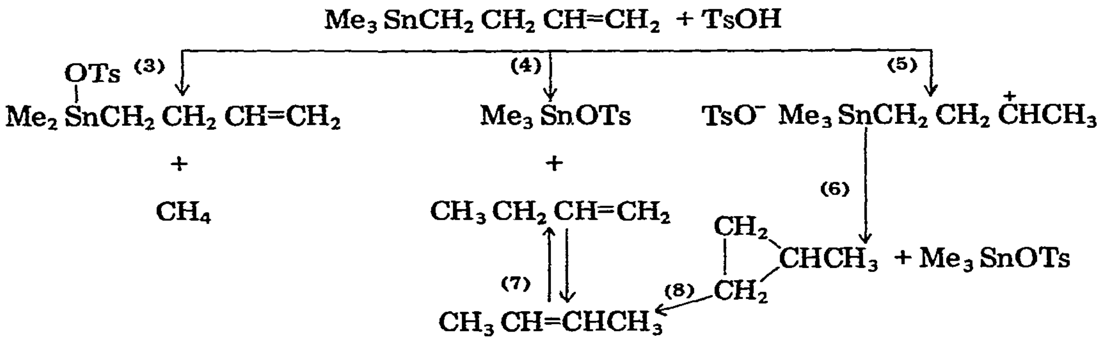
TABLE 2

EQUILIBRATION OF C_4H_8 ISOMERS BY TOLUENESULFONIC ACID

Substrate	Time (min)	Temp. (°C)	Products (%)			
			1-butene	*trans*-2-butene	*cis*-2-butene	methylcyclopropane
1-butene	60	110	10.7	52	37.3	0
cis-2-butene	45	150	11	49	40	0
methylcyclopropane	5	110	8	36	34	22
	20	110	10.5	50	39.5	0

These results can be rationalized in terms of Scheme 1. Protonolysis of 3-butenyltrimethyltin by toluenesulfonic acid formed in reaction 2 can occur in three ways: cleavage of a methyl—tin bond to form methane (eqn. 3); cleavage of a butenyl—tin bond forming 1-butene (eqn. 4); and protonation of the terminal atom of the double bond followed (or accompanied) by intramolecular electrophilic attack on a carbon—tin bond to form methylcyclopropane (eqns. 5 and 6). If contact with acid is sufficiently long equilibration of the C_4 products can, and does, occur to give a mixture of 1-butene, *cis*-2-butene and *trans*-2-butene in a 1/4/5 ratio.

SCHEME 1



As one test of the scheme the reaction between deuteriotoluenesulfonic acid ($C_7H_7SO_3D\cdot D_2O$) and 3-butenyltrimethyltin was carried out and the C_4 products were trapped at —113° and examined by PMR spectroscopy. The major deuterated products were those expected: $DCH_2CH_2CH{=}CH_2$ by eqn. 4; $DCH_2CH(CH_2)_2$ by eqns. 5 and 6; 2-butene-d_2 and 2-butene-d_3 by eqns. 7 and 8.

Integration indicated 2.15 protons per methyl group of the methylcyclopropane, suggesting that the reaction sequence 5 → 6 is irreversible. Similarly, the 1-butene formed contained 2.0 protons in the methyl group indicating that it was formed primarily by deuterolysis of the tin—butenyl carbon bond. These facts lead to the conclusion that the initially formed 2-butenes must result primarily, but not necessarily exclusively, from deuterolytic cleavage of the ring of methylcyclopropane (eqn. 9a). Loss of a proton from the secondary carbon could form 2-butenes containing deuterium atoms at each of the methyl groups;

$$\mathrm{TsOD} + \mathrm{CH_2DCH}\overset{\mathrm{CH_2}}{\underset{\mathrm{CH_2}}{<|}} \longrightarrow \mathrm{CH_2D\overset{+}{C}HCH_2CH_2D} \begin{cases} \rightarrow \mathrm{CH_2DCH{=}CHCH_2D} & \text{(9a)} \\ \rightarrow \mathrm{CHD{=}CHCH_2CH_2D} & \text{(9b)} \end{cases}$$

i.e., the methyl-proton/vinyl-proton ratio would 2.0. The observed value was 2.3. Since only this ratio, and not the total numbers of hydrogens and deuteriums, was determined it seems probable that some H—D exchange has occurred in the 2-butenes by deuteronation-deprotonation, and that there were three deuterium atoms in some of the 2-butene molecules. Formation of 1-butene by eqn. 9b would be expected to occur by loss of a proton faster than a deuteron leading to more 1-butene-d_2 than 1-butene-d_1. To the extent that this occurred the allylic-proton/terminal vinyl-proton ratio would tend toward 2, but the actual value was unity within the experimental error. In support of these conclusions are the observations made that the half-lives for isomerization of methylcyclopropane and of *cis*-2-butene to the equilibrium mixture of butenes are less than a tenth and a fifth, respectively, of the rate for 1-butene.

