THE PREPARATION AND PROPERTIES OF A SERIES OF OLEFINIC TIN COMPOUNDS

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(Received April 21st, 1964)

The preparation of many mono- and diallyl derivatives of tin has been reported in detail by Jones *et al.*[1], and by Gilman[2], among others. In these cases, the compounds in question were prepared by treating an alkyl- or aryltin halide with an ether solution of allylmagnesium bromide. Thus, allyltriethyltin, allyltri-*n*-butyltin, allyltriphenyltin and allyltri-*p*-tolyltin were prepared, as well as diallyldiethyltin and diallyldi-*n*-butyltin. Allyltri-*p*-tolyltin had not been previously reported.

Similarly, a series of β-methallyltin compounds has been prepared by the reaction of the appropriate tin halide with β-methallylmagnesium chloride in tetrahydrofuran. In this manner, the triethyl, tri-*n*-butyl, triphenyl and tri-*p*-tolyl derivatives were obtained. β-Methallyltriphenyltin has recently been reported by Seyferth[3]. Di-*n*-butyldi-β-methallyltin was prepared in a similar manner.

INFRARED DATA

In general, the spectra of all the allyl- and diallyltin compounds prepared show a $-C{=}C-$ stretching vibration at 1620 cm^{-1}. Other absorptions specifically due to the allyl group are the $=CH_2$ out-of-plane-bending mode which is found at 880 cm^{-1} and the $CH=$ out-of-plane-bending mode which may be the 985 cm^{-1} band. There is also a weak band at 930 cm^{-1} which is attributable to the allyl group. The 880 cm^{-1} absorption exhibits an overtone near 1750 cm^{-1}.

The range listed by Bellamy[4] for $=CH_2$ out-of-plane-bending modes for a series of olefins is 905–915 cm^{-1} while Egorov[5] lists this vibration as occurring at 880 cm^{-1} for allyltrimethyltin. Allyltriaryltin compounds show this absorption at 890 cm^{-1}. This was noted by Henry and Noltes[6] for allyltriphenyltin.

The allyltrialkyl- and diallyldialkyltin compounds all have a weak absorption at 3060 cm^{-1} due to the CH stretching vibration of the $=CH_2$ group. In phenyl and *p*-tolyl compounds this absorption is overlapped by the CH stretching modes of the aromatic ring at 3050 cm^{-1}.

The $C{=}C$ stretching mode for all the β-methallyltin compounds is found at 1625 cm^{-1}. The spectra of all the alkyl-β-methallyltin compounds exhibit a $=CH_2$ out-of-plane-deformation vibration at 860 cm^{-1}. As in the case of the allyl compounds, β-methallyltriphenyltin and β-methallyltri-*p*-tolyltin absorb at higher frequency. The $=CH_2$ out-of-plane-deformation was recorded at 868 cm^{-1} for these compounds.

The aromatic compounds, in addition to the normal CH and ring vibrations,

TABLE I

PHYSICAL PROPERTIES

Compound	*Boiling point*	*Melting point*	n_D
$(C_2H_5)_3SnCH_2CH{=}CH_2$	60–1°/7 mm		1.4868/24°
$(n\text{-}C_4H_9)_3SnCH_2CH{=}CH_2$	89°/0.3 mm		1.4863/22°
$(C_6H_5)_3SnCH_2CH{=}CH_2$		72–4°	
$(p\text{-}CH_3C_6H_4)_3SnCH_2CH{=}CH_2$		58–60°	
$(C_2H_5)_2Sn(CH_2CH{=}CH_2)_2$	98–100°/17 mm		1.5086/23°
$(n\text{-}C_4H_9)_2Sn(CH_2CH{=}CH_2)_2$	144–5°/17 mm		1.5023/25°
$(C_2H_5)_3SnCH_2C(CH_3){=}CH_2$	73–4°/4.2 mm		1.4882/24°
$(n\text{-}C_4H_9)_3SnCH_2C(CH_3){=}CH_2$	82–3°/0.1 mm		1.4830/22°
$(C_6H_5)_3SnCH_2C(CH_3){=}CH_2$		70–1°	
$(p\text{-}CH_3C_6H_4)_3SnCH_2C(CH_3){=}CH_2$		45.5–47°	
$(n\text{-}C_4H_9)_2Sn[CH_2C(CH_3){=}CH_2]_2$	142–3°/7 mm		1.4986/20°

