Transylidation of Some Stabilized Bismuthonium Ylides

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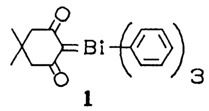
Synopsis. Triphenylbismuthonium diacylmethanides underwent the copper(I)-assisted transylidation with dimethyl sulfide and triphenylarsine in benzene at room temperature, giving the corresponding sulfonium and arsonium ylides in moderate to good yields, but they failed to exchange the ylide functionality with triphenylphosphine in most cases and with triphenylstibine in all cases examined, decomposition leading to the *C*- or *O*-phenylation of 1,3-dicarbonyl portion being the major reaction that took place.

Although the bismuthonium ylide was first obtained by Lloyd and Singer in 1967 as an unstable solid,[1] the chemistry of this class of compounds has remained yet unexplored. Recently, we reported some unique reactions of a stabilized bismuthonium ylide, triphenylbismuthonium 4,4-dimethyl-2,6-dioxocyclohexanide (**1**), with aldehydes,[2] alkynes,[3] isothiocyanate,[4] and sulfenes.[5] In the present paper, we describe the first example of the transylidation of bismuthonium ylides with organic sulfide, phosphine and arsine. In contrast to the ylides of lighter V$_B$ and VI$_B$ group elements, the exchange of the ylide functionality of bismuthonium ylides has been found to occur only with a limited range of neutral nucleophiles.

Moderately stabilized bismuthonium ylides (**2a**—**2d**) were generated by the interaction of sodium salts of the parent active methylene compounds with triphenylbismuth dichloride or triphenylbismuth oxide. These ylides were comparatively stable in solutions in inert organic solvents at room temperature, but attempts to isolate them led to complete decomposition, the *C*-phenylated 1,3-dicarbonyl compounds and triphenylbismuthine being the major products obtained. The ylides **2a**—**2d** underwent a facile ylide-exchange reaction with dimethyl sulfide in benzene at room temperature in the presence of copper(I) chloride, giving the corresponding dimethylsulfonium ylides (**3a**—**3d**) in moderate to good yields. The transylidation did not occur in the absence of copper(I) salt. Decrease in yields of the products was mainly attributed to the concurrent *C*-phenylation of the 1,3-dicarbonyl moiety. Diphenyl sulfide failed transylidation probably because of its low nucleophilicity. Highly stabilized bismuthonium ylide **1** was quite reluctant to undergo the ylide exchange (Table 1).

Table 1. Transylidation of Bismuthonium Ylides **1** and **2** with Dimethyl Sulfide

Ylide	R¹	R²	Reaction time/min	Yield of **3**/%
1	$OCCH_2C(CH_3)_2CH_2CO$		48 h	35[7]
2a	CH_3CO	CH_3CO	30	81[7]
2b	CH_3CO	C_6H_5CO	30	32[7]
2c	CH_3CO	CH_3OCO	30	27[7]
2d	$C_6H_5SO_2$	$C_6H_5SO_2$	30	20[6]



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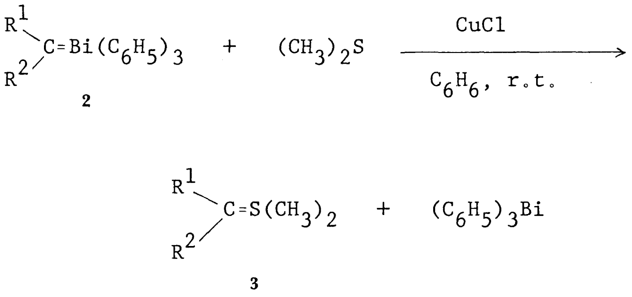

$$\begin{matrix}R^1\\ \quad\end{matrix}\!\!>C{=}Bi(C_6H_5)_3 + (CH_3)_2S \xrightarrow[C_6H_6,\ r.t.]{CuCl} \begin{matrix}R^1\\ \quad\end{matrix}\!\!>C{=}S(CH_3)_2 + (C_6H_5)_3Bi$$

$$R^1R^2C{=}Bi(C_6H_5)_3\ (\mathbf{2}) + (CH_3)_2S \xrightarrow[C_6H_6,\ r.t.]{CuCl} R^1R^2C{=}S(CH_3)_2\ (\mathbf{3}) + (C_6H_5)_3Bi$$

