The Reaction of Tris(diethylamino)bismuthine with Carbonyl Compounds and the Reactivity Comparison of Several Metal Amides

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Tris(diethylamino)bismuthine (I) reacted with the sterically unhindered carbonyl compounds to give the corresponding enamines. The reactivity of the metal amides $M(NR_2)_n$ (M=As, Sb, Bi, and Ti; R=Me and Et) toward the carbonyl compounds was examined. The order of reactivity: Bi>Sb>Ti>As was observed for the addition reaction that took place as the first step in the reaction. On the other hand, the order of enamine formation was Sb>Ti>As>Bi. The effectiveness of the amination reaction depends both on the reactivity of metal amides to carbonyl groups and also on the affinity for oxygen of metal atoms. Although bismuth amide gives the addition product very rapidly, because of its poor affinity for oxygen, the addition products decompose thermally on prolonged standing or on distillation giving large amounts of starting carbonyl compounds along with small amounts of enamines.

The preparation and reactions of tris(dialkylamino)bismuthines with heterocumulenes have been reported.[1] The reactions of these reagents with acetic anhydride and heterocumulenes were found to be much easier than those of arsine amide or stibine amide, and the reagents could be expected to be useful for aminating carbonyl compounds. The reactions of various carbonyl compounds with the following organometallic compounds have been reported: tributylmethylaminotin,[2–4] tris(dimethylamino)borane,[5,6] tris(dimethylamino)arsine,[7–9] tetrakis(dimethylamino)titanium,[4,7,10–13] and tris(dimethylamino)stibine.[14,15] The amination ability order of metal amides, $M(NR_2)_n$, towards carbonyl compounds has been found to be Ti>As>B>Sn.[7] Tris(dimethylamino)stibine was proved to have an amination ability towards carbonyl compounds comparable to that of tetrakis(dimethylamino)titanium.[14,15] Amination of carbonyl compounds by metal amides is known to be a very easy way for obtaining the versatile synthetic intermediate enamines, because the reaction is very fast and the by-product (metal oxide) can be separated easily. Therefore it is of significance to find out the factors which control the amination reactions. This paper reports the reaction of tris(diethylamino)bismuthine (I) with carbonyl compounds along with a comparison of the reactivity of various metal amides.

Experimental

General Remarks. All reactions were carried out under argon. IR and NMR spectra were taken on a JASCO A-1 spectrometer and a JEOL-C 60 HL spectrometer respectively. Glc analyses were carried out on a Shimadzu GC 6A apparatus, using PEG 6000 (10%) on Shimalite W-301 (1.0 m) and helium as a carrier gas.

Reagent. The preparation of tris(diethylamino)bismuthine (I), was reported previously.[1] Tris(diethylamino)arsine (II), -stibine (III), and tetrakis(diethylamino)titanium (IV) were prepared by the same method reported in the preparation of their dimethylamino derivatives; II: bp, 47—50 °C/0.08 mmHg; yield, 72%, III: bp, 59—62 °C/0.02 mmHg; yield, 82% and IV: bp, 96—98 °C/0.12 mmHg; yield, 64%.

The other commercial reagents were dried over calcium hydride and distilled before use.

Reaction of I with Benzaldehyde. To a solution of I (3.0 g, 7.07 mmol) in 10 ml of ether, benzaldehyde (0.74 g, 7.00 mmol) was added slowly with stirring. A slightly exothermic reaction took place giving a yellowish solution. After removal of the solvent, a viscous yellowish liquid remained. IR spectra of the liquid showed no absorption of carbonyl group and a new absorption at 1060 cm^{-1} (ν_{C-O}). NMR also showed no reasonance of aldehyde-proton but a new reasonance of –OCH–N moiety at δ 4.10. On distillation of the liquid under reduced pressure, benzaldehyde was recovered almost completely (0.65 g). The distillation residue was a dark black solid whose structure was not identified. Hydrolysis of the reaction mixture, and the following extraction with ether gave mostly (90%) benzaldehyde with several materials detected on a TLC. These materials was not identified.