Formation of dimethyltin ditosylate could occur by one or more of three reactions: Protonolysis of a methyl group from trimethyltin tosylate, protonolysis of the butenyl group from 3-butenyldimethyltin tosylate, or exchange between either of these substrates with trimethyltin tosylate (eqns. 10a and 10b).

$$\mathrm{(CH_3)_3SnOTs} \begin{cases} \xrightarrow{\mathrm{(CH_3)_2Sn(OTs)C_4H_7}} \mathrm{(CH_3)_3SnC_4H_7} + \mathrm{(CH_3)_2Sn(OTs)_2} & \text{(10a)} \\ \xrightarrow{\mathrm{(CH_3)_3SnOTs}} \mathrm{(CH_3)_4Sn} + \mathrm{(CH_3)_2Sn(OTs)_2} & \text{(10b)} \end{cases}$$

The formation of tetramethyltin could also occur by the analogous exchange between trimethyltin tosylate and 4-tosyloxybutyltrimethyltin tosylate, for which precedents involving trialkyltin chlorides exist [2, 3].

The formation of cyclopropanes by formal intramolecular electrophilic displacements on carbon—tin bonds has been observed previously by Scarpa [1, 4] and, particularly by Peterson and his collaborators [5, 6]. The latter have observed the 3-butenyltri-n-butyltin reacts with a variety of electrophiles to form cyclopropylcarbinyl compounds in yields high enough to be of synthetic utility. On the other hand, in the reaction with bromine in methylene chloride the trimethyltin analog yielded product of which one-fourth was methyl bromide, and the triphenyl analog gave only bromobenzene as the brominolysis product. Similarly Roberts [7] reports only methyl iodide (86%) in the iodinolysis of 3-butenyltrimethyltin in acetonitrile. These results suggest that the tendency toward cyclopropane formation from reaction of $R_3SnCH_2CH_2CH{=}CH_2$ with electrophiles depends strongly on the nature of R: The better R_3Sn is an electrofugal group (i.e., the better R is at inductive electron release) the more likely this reaction. Hence, the observed order is n-Bu > Me > Ph or R. A more polar solvent, on the other hand, would appear to favor simple products of direct electrophilic cleavage of the carbon—tin σ bonds over those of initial attack at the π bond. Other reaction parameters undoubtedly also affect the course of electrophilic attack on homoallylic organometallics. For example, 3-butenylmagnesium chloride and bromide give 1-butene upon treatment with benzoic acid or trifluoroacetic acid [8]. All of these results, taken together, indicate clearly that the product distribution obtained by chemical conversions of a mixture of 3-butenyl and cyclopropylcarbinyl organometallics may not reflect the original composition of this mixture.

Experimental

Gas-liquid partition chromatographic analysis and separation of gaseous products were carried out on 1/4 in. columns in tandem, one consisting of 15 ft. packed with dimethylsulfolane on Chromosorb W (60—80 mesh) and the other a 20 ft. section packed with silicone gum rubber on the same support. Infrared spectra were obtained on a Beckman IR 10 instrument. Proton magnetic resonance spectra were obtained with a Varian A-60A instrument. Chemical shifts are given in ppm downfield from internal tetramethylsilane.

3-Butenyltrimethyltin and 4-tosyloxytrimethyltin were prepared by the method of Scarpa [4].

p-Toluenesulfonic acid-O-*d*$\cdot D_2O$ was prepared by dissolving *p*-toluenesulfonyl chloride in deuterium oxide, evaporating to dryness and storing in a desiccator over potassium hydroxide pellets.

Methane, 1-butene, *cis*-2-butene, *trans*-2-butene and tetramethyltin obtained from commercial sources were used in the identification of reaction products. Identity of GLPC retention times, IR spectra and PMR spectra were used in assigning structures to reaction products. Methylcyclopropane was prepared in substantially quantitative yield by heating a mixture of *p*-toluenesulfonyl chloride (0.65 g) and 3-hydroxybutyltrimethyltin (1.10 g) in pyridine (5 ml) for 30 min.

