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THE PYROLYSIS OF SOME TRIMETHYLTIN BROMOACETATES AND RELATED METHYLMETAL ACETATE DERIVATIVES

TAKEHIRO OKADA and ROKURO OKAWARA

Department of Applied Chemistry, Osaka University, Yamadakami, Suita, Osaka (Japan)

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SUMMARY

The pyrolysis of $(CH_3)_3SnOCOCBr(C_6H_5)_2$, $(CH_3)_3SnOCOCHBr(C_6H_5)$, $(CH_3)_3SnOCOCBr(CH_3)_2$ and $(CH_3)_3Sb[OCOCHBr(C_6H_5)]_2$ gave trimethylmetal bromide and the corresponding polyester. In the pyrolysis of $(CH_3)_3SnOCOCBr(C_6H_5)_2$, a presumed reactive species, $^-O-CO-^+C(C_6H_5)_2$, was trapped by CBr_3CO_2H, CCl_3CO_2H and CH_3OH, respectively. It was also found that a similar elimination reaction through the formation of $(CH_3)_3SnOCOC(C_6H_5)_2OCOCX_3$ (X=Br and Cl) seems to occur in the reaction of $CX_3CO_2C(C_6H_5)_2CO_2H$ with $[(CH_3)_3Sn]_2S$.

INTRODUCTION

In the course of our study of the reactivity of organometal haloacetates, we have reported that the reaction with triphenylphosphine was effective as a source of haloketenes[1].

In this paper, we describe a novel elimination reaction found in the case of some trimethyltin phenyl or methyl substituted bromoacetates, trimethylantimony bis(phenylbromoacetate) and $(CH_3)_3SnOCOC(C_6H_5)_2OCOCX_3$ (X=Br and Cl), in contrast to the well known decarboxylation reaction in organotin carboxylates[2], having electron-withdrawing groups such as CN, Br and Cl at α-carbon.

EXPERIMENTAL

Materials

Bis(trimethyltin) sulfide[3] and trimethylstibine sulfide[4] were synthesized by standard methods described in the literature. Diphenylbromoacetic acid and phenylbromoacetic acid were prepared by the bromination of the corresponding acetic acids, according to the Hell–Volhard–Zelinsky method[5]. α-Bromoisobutyric acid was of reagent grade. All solvents were dried and purified by distillation from P_2O_5.

Preparation of trimethyltin bromoacetate derivatives; $(CH_3)_3SnOCOCBr(C_6H_5)_2$, $(CH_3)_3SnOCOCHBr(C_6H_5)$ and $(CH_3)_3SnOCOCBr(CH_3)_2$

$(CH_3)_3SnOCOCBr(C_6H_5)_2$ was prepared from $[(CH_3)_3Sn]_2S$ and $(C_6H_5)_2$-

$CBrCO_2H$ in ether at 0°, for this compound decomposes at room temperature, and other trimethyltin bromoacetate derivatives were similarly prepared at room temperature.

$(CH_3)_3SnOCOCBr(C_6H_5)_2$: yield 81%. (Found: Sn, 26.37. $C_{17}H_{19}BrO_2Sn$ calcd.: Sn, 26.15%.)

$(CH_3)_3SnOCOCHBr(C_6H_5)$: m.p. 130–132°; yield 95%. (Found: C, 34.78; H, 4.11. $C_{11}H_{15}BrO_2Sn$ calcd.: C, 35.06; H, 4.01%.)

$(CH_3)_3SnOCOCBr(CH_3)_2$: m.p. 137–139°; yield 56%. (Found: C, 25.51; H, 4.77, $C_7H_{15}BrO_2Sn$ calcd.: C, 25.49; H, 4.58%.)

Pyrolysis of $(CH_3)_3SnOCOCBr(C_6H_5)_2$

$(CH_3)_3SnOCOCBr(C_6H_5)_2$ (1.9 g) in benzene (20 ml) under an atmosphere of nitrogen was stirred overnight at room temperature. After benzene was removed *in vacuo*, the residual solid was washed by petroleum ether. The residue was a hard lacquer which yielded a white solid on solution in ether and evaporation. This white solid was identified as benzilic acid polyester* (0.8 g; 91%) by IR[6]. From the petroleum ether washings, $(CH_3)_3SnBr$** (0.99 g; 97%) was obtained.