show a very sharp band of strong intensity at 1070 cm^{-1}. This absorption is characteristic of phenyl and substituted phenyl groups bonded to tin.

EXPERIMENTAL PART

Allyltriethyltin

This compound was prepared in 75% yield by the interaction of allylmagnesium bromide and triethyltin chloride in accordance with the method of Jones *et al.*[1], b.p. 60–1°/7 mm, n_D^{24} 1.4868; (literature[1] b.p. 76–7°/10 mm). Similarly, *allyltri-n-butyltin* was also synthesized in 65.5% yield, b.p. 89°/0.3 mm, n_D^{22} 1.4863; (literature[1] b.p. 155°/17 mm). Using the method of Gilman and Eisch[2], *allyltriphenyltin* was prepared by the interaction of allylmagnesium bromide and triphenyltin chloride, 67.5% yield, m.p. 72–4°; (literature[2] m.p. 73–5°–74.5°).

Allyltri-p-tolyltin

To a 200 cc 3-necked flask equipped with magnetic stirrer, condenser, and addition funnel, containing 4.3 g (0.18 g-atom) of magnesium turnings and 60 cc of anhydrous ether, was added 7.3 g (0.06 mole) of allyl bromide in 60 cc of anhydrous ether with stirring and ice cooling. The Grignard reagent was transferred to an addition funnel and added dropwise to 15 g (0.035 mole) of tri-*p*-tolyltin chloride in 60 cc of dry benzene in a 500 cc 3-necked flask equipped as above. When addition had been completed, the mixture was refluxed for 18 h, hydrolyzed with 3% hydrochloric acid and the organic layer separated and dried over anhydrous calcium chloride. Removal of the solvent by distillation and subsequent refrigeration of the residue yielded a white solid. Recrystallization from 95% ethyl alcohol yielded 11 g (72.5%) of white needles, m.p. 58–60°. (Found: C, 66.87; H, 6.14; Sn, 27.52. $C_{24}H_{26}Sn$ calcd.: C, 66.51; H, 6.00; Sn, 27.48%.)

Triethyl-β-methallyltin

To 14.0 g (0.6 g-atom) of magnesium turnings and 150 cc of anhydrous tetrahydrofuran contained in a 500 cc 3-necked flask equipped with condenser, Trubore stirrer, addition funnel and nitrogen inlet tube, was slowly added 18.1 g (0.20 mole) of *β*-methallyl chloride in 100 cc of tetrahydrofuran with stirring and ice cooling. When addition had been completed, the Grignard reagent was filtered through glass wool