Reaction of I with Reactive Carbonyl Compounds. A typical

Table 1. Bp and yield of the amination products by means of $Bi(NEt_2)_3$

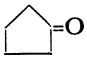
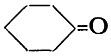
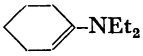
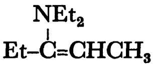
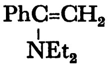
	Carbonyl compounds	Aminated products	Bp (°C/mmHg)	Yield (%)
V			60.5—62.0/10	29
VI			74.0—75.0/10	49
VII	$Et_2C=O$	 $Et-C(NEt_2)=CHCH_3$	68.0—69.0/35	28
VIII	PhCOMe	 $PhC(NEt_2)=CH_2$	60.0—61.0/1.0	4

Table 2. Relevant IR frequencies and NMR absorptions of the aminated products

	IR (C=C) cm^{-1}[a]	NMR (δ) ppm[b]		
V	1615	4.19(m, 1H)	3.04(q, 4H)	2.35(m, 4H)
		1.97(m, 2H)	1.03(t, 6H)	
VI	1630	4.49(m, 1H)	2.92(q, 4H)	2.04(m, 4H)
		1.59(m, 4H)	0.97(t, 6H)	
VII	1635	4.26(q, 1H)	2.91(q, 4H)	2.14(q, 2H)
		1.61(d, 3H)	0.99(t, 3H)	0.97(t, 6H)
VIII	1635	7.37—7.90(m, 5H)	4.14(s, 1H)	
		4.04(s, 1H)	2.96(q, 4H)	1.01(t, 6H)

a) Coated on NaCl Crystal. b) In $CHCl_3$ (V, VI and VII), in $CDCl_3$ (VIII).

reaction (with cyclohexanone) is described.

Details are given in Tables 1 and 2. To a solution of (I) (2.82 g, 5.92 mmol) in 10 ml of ether, cyclohexanone (0.87 g, 8.4 mmol) was added slowly with stirring. A slightly exothermic reaction took place giving a small amount of a yellowish grey precipitate. The precipitate was removed by filtration and the filtrate was condensed on a rotary evaporator. Distillation of the remaining viscous liquid which showed no carbonyl absorption on its IR spectra gave a large amount (0.44 g, 50% recovery) of cyclohexanone and the aminated product; *N,N*-diethylcyclohex-1-enylamine in 49% yield (0.39 g); bp, 74.0—75.0 °C/10 mmHg, NMR (in $CHCl_3$) δ 4.49 (m, 1H), 2.92 (q, 4H), 2.04 (m, 4H), 1.59 (m, 4H) and 0.37 (t, 6H), IR 1630 cm^{-1} ($\nu_{C=O}$). These spectroscopic data coincide with those of the reaction product of cyclohexanone with III[14,15] or IV.[4,7,10-13]

Reaction of Acetophenone with Various Metal Amides. The reactions of acetophenone with I—IV as well as with their dimethyl amino homologues were carried out under the same reaction conditions. To a solution of metal amide (5 mmol) in 10 ml of ether, acetophenone (0.9 g, 7.5 mmol) was added slowly with stirring. The reaction mixture was kept at 20 °C for 24 hr. The same treatment as above gave α-dimethylaminostyrene or α-diethylaminostyrene. The yields of the substituted styrenes are given in Table 3.

Measurements of the Rate of Carbonyl Compounds Consumption on the Reactions with I—IV. An equimolar (0.05 mol/l) reaction between metal amide and carbonyl compounds at an appropriate temperature was started by mixing each reagent dissolved in chlorobenzene containing a constant amount of *o*-dichlorobenzene as an internal standard. Aliquots of the reaction mixture were withdrawn at appropriate time intervals and the remaining amounts of the carbonyl compounds were determined by GLC analyses. The results are shown in Figs. 1 and 2.

Table 3. Yield (%) of the enamine in the reaction of $M(NR_2)_n$ with PhCOMe

R	M			
	As	Sb	Ti	Bi
Me	41	86	65	0
Et	12	78	38	4

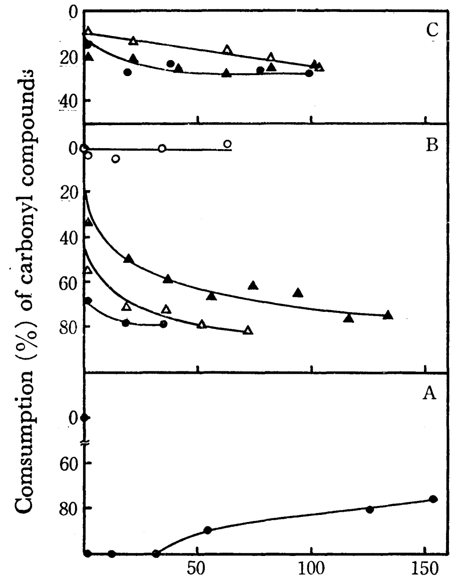


Fig. 1. Consumption (%) curves of the reactions between reactive carbonyl compounds and various metal amides.

A: Benzaldehyde, 100 °C; B: Acetophenone, 40 °C; C: Di-isopropyl ketone, 40 °C.

