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Journal of Organometallic Chemistry 690 (2005) 4280–4284

Journal of Organometallic Chemistry

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Chlorination of *p*-substituted triarylpnictogens by sulfuryl chloride: Difference in the reactivity and spectroscopic characteristics between bismuth and antimony

A.F.M. Mustafizur Rahman, Toshihiro Murafuji *, Motoko Ishibashi, Youhei Miyoshi, Yoshikazu Sugihara [1]

Department of Chemistry, Faculty of Science, Yamaguchi University, Yamaguchi 753-8512, Japan

Received 18 March 2005; received in revised form 9 June 2005; accepted 21 June 2005
Available online 11 August 2005

Abstract

Competitive oxidative chlorination of *p*-substituted triarylstibines **3** [$(p\text{-}XC_6H_4)_3Sb$; **a**: X = OMe, **c**: Cl, **d**: CO_2Et, **e**: CF_3, **f**: CN, **g**: NO_2] by sulfuryl chloride was carried out against **3b** (X = H) and the electronic effect of these substituents on the chlorination of **3** was compared with that of homologous triarylbismuthanes **1**. The relative ratios **4/4b** (Ar_3SbCl_2/Ph_3SbCl_2) decreased with increasing electron-withdrawing ability of the substituents (**a**: 53/47, **c**: 49/51, **d**: 46/54, **e**: 44/56, **f**: 40/60, **g**: 37/63), but the tendency was not so pronounced as observed in the chlorination of **1**. A Hammett plot of the **4/4b** ratios against the σ_p constants exhibited a good linear relationship with a negative slope, the value of which was almost half of that deduced from the **2/2b** (Ar_3BiCl_2/Ph_3BiCl_2) ratios. The difference in the reactivity between **1** and **3** may be explained by the effect of the electron-withdrawing substituents in the aromatic rings, which affects the p-character of the lone pair on the pnictogen atoms by increasing the positive metal charge and appears more remarkably in **1** than in **3**. The ^{13}C NMR study of **3** revealed that the chemical shifts of the ipso carbons (C1) attached to the antimony show a linear relationship against the σ_p constants with a positive slope (14.5). The value was smaller than that deduced from **1** (17.0), suggesting that the antimony center of **3** is less sensitive to the substituent effect. This is in accord with the tendency of the chlorination.

Keywords: Antimony; Bismuth; Oxidative chlorination; ^{13}C NMR study; Hammett plot

1. Introduction

Recently, we have reported the effect of substituents on the reactivity and spectroscopic characteristics of triarylbismuthanes **1** and their dichlorides **2** [1]. Competitive chlorination of **1** against **1b** by sulfuryl chloride revealed that the reactivity of **1** is dramatically lowered by the electron-accepting substituents. Thus, **1g** bearing a nitro group does not show any reactivity in the chlorination (**2g/2b** = 0/100). Such a marked electronic effect should be stressed since the lone pair of the bismuth atom is inherently an s-character and cannot efficiently overlap with the 2p orbitals of the aromatic ring carbons. To know how the electronic effect affects the reactivity of triarylpnictogen more clearly, homologous antimony system was chosen for comparison [2]. We describe here the oxidative chlorination of *p*-substituted triarylstibines **3** together with the spectroscopic characteristics of **3** and their dichlorides **4**, in comparison with the bismuth congeners (see Chart 1).

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* Corresponding author. Fax: +81 83 933 5738.
E-mail addresses: murafuji@yamaguchi-u.ac.jp (T. Murafuji), sugihara@yamaguchi-u.ac.jp (Y. Sugihara).

[1] Fax: +81 83 933 5730.

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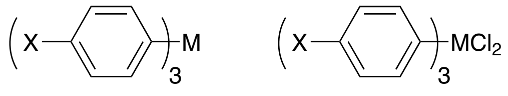
doi:10.1016/j.jorganchem.2005.06.040



1: M = Bi
3: M = Sb

2: M = Bi
4: M = Sb

X = **a**: MeO, **b**: H, **c**: Cl, **d**: CO_2Et,
e: CF_3, **f**: CN, **g**: NO_2

Chart 1.