TABLE 2

INFRARED ABSORPTION DATA

Allyltri-ethyltin	*Allyltri-n-butyltin*	*Allyltri-phenyltin*	*Allyltri-p-tolyltin*	*Triethyl-β-methallyltin*	*Tri-n-butyl-β-methallyltin*	*β-methallyl-triphenyltin*	*β-methallyl-tri-p-tolyltin*	*Diallyl-diethyltin*	*Diallyldi-n-butyltin*	*Di-n-butyl-di-β-meth-allyltin*
3060 (w)	3060 (w)	3050 (m)	3040 (m)	3060 (w)	3060 (w)	3050 (m)	3050 (m)	3060 (w)	3060 (w)	3060 (w)
2930 (s)	2930 (s)	3000 (w)	3000 (m)	2940 (s)	2980 (s)	3000 (w)	3000 (m)	2940 (s)	2950 (s)	2960 (s)
2900 (s)	2900 (s)	2900 (w)	2950 (m)	2900 (s)	2920 (s)	2900 (w)	2960 (m)	2900 (s)	2900 (s)	2920 (s)
2860 (s)	2840 (s)	1960 (w)	2900 (m)	2860 (s)	2860 (s)	1960 (w)	2910 (m)	2860 (s)	2840 (s)	2860 (s)
1755 (w)	1750 (w)	1875 (w)	2850 (w)	1625 (s)	1628 (m)	1875 (w)	2860 (w)	1620 (s)	1620 (s)	1625 (s)
1620 (s)	1620 (s)	1805 (w)	1895 (w)	1460–50 (m, broad)	1463 (m)	1810 (w)	1900 (w)	1460 (m)	1460 (m)	1450 (m, broad)
1463 (m)	1460 (s)	1620 (m)	1795 (w)	1420 (m)	1420 (w)	1628 (m)	1800 (w)	1420 (m)	1420 (m)	1420 (w)
1420 (m)	1420 (m)	1575 (w)	1620 (m)	1375 (m)	1375 (m)	1578 (w)	1628 (m)	1375 (m)	1375 (m)	1375 (m)
1375 (m)	1375 (m)	1480 (m)	1590 (m)	1275 (s)	1340 (w)	1480 (m)	1595 (m)	1255 (w)	1338 (w)	1340 (w)
1230 (w)	1355 (w)	1430 (s)	1490 (m)	1233 (w)	1275 (m)	1430 (s)	1495 (m)	1230 (w)	1290 (w)	1278 (s)
1185 (m)	1338 (w)	1328 (w)	1443 (w)	1185 (w)	1250 (w)	1375 (m)	1445 (m, broad)	1185 (s)	1250 (w)	1260 (sh)
1085 (m)	1290 (w)	1295 (w)	1420 (w)	1095 (m)	1180 (w)	1328 (w)	1390 (s)	1090 (m)	1188 (m)	1180 (w)
1020 (m)	1248 (w)	1260 (w)	1388 (s)	1013 (s)	1150 (w)	1295 (w)	1375 (w)	1020 (m, broad)	1150 (w)	1150 (w)
985 (m)	11880 (m)	1185 (m)	1310 (w)	990 (sh)	1100 (w)	1273 (m)	1313 (w)	988 (m)	1080 (m, broad)	1100 (m)
925 (w)	1150 (w)	1095 (w)	1255 (w)	975 (w)	1070 (m)	1255 (w)	1278 (m)	960 (w)	1025 (m)	1073 (m)
880 (s)	1075 (m)	1070 (s)	1187 (s)	958 (w)	1045 (w)	1185 (w)	1260 (w)	928 (m)	985 (m)	1023 (w)
725 (m)	1020 (m)	1020 (s)	1100 (w, broad)	943 (w)	1020 (w)	1100 (w, broad)	1213 (w)	880 (s)	960 (w)	995 (w)
	1000 (w)	995 (s)	1068 (s)	860 (s)	1000 (w)	1070 (s)	1190 (s)	795 (w)	930 (m)	975 (w)
	985 (m)	983 (m)	1030 (w)	820 (w)	975 (w)	1020 (m)	1115 (m, broad)	738 (m)	880 (s)	963 (w)
	960 (m)	927 (w)	1017 (m)	740 (m)	962 (w)	995 (m)	1072 (s)		840 (w)	860 (s)
	930 (w)	885 (s)	985 (w)	700 (m)	860 (s)	968 (w)	1015 (w)		810 (w)	825 (w)
	880 (s)	790 (m)	928 (w)		823 (w)	865 (s)	1020 (m)		733 (m)	750 (w)
	840 (w)	723 (s)	885 (m)		740 (w)	820 (w)	970 (w)			705 (m)
	768 (w)	695 (s)	790 (s)			723 (s)	950 (w)			
	725 (m)		730 (m)			695 (s)	868 (m)			
							795 (s)			
							745 (m)			
							705 (m)			