	R¹	R²
a :	CH_3CO	CH_3CO
b :	CH_3CO	C_6H_5CO
c :	CH_3CO	CH_3OCO
d :	$C_6H_5SO_2$	$C_6H_5SO_2$

Bismuthonium ylides also underwent transylidation with triphenylarsine under the catalysis of copper(I) salt to form arsonium ylides (**4a**) in moderate yields (Table 2). Attempts to effect transylidation with triphenylstibine were unsuccessful under the similar

Table 2. Transylidations with Pnictnide Nucleophiles

Nucleophile	Ylide **1**		Ylide **2a**	
	Reaction time/h	Yield/%	Reaction time/min	Yield/%
$(C_6H_5)_3P$	24	0[a]	30	18[8,b]
$(C_6H_5)_3As$	24	25[9]	30	52[9]
$(C_6H_5)_3Sb$	24	0[10,a]	30	0[10,c]

a) Dimedone was the major product obtained. b) 3-Phenyl-2,4-pentanedione (**6**) was obtained in 63% yield. c) Diketone **6** was obtained in 23% yield.

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conditions. In the latter case decomposition leading to the *C*-phenylated active methylene compounds and bismuth-containing polymeric substance was the only reaction that took place.

Results were rather embarrassing for the transylidation with triphenylphosphine. Stable ylide **1** failed to exchange the ylide functionality with triphenylphosphine; recovery of the starting ylide under mild conditions and decomposition to a yellow resinous substance under forced conditions were the respective results obtained. More reactive ylide **2a** underwent a partial ylide exchange with the phosphine to give the corresponding phosphonium ylide (**5a**) in a low yield (Table 2). The major product was 3-phenyl-2,4-pentanedione (**6**). Low efficiency in the ylide exchange may be attributed to the concomitant interaction of copper(I) chloride with triphenylphosphine to form a crystalline complex, which lacks the ability to promote the transylidation.

$$\underset{\mathbf{2a}}{(CH_3CO)_2C{=}Bi(C_6H_5)_3} + (C_6H_5)_3M \xrightarrow[C_6H_6\text{ , r.t.}]{CuCl}$$

$$(CH_3CO)_2C{=}M(C_6H_5)_3 + \underset{\mathbf{6}}{CH_3COC(C_6H_5){=}C(OH)CH_3}$$

4a: M=As

5a: M=P

$$+ (C_6H_5)_3Bi$$

Moderately stabilized bismuthonium ylide **2a** was found to react with 5,5-dimethyl-1,3-cyclohexanedione (dimedone) in the presence of an equimolar amount of triethylamine to exchange the carbanionic portion of the ylide, giving the highly stabilized ylide **1** in 69% isolated yield. In the absence of tertiary amine, however, no exchange reaction took place.

Recently, Varvoglis and co-worker reported the transylidation of phenyliodonium bis(aryl/alkylsulfonyl)methanides with a variety of nucleophiles such as pyridine, triphenylphosphine, triphenylarsine, dimethyl sulfide and sulfoxide.[6] In contrast to this, the bismuthonium ylides has been found to be subject to the copper(I) assisted transylidation only with a quite limited range of heteroatom nucleophiles.

Experimental

Bismuthonium ylides **2a**—**2d** were prepared by the reaction of the sodium salt of appropriate active methylene compounds with triphenylbismuth dichloride or oxide in tetrahydrofuran (THF) and used as a benzene solution without further purification. Ylide **1** was obtained as previously reported.[4]

Transylidation of Bismuthonium Ylides (1 and 2) with Heteroatom Nucleophiles. General Procedure: To a stirred suspension of sodium hydride (2 mmol; washed thoroughly with hexane prior to use) in dry THF (3 ml) cooled to 0 °C, a solution of an active methylene compound (1 mmol) in the same solvent (2 ml) was slowly added through the septum by means of a syringe under an atmosphere of nitrogen. After the cease of hydrogen evolution, a solution of triphenylbismuth dichloride (1.1 mmol) in THF (2 ml) was added and the mixture was stirred for 30 min. The resulting turbid, pale yellow solution was evaporated under reduced pressure to leave an oil containing a white powdery matter, to which was added a heteroatom nucleophile (1.0 mmol) in dry benzene (1 ml) followed by copper(I) chloride (0.2 mmol). The mixture which turned deep green (in the case of dimethyl sulfide) or blue (in other cases) was stirred for a time given in Tables 1 and 2, and then filtered to remove insolubles (sodium chloride and Bi-containing polymeric substances). The filtrate was evaporated and the residue was chromatographed over silica gel to give the corresponding ylides in yields as shown in the Tables. Products were known and identified by spectroscopic comparison to the authentic samples.

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