Thermal decomposition of 4-tosyloxybutyltrimethyltin

A round bottom distilling flask with a capacity of 0.75 ml with a condenser side-arm was connected to a mercury-filled gas buret. The system was designed to have a minimal dead volume (ca. 2.5 ml), and was fitted with a serum-capped side arm for gas sampling. In a typical experiment 0.5 g of the tosylate was placed in the flask, which was flushed with helium, and then heated to 160° for 2.5 h, when gas evolution ceased. The infrared spectrum of the gas showed the characteristic vibration-rotation envelopes of methane centered at 3000 and 1300 cm^{-1} and the olefinic bands of the butenes between 1600 and 1850 cm^{-1}. The gas chromatogram showed the presence of six compounds with retention times identical with those of methane, cyclopropane*, 1-butene, methylcyclopropane, *cis*-2-butene and *trans*-2-butene. Samples of the gases were collected in traps cooled with liquid nitrogen, and the PMR spectra in chloroform solution taken. 1-Butene was identified by the vinyl-proton multiplets at δ 4.5 and δ 6.0; methylene multiplet at δ 2.0 and the methyl triplet centered at δ 1.6. The 2-butenes showed the vinyl multiplet at δ 5.4 and the methyl multiplets at δ 1.6. Methylcyclopropane showed the methyl doublet at δ 1.03, and ring proton

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* The 4-tosyloxybutyltrimethyltin was prepared by hydrostannation of 3-butenol, followed by conversion of the alcohol to the tosylate. It was found that the 3-butenol was contaminated with about 5% of allyl alcohol which resulted in the presence of 3-tosyloxypropyltin in the product.

multiplets at δ 0.4, and δ 0.05. The cyclopropane singlet appeared at δ 0.63. Data on rate and gaseous product distribution at four temperatures are given in Table 1.

The small amount of liquid which condensed on the mercury of the gas buret was shown to be tetramethyltin by GLPC and a singlet at δ 0.06 as the only signal in the PMR spectrum.

The residual solid in the reaction flask was dissolved in D_2O and its PMR spectrum showed the presence of dimethyltin ditosylate (δ 1.03), trimethyltin tosylate (δ 0.63) and 3-butenyldimethyltin tosylate (methyl singlet at δ 0.60, and multiplets in the δ 4.5 and δ 6.0 regions). The infrared spectrum showed a sharp band at 1640 cm^{-1}, due to a terminal vinyl group.

Decompositions in anisole and dimethylformamide

To 4.5 ml of the solvent was added 0.5 g of the tosylate in the apparatus described above. The flask was placed in a bath at 165°, and the evolution of gas was observed. In anisole, after 5 h, the volume of gas was about 3% that expected for complete decomposition and contained only cyclopropane. When dimethylformamide was used as the solvent, gas was evolved with a half-life of 30 min. When decomposition was complete analysis of the gas by GLPC revealed it to consist of at least 95% methane.

Isolation of 3-butenyltrimethyltin

(a) A mixture containing 0.4 g each of lutidine and 4-tosyloxybutyltrimethyltin was heated for 2.5 h, after which the reaction mixture was black, and the only gas evolved was 2 ml of cyclopropane. Distillation of the residue yielded 0.024 g (12%) of 3% butenyltrimethyltin, characterized by its PMR spectrum. *(b)* In another experiment, designed to remove this compound by distillation before it could react with the toluenesulfonic acid formed concomitantly, 0.5 g of the tosyloxytin compound was heated in the reaction flask at 15 mm and 180°. The liquid which distilled (0.12 g) consisted primarily of 3-butenyltrimethyltin.

Reaction of 3-butenyltrimethyltin with p-toluenesulfonic acid

The reaction flask containing 0.22 g of *p*-toluenesulfonic acid and 0.28 g of 3-butenyltrimethyltin was placed in a preheated bath until gas evolution ceased. About 55% of the gas was methane. The C_4 products, 1-butene, *trans*-2-butene, *cis*-2-butene and methylcyclopropane, respectively, comprised 47, 17, 13 and 22% at 80°, and 34, 29, 23 and 14% at 170°. At 80° the reaction was complete within 1 h, and at 150° within 1 min.

In a similar experiment at 80—100° using $p\text{-}CH_3C_6H_4SO_3D \cdot D_2O$, the evolved gases were condensed in a trap cooled with liquid nitrogen, separated by GLPC, and the PMR spectra taken in CCl_4. The relative areas under the proton signals for the 1-butene were: C-1, 1.97; C-2, 1.02; C-3, 1.93 and C-4, 2.0. For the 2-butene mixture the areas were: C-1, 4.6; C-2, 2.0. For the methylcyclopropane the areas were: CH_3, 2.15, C-1, C-2, C-3 (*cis*, *cis*, *cis*; 3 protons), 3.0; C-2, C-3 (*cis* to CH_3), 1.97.

Equilibrations of C_4 isomers by p-toluenesulfonic acid

The reaction flask containing 1.5 g of *p*-toluenesulfonic acid was connected to the gas buret and charged with 50 ml of hydrocarbon. The flask was then immersed in an oil bath, and the gas was analyzed by GLPC at times and with results indicated in Table 2.

Acknowledgements

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society for support of this research. We also thank M & T Chemicals Inc., for gifts of chemicals.

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