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Preparation and Some Properties of Acyltin Compounds

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Synopsis. According to Quintard's method, acyltin compounds were prepared by the reaction of tributylstannylmagnesium chloride with an excess of aldehyde, and their physical data were described. These compounds were sensitive to oxygen air to give the corresponding tributyltin carboxylates. Free radical chain mechanism was suggested.

For lack of a suitable synthetic method, acyltin compounds have been virtually unkown and are believed to be very labile compounds.[1,2] Recently, the acyltins have been reported by Quintard et al. to form through the reaction of tributylstannylmagnesium chloride prepared in situ from isopropylmagnesium chloride and tributyltin hydride, with an excess of aldehyde.[3]

$$\mathrm{Bu_3SnMgCl+2\ RCHO \rightarrow Bu_3SnCOR+RCH_2OMgCl}$$

However, physical data of the acyltins thus formed were not fully provided.[3] In this note, several trials of the syntheses of acyltins, and some of their physical data were described.

The reaction presented by Quintard et al. is interesting and thought to be a kind of Cannizzaro reaction of aldehyde involving Grignard reagent instead of a base. In 1925, the reaction of Grignard reagent with benzaldehyde giving benzyl alcohol was reported.[4] We re-examined the reaction of some ordinary Grignard reagents with excess of aldehydes,

$$\begin{array}{llll} \mathrm{RMgBr + 2PhCHO} \rightarrow & \rightarrow \mathrm{PhCOR} & + & \mathrm{PhCH_2OH} \\ \quad \mathrm{R{=}Et,\ Ph} & \quad \mathrm{Et;\ 77\%,} & & \mathrm{Et;\ 83\%} \\ & \quad \mathrm{Ph;\ 60\%} & & \mathrm{Ph;\ 61\%} \end{array}$$

$$\mathrm{EtMgCl + 2PhCH_2CH_2CHO} \rightarrow \rightarrow$$

$$\begin{array}{ccc} \mathrm{EtCOCH_2CH_2Ph} & + & \mathrm{PhCH_2CH_2CH_2OH} \\ 44\% & & 49\% \end{array}$$

and found that Cannizzaro type reactions between the Grignard reagent and an excess of aldehyde actually occurred to give the corresponding ketones and alcohols in moderate to good yields, even with aldehydes bearing α-hydrogen atoms.[5]

Based on the above results, the reactions of various tributylstannylmetal compounds ($\mathrm{Bu_3Sn{-}M}$) with an excess of propanal were carried out, expecting to give the propanoyltributyltin. Tributylstannylmagnesium chloride was the best reagent which reacted with an excess of aldehyde to give the acyltins in 84% yield. The reaction with diethyl(tributylstannyl)aluminum also gave the acyltins, although the yields were low (18%). The reaction with other reagents, $\mathrm{Bu_3Sn{-}M}$ (M: Li, ZnCl, $\mathrm{ZnSnBu_3}$, $\mathrm{SiMe_3}$, $\mathrm{SnBu_3}$ etc.) did not give the acyltins.

The following two coupling reactions were also carried out for the purpose of preparation of acyltins.

$$\mathrm{Bu_3SnLi + EtCOBr \longrightarrow Bu_3SnCOEt + LiBr}$$

$$\mathrm{Bu_3SnSnBu_3 + EtCOCl \xrightarrow{[Pd]} Bu_3SnCOEt + Bu_3SnCl}$$

These two reactions gave the propanoyltributyltin, although the yields (12 and 15% yields, respectively) were not satisfactory.[6] At present, Quintard's method was found to be the best for the preparation of acyltins.

