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Acyl derivatives of main group metals: preparation of benzoyl derivatives of some group V and VI metals and metalloids

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Abstract

3,5-Dinitrobenzoyl chloride (**1**) adds oxidatively to triarylantimony to give the first benzoyl derivatives of antimony, $Ar_3Sb[COC_6H_3(NO_2)_2]Cl$. Triphenyl-phosphine and -arsine, and also bis(*p*-methoxyphenyl)tellurium(II) react with **1** in the same way. Conductivity and molecular weight data show that the benzoyl derivatives exist in solution as monomeric species. The metal–acyl bond in the compounds is stable towards MeOH, MeI, and CdX_2.

Reaction of **1** with triphenylbismuth leads to the cleavage of one Bi–Ph bond. Attempts to prepare the benzoyl derivative, $Ph_3PbCOC_6H_3(NO_2)_2$, by the reaction of **1** with hexaphenyldilead were unsuccessful, but one Pb–Ph bond was cleaved of Ph_4Pb in the presence of **1**.

Introduction

Acyl derivatives of main group metals are known to be difficult to make, partly because of unavailability of acyl analogues of Grignard reagents and partly because of their instability at room temperature. Thus, whereas R_3SiCOR' and R_3GeCOR' are stable, the Sn and Pb analogues are unstable at room temperature [1,2]. It has been suggested that for the derivatives to be stable the acyl group must be of a special nature and isolation of stable $Ph_3PbCOOEt$ and $Ph_3PbCONMe_2$ substantiates this view [2].

Several methods have been used for the preparation of acyl-silicon and -germanium compounds [1], but they require rather special reagents and so are not very convenient and general. Ph_3SnCOR and Ph_3PbCOR have been prepared by the reaction of Ph_3MLi with RCOCl at low temperatures [2].

Acyl complexes of transition metals may be formed by the oxidative addition of RCOCl to a low valent metal [3], but the analogous reaction with main group metals and metalloids in a low oxidation state seems not to have been exploited as a general route to M–COR bonded compounds, though some acylgermanium com-

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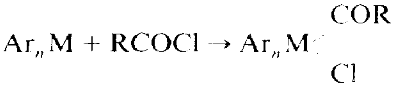
pounds have been obtained by the reaction of RCOCl with germylenes [4]. We describe here the outcome of the reactions of some acyl chlorides with Ar_nM (M = Bi, Sb, As, P; $n = 3$ and M = Te; $n = 2$), Ph_4Pb and Ph_6Pb_2.

Results and discussion

Acetyl chloride, benzoyl chloride or chloroacetyl chloride did not react with triphenyl-antimony or -bismuth in refluxing dichloromethane or carbon tetrachloride (but see ref. 5), but 3,5-dinitrobenzoyl chloride (**1**) added oxidatively to Ar_3M (M = Sb, As, P) and $(p\text{-}MeOC_6H_4)_2Te^{II}$ to give the corresponding benzoyl derivatives (eq. 1, H = $3,5\text{-}(NO_2)_2C_6H_3$).



$$Ar_nM + RCOCl \rightarrow Ar_nM\begin{matrix}COR\\ \\ Cl\end{matrix} \qquad (1)$$

(M = Sb; Ar = C_6H_5 or $p\text{-}CH_3C_6H_4$ and $n = 3$.
M = P or As; Ar = C_6H_5 and $n = 3$.
M = Te; Ar = $p\text{-}CH_3OC_6H_4$ and $n = 2$)

The analytical and IR data are given in Table 1. All the benzoyl derivatives are pale yellow solids, soluble in benzene, chloroform, and dichloromethane, and are monomeric. The molar conductance of 10^{-3} *M* solutions of the $Ph_3M(COR)Cl$, in acetonitrile, were 4–7 ohm^{-1} mol^{-1} cm^2 showing that there is very little, if any, ionization of these compounds [6]. Their melting points are also consistent with a non-ionic structure.

The IR spectra of the benzoyl derivatives (except that of Te) show the carbonyl stretching frequency at 1660–1710 cm^{-1}, which is lower than that for organic ketones (~ 1725 cm^{-1}). However, the $\nu(CO)$ value for $(MeOC_6H_4)_2Te[COC_6H_3(NO_2)_2]Cl$ is surprisingly high (1735 cm^{-1}). In the series $Ph_3M[COC_6H_3(NO_2)_2]Cl$ (M = P, As, Sb), there is a general decrease in $\nu(CO)$ with increasing mass of the central atom.

