value in the synthesis of heterocyclic rings. It should be pointed out that insertion products such as II may have been formed in other Beckmann or Schmidt reactions and were inadvertently missed since they would remain in the oft-discarded diluted acidic solution from which the usual neutral products are removed by filtration or extraction.

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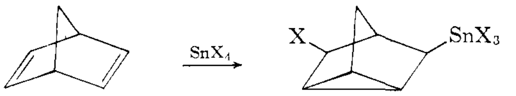
TIN TETRAHALIDE ADDUCTS OF BICYCLOHEPTADIENE AND THEIR FRAGMENTATION[1]

Sir:

Although olefins generally are known to be attacked by electrophilic reagents, few studies have been published on the interaction of olefins with strong Lewis acids other than boron hydrides.[2] Recently it has shown that BCl_3 and $C_6H_5BCl_2$ will add to several reactive olefins, including bicycloheptadiene.[3]

We now wish to report the addition of $SnCl_4$ and $SnBr_4$ to bicycloheptadiene (I) to yield crystalline 1:1 adducts, which like the boron halide adducts[3] are formulated as substituted nortricyclenes (II).

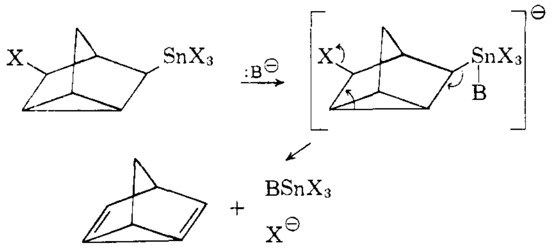


I II

These products presumably arise through homoconjugative addition of the type described by Winstein and Shatavsky.[4] The compounds are prepared simply by mixing the reactants in approximately equimolar proportion in dry isopentane at 0° and allowing the solution to stand. The colorless crystals which form may be recrystallized from fresh isopentane; m.p. for $C_7H_{10}SnCl_4$, 60.5–61.5°; for $C_7H_{10}SnBr_4$, 58–59°.

The infrared spectra of the two compounds provide strong support for the nortricyclene structure. Both compounds have strong bands at 3070 and 1020 cm.$^{-1}$, which are diagnostic for the cyclopropane ring in nortricyclenes.[5] A band also appears in the 800–818 cm.$^{-1}$ region in both compounds, consistent with the fact that the cyclopropyl ring is not substituted.[5] The complex proton magnetic spectra of the two compounds are very similar, differing only in slight shifts of peak positions and in relative intensities. These n.m.r. spectra have not yielded to analysis, perhaps because several stereoisomers are present. However, protons in at least eight different environments are found, consistent with the nortricyclene structure and inconsistent with alternative pi-complex formulations.

Upon treatment with water or bases the compounds undergo a remarkable fragmentation reaction,[6] with the reformation of bicycloheptadiene and a tin-containing fragment. This reaction may be explained as a delta-elimination brought about by attack of the base at tin



The fragmentation is quantitative and was used for approximate analysis of the compounds, sufficient to show that they are 1:1 adducts. In a typical hydrolysis, the $SnCl_4$ adduct gave bicycloheptadiene, 25.9; Sn, 35.8; Cl, 38.0 (calcd. for $C_7H_{10}SnCl_4$; bicycloheptadiene, 26.5; Sn, 33.4; Cl, 40.0). The $SnBr_4$ adduct gave bicycloheptadiene, 16.3; Sn, 19.6; Br, 60 (calcd. for $C_7H_{10}SnBr_4$, bicycloheptadiene, 17.6; Sn, 22.3; Br, 60.1). Conventional combustion analyses were impractical because of the instability of the compounds.

The adducts are stable pure or under hydrocarbons at 0° or below, but at room temperature or in contact with polar solvents they decompose with the formation of tarry masses apparently containing polymerized material It seems not unlikely that similar adducts may be formed during the polymerization of diolefins by $SnCl_4$. Experiments are under way with other Lewis acids and olefins to determine the generality of the addition reaction. Preliminary results indicate that $GeBr_4$ and $C_6H_5SnCl_3$ form adducts with bicycloheptadiene, but that SnI_4, $SiCl_4$ and $(C_6H_5)_2SnCl_2$ do not.

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