Table 1 shows the physical properties of acyltins thus obtained. Propanoyl- and 2-methylpropanoyltributyltin were greenish yellow liquid with the absorption at ca. 380nm and could be distilled under reduced pressure. Their GC-MS(CI) showed the parent peak with the reasonable isotopic patterns. ^{1}H NMR, ^{13}C NMR, and IR spectrum were also reasonable. On the other hand, benzoyltributyltin was thermally unstable and decomposed to give the white solid on distillation under reduced pressure. Its GC-MS showed the pattern quite different from that of GLC and benzil was detected, showing that the

Table 1. Physical Data of Acyltins

	$\mathrm{Bu_3SnCOCH_2CH_3}$	$\mathrm{Bu_3SnCOCH(CH_3)_2}$	$\mathrm{Bu_3SnCOPh}$
^{1}H NMR($\mathrm{CCl_4}$) δ:	0.70—1.80(m, Bu, $\mathrm{CH_3}$) 2.66(q, J=7 Hz, $\mathrm{CH_2}$)	0.65—1.85(m, Bu, $\mathrm{CH_3}$) 2.35(h, J=6 Hz, CH)	0.63—1.80(m, Bu) 7.26—8.26(m, Ph)
^{13}C NMR($\mathrm{CDCl_3}$) δ:	13.6, 27.2, 29.1, 10.5 (Bu) 250.1 (CO) 48.9 ($\mathrm{CH_2}$) 6.2 ($\mathrm{CH_3}$)	13.6, 27.4, 29.3, 11.0 (Bu) 249.8 (CO) 50.7 (CH) 15.8 ($\mathrm{CH_3}$)	13.6, 27.3, 29.2, 11.5 (Bu) 241.3 (CO) 142.9, 127.6, 128.6, 132.4 (Ph)
UV(hexane)	385, 370 nm	390, 375 nm	440 nm
IR(neat)	1640 (CO) cm^{-1}	1640 (CO) cm^{-1}	1610 (CO) cm^{-1}
Bp[a]	107 °C/0.5 mmHg	119 °C/0.8 mmHg	Decomposed
GC-MS(CI) m/z, M$^+$:	345, 346, 347, 349	359, 361, 362, 363[b]	Decomposed[c]

a) 1 mmHg = 133.322 Pa. b) Peak at 360 was not detected. c) Decomposition was occurred in the MS chamber and benzil was detected.

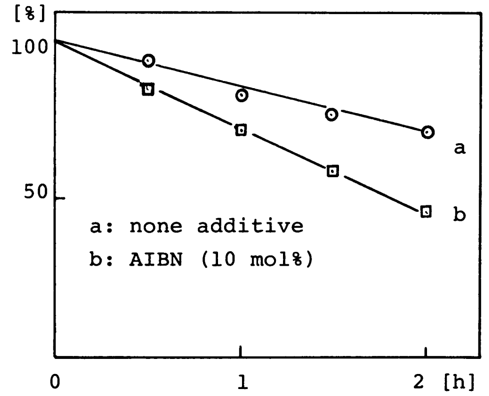

Fig. 1. Effect of AIBN on the disappearance of $Bu_3SnCOEt$ at 60 °C.

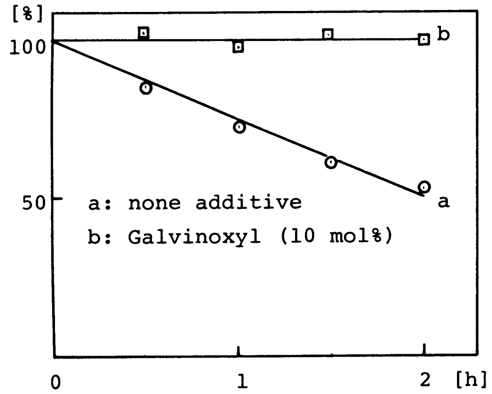

Fig. 2. Effect of Galvinoxyl on the disappearance of $Bu_3SnCOEt$ at room temperature.

benzoyltin decomposed in the GC-MS chamber. However, the product before distillation showed the reasonable spectroscopic data.