The ^1H NMR spectra of the benzoyl derivatives are not very informative. Thus, the spectrum of $(p\text{-}CH_3C_6H_4)_3Sb(COR)Cl$, in $CDCl_3$, consists of a singlet (9H) at

Table 1

Analytical and IR data for the benzoyl derivatives, $Ar_nM[COC_6H_3(NO_2)_2]Cl$

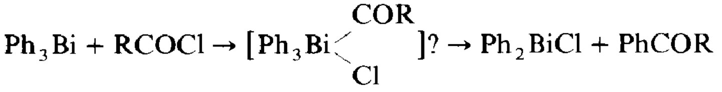
Ar_nM	m.p. (°C)	Analyses (Found (calc.) (%))		$\nu(CO)$ (cm^{-1})
		C	H	
Ph_3Sb [a]	148	51.2	3.3	1670
		(51.5)	(3.1)	
$(p\text{-}MeC_6H_4)_3Sb$	112–113	54.0	3.7	1660
		(53.7)	(3.9)	
Ph_3As	88–89	55.8	3.3	1705
		(56.0)	(3.4)	
Ph_3P [b]	107–108	60.4	3.6	1710
		(60.9)	(3.7)	
$(p\text{-}MeOC_6H_4)_2Te$ [c]	78–80	43.8	3.2	1735
		(44.1)	(3.0)	

[a] Cl: found 5.9; calc. 6.1%. [b] Cl: found 7.0; calc. 7.2%; [c] Te: found 21.7; calc. 22.0%.

2.3 ppm due to CH_3 group and a multiplet (15H) centred at 7.85 ppm due to the aryl protons.

The Sb–COR bond in $Ar_3Sb(COR)Cl$ was found to be stable to MeOH and MeI, which is interesting because **1** itself reacts with MeOH to give the corresponding ester. $Ph_3Sb(COR)Cl$ also failed to react with $Cd(ClO_4)_2$, as did $Ph_3P(COR)Cl$ with $CdBr_2$. Both Ph_3Sb and Ph_3P are known to form stable 2:1 complexes with $Cd(ClO_4)_2$ and $CdBr_2$ respectively [7,8]. These observations rule out the possibility of $[Ar_3M{:}\rightarrow RCOCl]$ as an alternative structure for the benzoyl derivatives (cf. $R_3M \rightarrow ICCl_3$ [9]).

The reaction of **1** with triphenylbismuth in dichlomethane resulted in the cleavage of one Bi–Ph bond (eq. 2), but the benzoyl derivative, $Ph_3Bi(COR)Cl$, if formed, was not isolated.



$$Ph_3Bi + RCOCl \rightarrow [Ph_3Bi\langle^{COR}_{Cl}]? \rightarrow Ph_2BiCl + PhCOR \quad (2)$$

This difference in the reactivity of **1** towards Ph_3Sb and Ph_3Bi is not wholly unexpected. Similar observations have been made in the reactions with XCN (X = I, Br); thus, whereas oxidative addition products, $Ph_3Sb(CN)X$, were obtained with Ph_3Sb, triarylbismuth gave the cleavage products, Ar_2BiX [10,11]. On the assumption that the most likely pathway for reaction shown in eq. 1 involves initial nucleophilic attack of Ar_nM: on the benzoylic carbon, the difference in the reactivities of Ph_3Sb and Ph_3Bi may be attributed to the poor donor property of the latter coupled with the general instability of the bismuthonium compounds, R_4BiX [12].

In an attempt to prepare a benzoyllead compound, hexaphenyldilead was treated with **1** in refluxing dichloromethane, but was recovered unchanged after ~ 1 h. Compound **1** did, however, cleave one Pb–Ph bond of Ph_4Pb in dichloromethane to give Ph_3PbCl in quantitative yield.

Experimental

Ph_3As, Ar_3Sb, Ph_3Bi, $(p\text{-}MeOC_6H_4)_2Te$, Ph_4Pb and $3,5\text{-}(NO_2)_2C_6H_3COCl$ were prepared by standard methods. All manipulations were performed under anaerobic conditions. IR spectra were recorded on Perkin–Elmer 577 spectrometer as CsI discs or Nujol mulls. Conductivity measurements were made on Philips Magic Eye model PR 9500 conductivity bridge with a dip type conductivity cell.