2. Results and discussion

Substituted triarylstibines **3** were synthesized from the corresponding aryllithium or aryl-magnesium in accordance with the method for the synthesis of **1** [3]. Competitive chlorination of **3** was carried out against **3b** (Eq. (1)) and the result is summarized in Table 1. The relative ratios **4**/**4b** (estimated by ^1H NMR) decreased with increasing electron-withdrawing nature of the *p*-substituent, but the tendency was not so pronounced as that of **2**/**2b**. As shown in Fig. 1, a Hammett plot of **4**/**4b** against σ_p constants [4] showed a good linear relationship ($n = 6$, $r = 0.95$) with a negative slope (-0.51), which is almost half of the **2**/**2b** value (-0.97). The nuclear quadrupole resonance study of certain substituted triarylstibines has suggested that the efficient means of transmission of the substituent effect to the antimony atom is through the Sb–C σ bonds owing to the mismatch with the p orbitals of the ring carbons used in π interaction and that changes in the σ and π network are competitive [5]. The effect of electron-withdrawing substituents on the structure and stabilities of compounds containing heavier main group elements has been studied from the viewpoint of sp-hybridization [6]. In substituted lead compounds, an increasing positive metal charge due to electronegative substituents increases the size differences between the 6s and 6p orbitals by greater contraction of the 6s orbital and makes the efficient sp-hybridization less favorable [6a]. This destabilizes electronegatively substituted Pb(IV) compounds. Thus, such an effect of the electron-withdrawing substituents may reduce the p-character of the lone pair on the pnictogen atoms, lowering the reactivity of **1** and **3**. It is known that configurational inversion at the trivalent antimony and bismuth centers can take place via the edge inversion process [6b] when these central atoms are substituted by electron-withdrawing substituents [6c,6d], although the inversion at the pnictogen centers is a slow process except for the classical vertex inversion typified by nitrogen. The trigonal transition state of the classical vertex inversion is destabilized by the similar electronic effect while the T-shaped transition state of the edge inversion is rather favorable [6e]. The pronounced substituent effect in **1** compared to that in **3** seems to be due to the larger orbital size and more electropositive nature of bismuth atom than antimony atom. We have observed the predominant chlorination of **3b** over **1b** (**4b**/**2b** = 62/38) in the competitive chlorination and ascribed this result to the higher p-character of the lone pair on the antimony atom [1]. This is reflected in the C–Sb–C bond angles of **3b** [98.0(3)°, 96.0(3)°, 95.7(3)° and 97.5(3)°, 95.5(4)°, 95.1(3)° for the two independent molecules in the asymmetric unit] [7], which are larger than the C–Bi–C bond angles of **1b** [96(1)°, 94(1)° and 92(1)°] [8].

Table 1
Relative ratios in the competitive reaction

	(a)	(c)	(d)	(e)	(f)	(g)
2/2b	53/47	33/67	29/71	35/65	16/84	0/100
4/4b	53/47	49/51	46/54	44/56	40/60	37/63

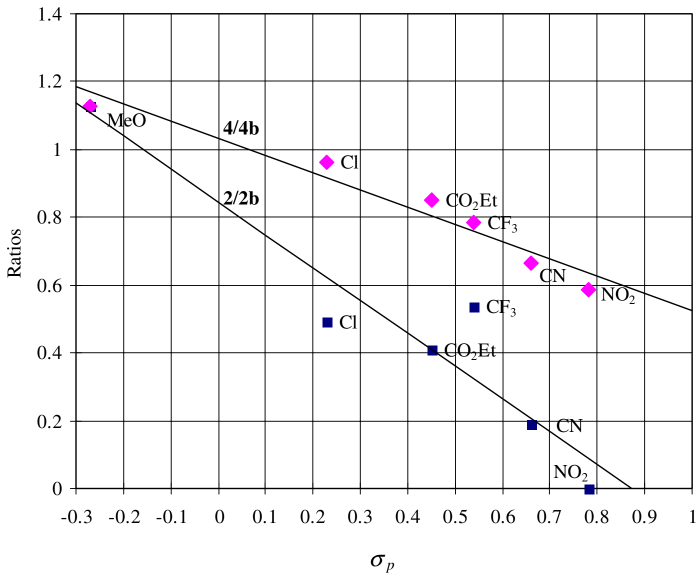


Fig. 1. Hammett plots.