This pyrolysis reaction was also carried out in the presence of an equimolar amount of CBr_3CO_2H, excess CCl_3CO_2H or excess CH_3OH. After the solvent was removed *in vacuo*, petroleum ether was added to the residue, giving the white precipitates, respectively, as shown below.

$CBr_3CO_2C(C_6H_5)_2CO_2H$: m.p. 163–164°; IR (nujol mull): ν(C=O) 1762 and 1718 cm^{-1}; NMR ($CDCl_3$) (δ): 7.31 ppm (m, C_6H_5); mass spectrum (70 eV): *m/e* (rel. intensity) 510 (37, $M^+ + 6$), 508 (100, $M^+ + 4$), 506 (100, $M^+ + 2$) and 504 (37, M^+); yield 84%. (Found: C, 38.20; H, 2.15. $C_{16}H_{11}Br_3O_4$ calcd.: C, 37.90; H, 2.19%.)

$CCl_3CO_2C(C_6H_5)_2CO_2H$: m.p. 90–91°; IR (nujol mull): ν(C=O) 1779 and 1724 cm^{-1}; NMR ($CDCl_3$) (δ): 7.35 ppm (m, C_6H_5); mass spectrum (70 eV): *m/e* (rel. intensity) 378 (12, $M^+ + 6$), 376 (45, $M^+ + 4$), 374 (95, $M^+ + 2$) and 372 (100, M^+); yield 51%. (Found: C, 51.13; H, 2.83. $C_{16}H_{11}Cl_3O_4$ calcd.: C, 51.43; H, 2.97%.)

$CH_3OC(C_6H_5)_2CO_2H$: yield 70%. (This compound was identified by its m.p.[7], IR, NMR, mass spectrum and elemental analysis.)

Pyrolysis of $(CH_3)_3SnOCOCHBr(C_6H_5)$ and $(CH_3)_3SnOCOCBr(CH_3)_2$

$(CH_3)_3SnOCOCHBr(C_6H_5)$ (2.0 g) in pseudocumene (b.p. 168–169°) (15 ml) was refluxed for 15 h. The solvent and $(CH_3)_3SnBr$ (1.2 g; 92%) were removed by distillation under reduced pressure. After the residual viscous solid had been washed by petroleum ether several times, ether was added and evaporated *in vacuo*, giving a white solid. This solid was thought to be mandelic acid polyester (0.6 g; 86%) by IR ($CDCl_3$) [ν(C=O) 1753 cm^{-1}] and NMR [δ 4.75 (OCOCH) and 7.26 ppm ($OCOCC_6H_5$) in $CDCl_3$ in the relative intensity of 1/5].

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* This polyester melted over a 20° range (ca. 64–87°) depending upon its form. The melt evolved gas at 190–200° and turned red in color. A determination with vapor phase osmometer gave a molecular weight of 1500, corresponding to $n=7$ in formula (I).

** $(CH_3)_3SnBr$ was identified by IR and its yield was estimated by NMR, using cyclohexane as a reference.

Refluxing of $(CH_3)_3SnOCOCBr(CH_3)_2$ (2.0 g) in pseudocumene (15 ml) for 48 h gave $(CH_3)_3SnBr$ (1.4 g; 95%) and α-hydroxyisobutyric acid polyester (0.43 g; 83%), which was identified by IR[8].

Reaction of $[(CH_3)_3Sn]_2S$ *with* $CX_3CO_2C(C_6H_5)_2CO_2H$ *(X = Br and Cl)*

Into the mixture of $CBr_3CO_2C(C_6H_5)_2CO_2H$ (1.5 g) and $[(CH_3)_3Sn]_2S$ (0.53 g) in benzene (15 ml), nitrogen gas was bubbled through to remove the H_2S. After stirring overnight, the white precipitate was filtered off. The filtrate gave benzilic acid polyester (0.54 g; 87%). The white precipitate was identified as $(CH_3)_3SnOCOCBr_3$ (1.1 g; 82%) by comparing its m.p. and IR spectrum with those of an authentic sample[9].