Reactions of 1 with Ar_3Sb, Ph_3As, Ph_3P and $(p\text{-}MeOC_6H_4)_2Te$

A typical experiment is described: A solution of Ph_3Sb (0.50 g, 1.4 mmol) and **1** (0.33 g, 1.4 mmol) in benzene or dichloromethane was refluxed for 5 h with stirring. The solvent was distilled off and the residue crystallised from dichloromethane/petroleum ether to give $Ph_3Sb[COC_6H_3(NO_2)_2]Cl$ in > 90% yield.

$(p\text{-}MeC_6H_4)_3Sb[COC_6H_3(NO_2)_2]Cl$, $Ph_3As[COC_6H_3(NO_2)_2]Cl$, $Ph_3P[COC_6H_3(NO_2)_2]Cl$ and $(p\text{-}MeOC_6H_4)_2Te[COC_6H_3(NO_2)_2]Cl$ were prepared similarly.

Reactions of 1 with Ph_3Bi and Ph_4Pb

A solution of Ph_3Bi (0.5 g, 1.1 mmol) in dichloromethane (5 ml) was added to one of **1** (0.26 g, 1.1 mmol) in the same solvent (5 ml) at 0 °C. The mixture was stirred for ~ 4 h during which a white solid gradually separated out. It was filtered off and dried under reduced pressure to give Ph_2BiCl (~ 80%) m.p. 183–184 °C (lit [13] m.p. 184 °C), Found: C, 35.7; H, 2.6. $C_{12}H_{10}ClBi$ calcd.: C, 36.1; H, 2.5%. The filtrate on treatment with 2,4-dinitrophenylhydrazine afforded the corresponding hydrazone derivative, m.p. 190–192 °C (authentic IR spectrum). In another experiment, the filtrate was concentrated to give the ketone, $PhCOC_6H_3(NO_2)_2$, m.p. 131 °(lit. [14] m.p. 131 °C).

Ph_4Pb reacted similarly with **1** in refluxing dichloromethane to give Ph_3PbCl (~ 90%), m.p. 203–205 °C (lit. [15] m.p. 205 °C) and the ketone which was characterised as above.

Attempted reaction of 1 with Ph_6Pb_2

A mixture of the lead compound (0.5 mmol) and **1** (0.5 mmol) was heated together in refluxing dichloromethane (10 ml) for 1 h. After removing the dichloromethane under reduced pressure, the residue was washed with acetone. It was found to be unreacted hexaphenyldilead, m.p. 168–170 °(d) (lit. [15] m.p. 170 °(d)) in > 80% yield.

Attempted reactions of $Ph_3M[COC_6H_3(NO_2)_2]Cl$ (M = Sb, P) with MeOH, MeI and CdX_2

(a) To a solution of the benzoyl derivative (0.2 g) in benzene (10 ml) was added MeOH (1 ml). The reaction mixture was refluxed for 1 h. Removal of the volatiles under reduced pressure showed the unchanged benzoyl derivative, to be recovered in quantitative yield (authentic IR spectrum).

Under similar conditions, **1** and MeOH gave $MeOOCC_6H_3(NO_2)_2$, m.p. 111-112 °C [lit. [15] m.p. 112 °C]

(b) The benzoyl derivatives were recovered unchanged when stirred (1 h) with a slight excess of MeI in ether.

(c) $Ph_3Sb[COC_6H_3(NO_2)_2]Cl$ (1 mmol) and $Cd(ClO_4)_2$ (0.5 mmol) (prepared from CdI_2 and $AgClO_4$) were stirred together in refluxing dichloromethane (20 ml) for ~ 4 h. After distillation of the solvent, the residue was extracted with benzene. Removal of the benzene under reduced pressure left the unchanged benzoyl derivative in quantitative yield.

The phosphine derivative was recovered unchanged when treated with $CdBr_2$ under similar conditions.

Attempted reactions of Ph_3Sb and Ph_3Bi with other acyl chlorides

In the following reactions, the reactants were recovered unchanged:

(a) Ph_3Sb and CH_3COCl or C_6H_5COCl in refluxing dichloromethane (5 h); (b) Ph_3Bi and CH_3COCl or C_6H_5COCl in refluxing CCl_4 (4 h); (c) Ph_3Sb or Ph_3Bi and $ClCH_2COCl$ in refluxing dichloromethane (4 h); and (d) Ph_3bi and 1 chloropyridine in refluxing dichloromethane (5 h).

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