1,2-Addition of Tin Tetrachloride to Bicyclo[2.2.1]hepta-2,5-diene and 2,3-Benzobicyclo[2.2.1]hepta-2,5-diene

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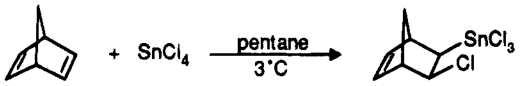
Organotin halides are key intermediates in the industrial[1] and laboratory[2] preparation of several important classes of organotin compounds: unsymmetrical tetraorganostannanes, stannyl hydrides, organostannoxanes, hydroxyorganostannanes, alkoxyorganostannanes, or (acyloxy)organostannanes.[3] The principal routes involve the electrophilic cleavage of tetraorganostannanes by hydrogen halides, halogens, or tin tetrahalides and are general enough to be used for the preparation of tri-, di-, or monohaloorganostannanes.[4] In the case of trihaloorganostannanes,[5] more specific reactions can also be used,[6−13] such as the 1,4−addition reaction of tetrachlorostannane to bicyclo[2.2.1hepta-2,5-diene. This addition leads to trichloro(5-chlorotricyclo[2.2.1.$0^{2.6}$]hept-2-yl)stannane (**1**).[14] Our interest in trichloroorganostannanes as key intermediates for the preparation of functional trialkoxyorganostannanes[15] as precursors of hybrid organic−inorganic materials led us to try to prepare **1** following the precedented route.

1

When a mixture of an equimolecular amount of norbornadiene and tin tetrachloride in pentane is left at 3 °C for 18 h, colorless crystals (mp 60 °C dec) were formed in a 72% yield, as described. However, examination of the ^{1}H NMR spectrum revealed some discrepancies between this compound and the proposed structure, which itself was only supported by an IR study and an uninformative NMR spectrum. In particular, the presence of two ethylenic hydrogens is clearly indicative of 1,2-addition leading to trichloro(3-chlorobicyclo[2.2.1]-5-hepten-2−yl)stannane (**2**), which rules out the previous conclusions of skeletal rearrangement. It is, however, possible that our adduct could be either an intermediate in the formation of the reported trichloro(5-chlorotricyclo-[2.2.1.$0^{2.6}$]hept-2-yl)stannane (**1**), or a rearranged product formed from it.



2

A ^{1}H−^{13}C heteronuclear correlation experiment allowed the unambiguous assignment of both hydrogens and carbons.[16] As only one set of resonances was observed in ^{1}H, ^{13}C, and ^{119}Sn NMR spectroscopies, it was concluded that the reaction was stereospecific. Four products in principle could be formed, from exo-syn, endo-syn, or the two possible anti-additions. The stereochemical determination was based on the values of hydrogen−hydrogen,[17] tin−hydrogen, and tin−carbon[18] ^{3}J and ^{4}J coupling constants of which the angular dependencies are well-known. The value of the coupling constant between H_2 and H_3 is 6.9 Hz which is compatible with a cis relationship and rules out a trans addition of tin tetrachloride. The values of the coupling constants between, respectively, H_2 and H_1, and H_3 and H_4, are less than 1 Hz which shows that H_2 and H_3 are in endo positions and thus tin and chlorine are in exo positions. The long range coupling recorded between H_2 and H_{7s}, and H_3 and H_{7s}, is indicative of an endo position for H_2 and H_3.[19] The fact that tin and H_1 are strongly coupled ($J_{Sn-H} = 45$ Hz) is also indicative of an exo position for the metal. This study was confirmed by ^{13}C NMR spectroscopy as a value of $^{3}J_{Sn-C}$ between the tin and the bridged carbon (C_7) lower than 5 Hz was observed.[20] In the ^{119}Sn NMR, the tin resonance was found at −87 ppm.

Trichlorophenylstannane or trichloromethylstannane did not undergo a similar addition to bicyclo[2.2.1]hepta-2,5-diene. Other dienes such as bicyclo[2.2.2]octadiene

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(16) Trichloro(3-chlorobicyclo[2.2.1]-5-hepten-2-yl)stannane (**2**): yield 72%; ^{1}H NMR (250 MHz), ($CDCl_3$) δ 6.36 (dd, 1 H_6, $^{3}J_{H6-H5} = 5.6$ Hz, $^{3}J_{H6-H1} = 2.9$ Hz), 6.20 (dd, 1 H_5, $^{3}J_{H6-H5} = 5.6$ Hz, $^{3}J_{H5-H4} = 2.9$ Hz), 4.26 (ddd, 1H_3, $^{3}J_{H3-H2} = 6.9$ Hz, $^{3}J_{H3-H4} = 0.6$ Hz, $^{4}J_{H3-H7s} = 1.6$ Hz, $^{3}J_{Sn-H} = 89$ Hz), 3.53 (bs, H_1, $^{3}J_{Sn-H} = 41$ Hz), 3.27 (dd, H_2, $^{3}J_{H2-H3} = 6.9$ Hz, $^{4}J_{H2-H7s} = 2.6$ Hz, $^{2}J_{Sn-H} = 44$ Hz), 3.25 (bs, H_4), 2.31 (d, H_{7a}, $^{2}J_{H7a-H7s} = 9.6$ Hz), 1.94 (dm, H_{7s}); ^{13}C NMR ($CDCl_3$) δ 140.4 (C_6, $J_{Sn-C} = 138$ Hz), 135.8 (C_5, $^{2}J_{Sn-C} = 18$ Hz), 65.5 (C_2, $J_{Sn-C} = 750$ Hz), 58.7 (C_3, $J_{Sn-C} = 18$ Hz), 53.8 (C_4), 46.1 (C_7), 45.2 (C_1, $J_{Sn-C} = 25$ Hz); ^{119}Sn NMR δ −87.8.

