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Preliminary communication

Deoxymetalations. 1,3 eliminations of organotin alcohols

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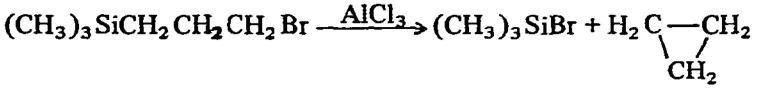
In a previous report we have noted that β-hydroxyalkyl triphenylmetal compounds undergo a rapid 1,2 elimination reaction to produce a triphenylmetal salt and alkene[1].

$$Ph_3MCR_2CR_2OH \xrightarrow[HOAc]{H^+} Ph_3MOAc + R_2C{=}CR_2 + H^+$$

(M = Sn, Pb)

As an extension of this work we have investigated the reactions of γ-hydroxyalkyl trimethyltin compounds as possible 1,3 elimination precursors.

A reaction analogous to the 1,3 elimination of hydrogen halides from organic compounds was reported by Sommer and co-workers in 1949[2]. They found that certain γ-haloalkyl organosilicon compounds undergo 1,3 elimination to give cyclopropane.



$$(CH_3)_3SiCH_2CH_2CH_2Br \xrightarrow{AlCl_3} (CH_3)_3SiBr + H_2C\!-\!CH_2\ (\text{ring closed by } CH_2)$$

Gilman and Marrs[3] have also reported that 3-triphenylsilylpropyl *p*-toluenesulfonate, when subjected to formolysis, yields products indicative of 1,3 elimination:

$$Ph_3SiCH_2CH_2CH_2OSO_2C_7H_7 \xrightarrow[HCO_2Na]{HCO_2H} Ph_3SiOSiPh_3 + Ph_3SiOH +$$
$$+ PH_3SiCH_2CH_2CH_2OH$$

The cleavage of the Si–C bond to give $Ph_3SiOSiPh_3$ and Ph_3SiOH suggests that 1,3 elimination has occurred, however no cyclopropane was found.

With a view toward a better system for 1,3 elimination, a series of γ-hydroxyalkyl trimethyltin compounds was prepared by the reaction of trimethyltin hydride with an excess of the appropriate unsaturated alcohol (reflux, 5 hours):

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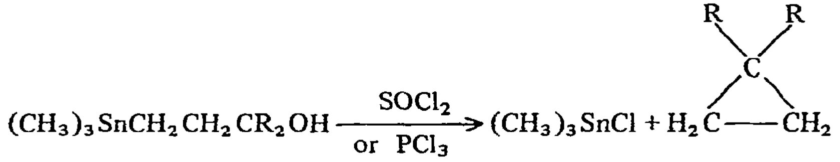
$$(CH_3)_3SnH + CH_2{=}CH{-}CR_2OH \longrightarrow (CH_3)_3SnCH_2CH_2CR_2OH$$
$$(R_2 = H, H;\ H, CH_3;\ CH_3, CH_3)$$

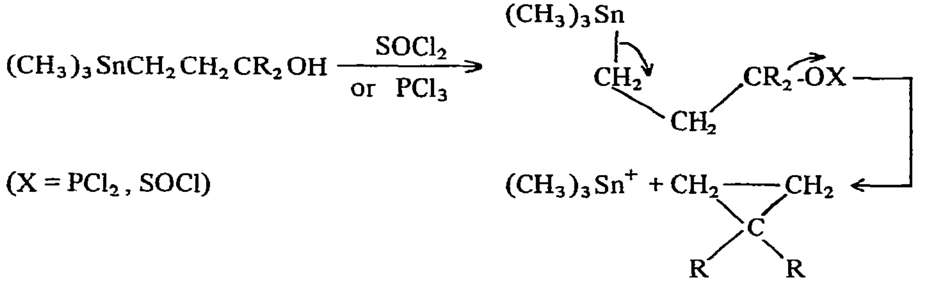
The compounds prepared were 3-(trimethylstannyl)propanol (b.p. 64°/ 1.5 mm), 3-(trimethylstannyl)-2-butanol (b.p. 66°/ 2.0 mm), and 3-(trimethylstannyl)-2-methyl-2-butanol (b.p. 52°/ 0.2 mm) in yields of 68, 57, and 29 % respectively. The IR and NMR spectra of these materials are consistent with the proposed structures. These products are air and water stable; however, when treated with an excess of thionyl chloride or phosphorous trichloride, a rapid elimination reaction occurs to produce a cyclopropane and trimethyltin chloride:



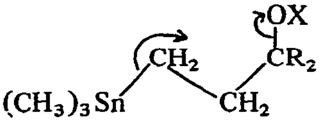
Reaction of either thionyl chloride or phosphorous trichloride with 3-(trimethylstannyl)-propanol produced trimethyltin chloride and cyclopropane (90 % yield). Analogously, 3-(trimethylstannyl)-2-butanol produced trimethyltin chloride and methylcyclopropane 80–85 % yield), while 3-(trimethylstannyl)-2-methyl-2-butanol gave trimethyltin chloride and 1,1-dimethylcyclopropane in 90 % yield.

The structures of the cyclic alkanes were confirmed by comparison of mass spectra, infrared spectra, and gas chromatographic retention times with those of the known compounds. The trimethyltin chloride was identified by comparison of its NMR spectra (chemical shift and the ^{117}Sn—^{119}Sn coupling constants) to that of an authentic sample of trimethyltin chloride.

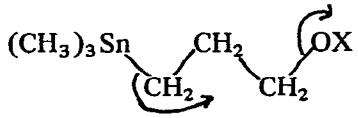
A possible mechanism for the formation of the cyclopropane ring is shown below:



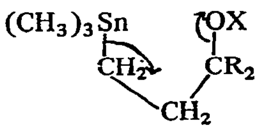
The question of the timing of the C—O and C—Sn bond breaking is still under investigation. The scheme shown here is not meant to imply a concerted reaction. Indeed, evidence presented later in this paper may indicate that, at least in some cases, a carbonium ion is involved in this reaction. The conformation of the transition state as shown above is the *exo*-sickle[4]. Other possible conformations are the *endo*-sickle, the W and the U. The stereochemistry at the reacting carbons are, retention—inversion, inversion—retention, inversion—inversion, and retention—retention respectively. In each case, the stereochemistry at the tin-bearing carbon is given first.



endo-S

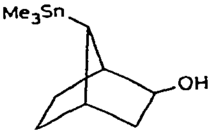


W

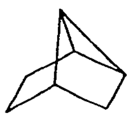


U

To examine the stereoelectronic requirements of the elimination, *anti*-7-trimethylstannyl-2-*exo*-norbornanol (I) was synthesized from the 7-norbornenyl Grignard reagent[5] by stannylation followed by hydroboration-oxidation and separation from the product mixture. This compound has the inversion–retention sickle configuration. When I was allowed to react with neat $SOCl_2$, PCl_3, or $SOCl_2$ in carbon tetrachloride solution, the major products as identified by NMR and GLC, were norbornene, 2-*exo*-norbornyl chloride, and trimethyltin chloride. The expected 1,3 elimination product, tricyclo-[4.1.0.0.^{3,7}]heptane[6,★] (II) was not observed.

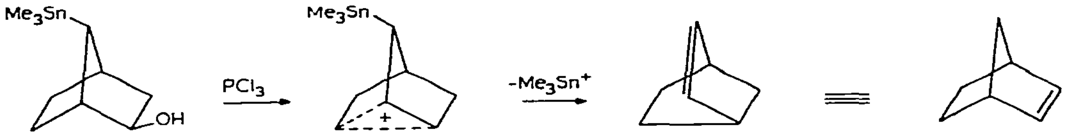


(I)



(II)

The particular geometry of I, the *endo*-sickle, appears to be an unfavorable configuration for a concerted 1,3 cyclization. A reasonable postulate for the formation of norbornene is from the non-classical ion (or a rapidly equilibrating classical ion) that occurs during the reaction of $SOCl_2$ or PCl_3 with *exo*-norbornanols. A rapid elimination is known to occur when a positive charge is β to a tin–carbon bond[1].



Norbornyl chloride then arises from further reaction of norbornene with HCl produced during the reaction. Both norbornene and norbornyl chloride are possible products of attack of HCl on II. Electrophilic cleavage of II should favor the formation of norbornyl chloride, however, norbornene is produced in greater amounts. As further support, II is being synthesized and its stability under the reaction conditions determined. The highly strained nature of II may also affect the relative amounts of 1,3 elimination and rearrangement-elimination.

★ *Chemical Abstracts* lists this compound as tricyclo[3.2.0.0^{2,7}]heptane.

Further work is in progress with other compounds having defined geometry to further elucidate the stereochemical requirements of the 1,3 elimination.

ACKNOWLEDGMENT

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