into an addition funnel mounted above a 1-liter 3-necked flask equipped as above. Triethyltin chloride (30 g, 0.124 mole) was placed in the flask with 100 cc of anhydrous pentane and the β-methallylmagnesium chloride slowly added. When addition had been completed, the system was refluxed for 6 h and the organic layer separated and dried over anhydrous calcium chloride. The solvent was removed by flash distillation over a steam bath and the pale yellow liquid vacuum distilled yielding 18.3 g (56.5 %) of triethyl-β-methallyltin, b.p. 73–4°/4.2 mm, n_D^{24} 1.4882. (Found: Sn, 45.69. $C_{10}H_{22}Sn$ calcd.: Sn, 45.59 %.)

Tri-n-butyl-β-methallyltin was prepared in an analogous manner, 78.5 % yield, b.p. 82–3°/0.1 mm, n_D^{22} 1.4830. (Found: C, 55.85; H, 9.80; Sn, 34.00. $C_{16}H_{34}Sn$ calcd.: C, 55.68; H, 9.93; Sn, 34.40 %.)

Triphenyl-β-methallyltin was prepared similarly, in 61.7 % yield, m.p. 70–1°; (literature[3] m.p. 72–3°).

Tri-p-tolyl-β-methallyltin was prepared as described above, in 69.5 % yield, m.p. 45.5–47.0°. (Found: C, 66.78; H, 6.53; Sn, 26.05. $C_{25}H_{28}Sn$ calcd.: C, 67.14; H, 6.31; Sn, 26.54 %.)

Diethyldiallyltin was prepared by the method of Jones *et al.*[1], in 25.2 % yield, b.p. 98–100°/17 mm, n_D^{23} 1.5086; (literature[1] b.p. 99–100°/17 mm). From the same source[1], *di-n-butyldiallyltin* was also prepared, 39.2 % yield, b.p. 144–5°/15 mm, n_D^{20} 1.5023; (literature[1,7] b.p. 145–6°/17 mm, n_D^{25} 1.4986).

Di-n-butyldi-β-methallyltin was prepared by the same general method as outlined in detail above, in 83.2 % yield, b.p. 142–3°/7.0 mm, n_D^{20} 1.4986.

SUMMARY

A series of allyl- and β-methallyltin compounds have been prepared by the action of the olefinic Grignard reagent on the appropriate tin halide and their infrared spectra recorded. The compounds prepared include $(C_2H_5)_3SnR$; $(n\text{-}C_4H_9)_3SnR$; $(C_6H_5)_3SnR$; $(p\text{-}CH_3C_6H_4)_3SnR$; $(C_2H_5)_2SnR_2$; $(n\text{-}C_4H_9)_2SnR_2$ (R = allyl); $(C_2H_5)_3SnR$; $(n\text{-}C_4H_9)_3SnR'$; $(C_6H_5)_3SnR'$; $(p\text{-}CH_3C_6H_4)_3SnR'$ and $(n\text{-}C_4H_9)_2SnR'_2$ (R' = β-methallyl).

REFERENCES

1 W. J. JONES, D. P. EVANS, T. GULWELL AND D. C. GRIFFITHS, *J. Chem. Soc.*, (1947) 1446.
2 H. GILMAN AND J. EISCH, *J. Org. Chem.*, 20 (1955) 763.
3 D. SEYFERTH AND M. H. WEINER, *J. Org. Chem.*, 26 (1961) 4797.
4 L. J. BELLAMY, *The Infrared Spectra of Complex Molecules*, Wiley, New York, 2nd Ed., 1958.
5 YU. P. EGOROV, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk.*, (1957) 131.
6 M. C. HENRY AND J. G. NOLTES, *J. Am. Chem. Soc.*, 82 (1960) 555.
7 D. ROSENBERG, E. DEBRECZENI AND E. L. WEINBERG, *J. Am. Chem. Soc.*, 81 (1959) 972.