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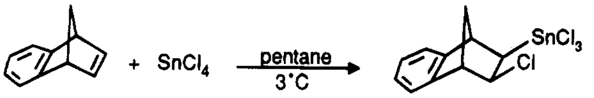
or 1,3-cyclohexadiene did not react with tin tetrachloride. Steric hinderance at the 7 position in 7,7-dimethylbicyclo[2.2.1]hepta-2,5-diene inhibited the reaction, which is consistant with hypothesis of exo attack on the double bond. The addition reaction may plausibly be assisted by the double bond since bicyclo[2.2.1]heptene was inert toward tin tetrachloride. The presence of a methoxyl group in 7-methoxybicyclo[2.2.1]hepta-2,5-diene or 1-(methoxymethyl)bicyclo[2.2.1]hepta-2,5-diene as a potential stabilizing ligand of electrophilic tin did not help the reaction to proceed. As polar solvents such as diethyl ether, acetone, dimethyl sulfoxide, favor β-elimination,[11,21] the ether group present on these dienes disfavored the reverse addition reaction, probably in raising the polarity of the medium. Despite all of these failures, the reaction was successfully extended to 2,3-benzobicyclo[2.2.1]hepta-2,5-diene (**3**) which gave an oily unstable adduct, the trichloro(3-chloro-5,6-benzobicyclo[2.2.1]hepten-2-yl)stannane **4**, presenting the same characteristics as trichloro(3-chlorobicyclo[2.2.1]-5-hepten-2-yl)stannane **2** in ^{1}H, ^{13}C, and ^{119}Sn NMR spectroscopies.[22]



3 **4**

Alkylation of both adducts with tetramethylstannane was unsuccessful. Redistribution products of the alkylating agent, and bicyclo[2.2.1]hepta-2,5-diene were recovered.

Bicyclo[2.2.1]heptene and bicyclo[2.2.1]hepta-2,5-diene have been widely used for studies of the course of addition processes because of their very high reactivity in all the types of addition reactions.[23] Usually they show a high preference for exo-attack of the double bond as demonstrated by the electrophilic addition of hydrochloric acid. The same stereochemistry was also reported with thallium acetate[24] and with phosphorus tribromide.[25] In the last case the interpretation of the ^{1}H NMR spectrum looks erroneous: the measured $J_{H1-H2} = 1.6$ Hz and $J_{H4-H5} = 2.1$ Hz in dichloro(3-chlorobicyclo[2.2.1]-5-hepten-2-yl)phosphane, contradictory with the proposed stereochemistry, must be in fact attributed to J_{H1-H7} and J_{H4-H5} respectively. With tin tetrachloride, we have shown that electrophilic addition follows the same 1,2-addition pathway.

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(22) Trichloro(3-chloro-5,6-benzobicyclo[2.2.1]hepten-2-yl)stannane (**4**): yield 65%; ^{1}H NMR (250 MHz) (CDCl$_3$) δ 7.20–7.38 (m, 4H), 4.38 (ddd, H$_3$, $^3J_{H3-H2} = 6.9$ Hz, $^4J_{H3-H7s} = 2.3$ Hz, $^3J_{H3-H4} = 0.5$ Hz, $^3J_{Sn-H} = 89$ Hz), 3.97 (bs, H$_1$, $^3J_{Sn-H} = 58$ Hz), 3.79 (bs, H$_4$, $^4J_{Sn-H} = 19$ Hz), 3.42 (dd, H$_2$, $^3J_{H2-H5} = 6.9$ Hz, $^4J_{H2-H7s} = 2.4$ Hz, $^2J_{Sn-H} = 56$ Hz), 2.68 (dt, H$_{7a}$, $^2J_{H7a-H7s} = 10.4$ Hz, $^3J_{H7a-H1,4} = 1.1$ Hz), 2.26 (dm, H$_{7s}$, $^2J_{H7s-7a} = 10.4$ Hz); ^{13}C NMR δ 146.4 (C$_6$, $^3J_{Sn-C} = 142$ Hz), 142.7 (C$_5$), 128.2, 127.7, ($J_{Sn-C} = 10$ Hz), 123.1 ($J_{Sn-C} = 9$ Hz), 121.5 ($J_{Sn-C} = 12$ Hz), 67.3, (C$_2$, $^1J_{Sn-C} = 752$ Hz), 60.7 (C$_3$, $^2J_{Sn-C} = 70$ Hz), 53.4 (C$_4$, $^3J_{Sn-C} = 10$ Hz), 46.8 (C$_1$, $^2J_{Sn-C} = 24$ Hz), 46.6 (C$_7$); ^{119}Sn NMR δ -86 ppm.

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