The acyltins were fairly stable under dark and inert atmosphere, being capable to be kept more than a month. One of the most characteristic reactions of acyltin was oxidation by molecular oxygen, giving the corresponding tributyltin carboxylates quantitatively. As Figs. 1 and 2 show, the autoxidation was completely inhibited in the presence of galvinoxyl (10 mol%) and was slightly accelerated by addition of AIBN (azobisisobutyronitrile). Based on these observations, free radical chain mechanism involving attack of acylperoxyl radical to a tin atom, followed by Baeyer–Villiger type oxidation, may be suggested.

$$Bu_3SnCOR \longrightarrow Bu_3Sn\cdot + R\dot{C}O$$

$$R\dot{C}O + O_2 \longrightarrow RCOOO\cdot$$

$$RCOOO\cdot + Bu_3SnCOR \longrightarrow RCOOOSnBu_3 + R\dot{C}O$$

$$RCOOOSnBu_3 + Bu_3SnCOR \longrightarrow 2RCOOSnBu_3$$

Moreover, propanoyltributyltin was found to reduce Tollens reagent. Thus, acyltin shows chemical behavior quite similar to aldehyde.

Experimental

Infrared spectra were recorded on a JASCO Model A-100 infrared spectrometer. ^1H NMR spectra (in carbon tetrachloride with tetramethylsilane internal standard) were run on a Varian Associates Model EM-360 spectrometer. ^{13}C NMR spectra (in deuteriochloroform with tetramethylsilane internal standard) were taken on a Hitach Model R-90H spectrometer. GC-MS spectra (Chemical Ionization) were recorded on a Shimadzu Model QP-1000 spectrometer. UV spectra (in hexane) were taken on a Hitachi Model 200-10 spectrophotometer. GLC analyses (10% of SF-96 on Celite 545) were performed by Ohkura Model 202 instrument.

Materials. Ethyl- and phenylmagnesium bromide were prepared by a standard method. Benzaldehyde, propanal, 2-methylpropanal, 3-phenyl-1-propanal, propanoyl chloride and bromide, propiophenone, benzophenone, benzyl alcohol, 1-phenyl-3-pentanone, 3-phenylpropanol, galvinoxyl, and AIBN were commercially available and used without further purification. Bu_3SnLi,7) $Bu_3SnZnCl$,8) $Bu_3SnZnBr$,8) $(Bu_3Sn)_2Zn$,8) $Bu_3SnSiMe_3$,7) $Bu_3SnSnBu_3$,7) $Bu_3SnAlEt_2$,8) $Bu_3SnMgCl$,4) $Bu_3SnOCOEt$,9) $Bu_3SnOCOCHMe_2$,9) and $Bu_3SnOCOPh$9) were prepared from the method described in the literatures.

Cannizzaro Type Reaction of Aldehyde with Grignard and Stannylmetal Reagents. After dropwise addition of benzaldehyde into an ethereal solution of ethyl Grignard reagent, the solution was refluxed for 2 h. The resulting reaction mixture was hydrolyzed with aqueous saturated ammonium chloride, and extracted with ether. The extracts were analyzed by GLC and ethyl phenyl ketone and benzyl alcohol were detected as products. Other reactions with Grignard reagents and the reactions of propanal with various stannylmetals were also carried out similarly.

Preparation of Acyltributyltins. Tributyltin hydride (45 g, 0.15mmol) was added to a solution of the Grignard reagent prepared from 14.1 g of isopropyl chloride (0.18 mol) and 4.4 g of magnesium (0.18 mol). The solution was then refluxed for an hour. The flask was cooled with an ice bath and 26.1 g of propanal (0.45 mol) was added into the solution dropwisely, which was further refluxing for an hour. Subsequent treatment of the resulting reaction mixture with aqueous ammonium chloride was carried out. Distillation under reduced pressure gave 32 g of propanoyltributyltin (62% yield). 2-Methylpropanoyltin (59%) and crude benzoyltin (64% yield) were obtained similarly. However, the latter was decomposed on heating under reduced pressure. Physical data of acyltins are shown in Table 1.

Reaction of Propanoyltributyltin with Oxygen. The disappearance of propanoyltributyltin in the presence of Galvinoxyl or AIBN was followed by GLC. The results are shown in Figs. 1 and 2.

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