○: with As–N; △: with Sb–N; ●: with Bi–N; ▲: with Ti–N.

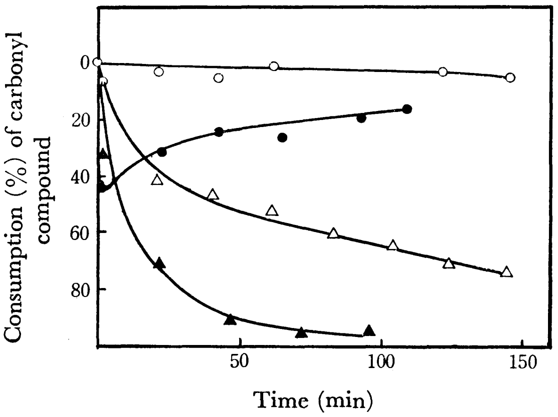


Fig. 2. Consumption (%) curves of the reactions between *N,N*-Dimethylformamide and various metal amides.

○: with As–N; △: with Sb–N; ●: with Bi–N; ▲: with Ti–N.

Results and Discussion

The amination of various carbonyl compounds with tris(dimethylamino)stibine has been studied,[14] and the amination ability is found to be comparable to that of tetrakis(dimethylamino)titanium which has been known as the most effective amination reagent so far.[7] Bismuth amide has labile bonds and could be expected to be an effective amination reagent. In fact bismuth amides are very reactive towards acetic anhydride and heterocumulenes and also towards moisture and oxygen in air.[1] Contrary to expectation, I gave only poor yields of amination products even in the reactions with reactive carbonyl compounds such as cyclohexanone, cyclopentanone, diethyl ketone and acetophenone (Table 1). The structures of the amination products were determined by comparison of their IR and NMR spectra with those of the reaction products obtained in the reaction between III or IV and the corresponding carbonyl compounds.[4,7,10-15] The reaction mixture of I with these carbonyl compounds shows no carbonyl absorption on their IR spectra. This result together with that of the reaction of I with benzaldehyde indicate that I could react with such carbonyl compounds quantitatively. Distillation of the reaction mixture under reduced pressure, however, gave only small amounts of aminated product and large amounts of starting carbonyl compounds (Table 1). Table 2 shows the yields of the enamines in the reaction of acetophenone with various metal amides. Bismuth amides gave the least amounts of the enamines among the metal amides examined. These unexpected observations prompted us to compare the reactivity of several metal amides. Figure 1 shows the consumption curves of benzaldehyde (A), acetophenone (B), and di-isopropyl ketone (C), in the reaction with compounds I—IV. The corresponding consumption curves of DMF with the same metal amides are shown in Fig. 2. They show only the consumption of the carbonyl compounds and not the formation of aminated products. It has been proposed that the reaction mechanism includes an addition step of metal–nitrogen bond to carbonyl groups (step A), followed by a deoxygenation step of carbonyl oxygen by metal moieties forming metal oxides (step B).[7,14] The results (Figs. 1 and 2) reveal that the bismuth amide has the highest reactivity in the addition step (step A) and reactivity order of $M(NEt_2)_n$ (n=3 or 4) is Bi>Sb>Ti>As in this step. The effectiveness of amination reaction is Sb>Ti>As>Bi based on the yield of the amination products (Table 3). This result can be explained in terms of the affinity for oxygen of the metal atoms. The properties of group Va metals have not been compared, but they could be parallel to factors such as the metal–oxygen bond energies, and the tendency of the quarternary onium salt formation. The σ-bond energies for the phosphorus–, arsenic–, and stibine–oxygen bonds have been reported to be 86,[16] 72 and 71 kcal/mol,[17] respectively. There have been several observations of the fact that the stability order of quinqivalence state of group Va metal is P>As>Sb>Bi.[18] Because of the poor affinity of bismuth atom for oxygen, the addition products decomposed thermally giving mostly original carbonyl compounds and unidentified decomposition products of bismuth amide. This is shown in the reaction of I with benzaldehyde (Fig. 1-A). Reappearance of benzaldehyde from the reaction mixture was observed at a high temperature (100 °C). In the reaction with amide carbonyls, group Va metal amides are apparently inferior to titanium amide from a preparative viewpoint.[14] Figure 2 shows, however, I could add to the amide carbonyl group much faster than IV, but the thermal decomposition of the addition products occurred again easily, giving the starting amide carbonyl. The reason why titanium amide could have a large reactivity towards amide carbonyl is not known but it may be partly ascribed to the fact that the titanium atom is a transition metal and has vacant d orbitals which increase the interactions with the lone pairs of the oxygen atom.

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