In the case of the reaction with $CCl_3CO_2C(C_6H_5)_2CO_2H$, benzilic acid polyester and $(CH_3)_3SnOCOCCl_3$ [10] were obtained almost quantitatively.

Reaction of $(CH_3)_3SbS$ *with* $(C_6H_5)CHBrCO_2H$

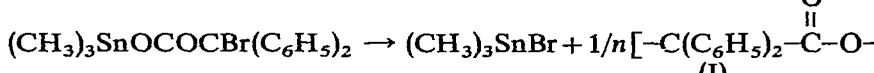
$(CH_3)_3SbS$ (1.0 g) was added to a xylene (b.p. 139.5–141.5°) (20 ml) solution of $(C_6H_5)CHBrCO_2H$ (2.2 g) with stirring. After the white powder of $(CH_3)_3SbS$ disappeared, the existence of $(CH_3)_3Sb[OCOCHBr(C_6H_5)]_2$ in the solution was shown by the IR spectrum [a strong absorption band at 1658 cm^{-1}, ν(C=O)] and the NMR spectrum [two singlets at δ 1.49 ($Sb-CH_3$) and 5.10 ppm (OCOCHBr) in a relative intensity of 9/2]. After nitrogen gas had been bubbled into this solution to remove the H_2S, the solution was refluxed for 24 h. The solvent was removed *in vacuo* and ether was added to the residue, giving a white precipitate of $(CH_3)_3SbBr_2$ [11] (1.4 g; 87%). From the filtrate, mandelic acid polyester (1.3 g; 93%) was obtained.

Physical measurements

The IR spectra were obtained using a Hitachi 225 spectrophotometer equipped with gratings. The NMR spectra were measured on a Japan Electron Optics JNM-3 H-60 spectrometer at 60 MHz. Mass spectra were recorded with a Hitachi mass spectrometer Model RMU-6E and the molecular weight was determined at 41° using a Hitachi–Perkin–Elmer 115 molecular weight apparatus.

RESULTS AND DISCUSSION

$(CH_3)_3SnOCOCBr(C_6H_5)_2$, $(CH_3)_3SnOCOCHBr(C_6H_5)$, $(CH_3)_3SnOCOCBr(CH_3)_2$ and $(CH_3)_3Sb[OCOCHBr(C_6H_5)]_2$ were pyrolysed to trimethylmetal bromide and the corresponding polyester at the appropriate temperature almost quantitatively.



$$(CH_3)_3SnOCOCBr(C_6H_5)_2 \longrightarrow (CH_3)_3SnBr + 1/n[-C(C_6H_5)_2-\overset{\overset{O}{\|}}{C}-O-]_n$$

(I)

(97%) (91%)

In the reaction of $CX_3CO_2C(C_6H_5)_2CO_2H$ (X = Br and Cl) with $[(CH_3)_3Sn]_2S$, a similar elimination reaction through the formation of $(CH_3)_3SnOCOC(C_6H_5)_2OCOCX_3$ seemed to occur.

When the pyrolysis of $(CH_3)_3SnOCOCBr(C_6H_5)_2$ was carried out in the presence of tribromoacetic acid, the (tribromoacetoxy)diphenylacetic acid was obtained almost quantitatively with $(CH_3)_3SnBr$. Also, in the presence of CCl_3CO_2H and CH_3OH, the corresponding α-functionally substituted diphenylacetic acids were obtained in moderate yields. These results show that a 1,3-dipolar ionic isomer[7] of diphenyl-α-lactone itself, $^{-}O{-}CO{-}^{+}C(C_6H_5)_2$, or its precursor exists as a reactive species in the course of the elimination reaction.

This novel elimination reaction found in the above organometal acetates may be mainly due to the capability of the substituents such as phenyl and methyl groups, stabilizing the $^{\delta+}C{-}^{\delta-}Y$ ($Y{=}Br$ or $OCOCX_3$) forms at α-position.

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