Insertion of Ketene and Diphenylketene to the Pnictogen-Heteroatom Bonds

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Synopsis. Ketene and diphenylketene insert across the heteroatom-metal bond of amino-, alkoxy-, and alkylthiopnictogens, $R_{3-n}MX_n$, to give the corresponding α-metallated acetamides, esters, and thioesters, $R_{3-n}M(CH_2COX)_n$ and $R_{3-n}M(CPh_2COX)_n$ (M=As, Sb, Bi; X=NR_2, OR, SR; n=1,3), respectively.

Ketene has been known to react with various organometallic compounds, especially with the compounds containing the group 3B and 4B elements.[1] However, the reactions of ketene with analogous arsenic, antimony, and bismuth compounds have been received scarce attention so for. Lustenko et al.[2] reported that alkoxyarsines and -stibines react with ketene to give alkoxycarbonylmethylarsines and -stibines. However, there is no report dealing with the reaction of ketene with group 5B metal amides and thiolates. As a part of our continuing work[3] on the reaction of group 5B metal compounds with multiply bonded reagents, the reactions of ketene and diphenylketene with amides, alkoxides, and alkanethiolates of arsenic, antimony, or bismuth have been investigated.

Ketene, generated by the pyrolysis of diketene, reacted with dialkylaminodialkylarsines in ether at about −20 °C to give *N,N*-dialkyl(dialkylarsino)-acetamides. The reaction of dialkylaminodimethylstibines with ketene proceeded more readily to yield *N,N*-dialkyl(dimethylstibino)acetamides (Table 1).

$$R_2M\text{-}NR'_2 + CH_2{=}C{=}O \longrightarrow R_2MCH_2CONR'_2$$
(M = As, Sb; R = Me, Ph; R' = Me, Et)

These insertion products were obtained as thermally stable (up to ca. 200 °C) and distillable liquids. The structure of the products was determined on the basis of IR, NMR, and mass spectra and elemental analyses. The IR spectra of the arsinoacetamides show a strong C=O stretching vibration at 1630—1622 cm^{-1}. The corresponding C=O stretching band of antimony analogues is located at a lower frequency (1620—1613 cm^{-1}). This may be explained by increased electron density on the α-methylene carbon and intramolecular coordination of carbonyl oxygen to antimony. The ^1H NMR spectra of these adducts contain a singlet peak of the methylene protons attached directly to the metal atoms at δ=2.5—3.1 and also characteristic peaks due to magnetically nonequivalent two alkyl groups on the nitrogen atom of amide groups, namely, two singlets at δ=2.7—3.1 for the dimethylamides and two quartets at δ=3.0—3.5 and two triplets at δ=0.9—1.2 for the diethylamides.

Tris(dialkylamino)bismuthines readily reacted with ketene at −50 °C with liberation of heat, and three moleclues of ketene inserted into the Bi-N bonds to give tris(dialkylcarbamoylmethyl)bismuthines. On the treatments of ketene with tris(dialkylamino)arsines at 0 °C or with tris(dialkylamino)stibines at −20 °C, the corresponding addition products containing arsenic or antimony were obtained.

$$M(NR_2)_3 + 3CH_2{=}C{=}O \longrightarrow M(CH_2CONR_2)_3$$
(M = As, Sb, Bi; R = Me, Et)

These adducts are reddish brown viscous liquids or waxy solid which, on attempted vacuum (ca. 10^{-2} Pa) distillation by heating up to 250 °C, decomposed to *N,N*-dialkylacetamides (70—80%) and unidentified black residues containing metals. Nevertheless, the formation of adducts was confirmed by ^1H NMR, ^{13}C NMR and IR spectra. In the ^1H and ^{13}C NMR spectra of the adducts, the methylene groups attached to the metals, in general, appeared at somewhat lower

Table 1. Preparative, Analytical, and Mass Spectral Data for the α-Metallated Acetamides

Compound	Bp/°C(Pa)	Yield/%	Calcd(Found)/%			MS, *m/z* (rel intensity)[a]
			C	H	N	
$Me_2AsCH_2CONEt_2$	60—61(4.0)	81	42.27 (43.84)	8.13 (8.28)	6.47 (6.39)	219(M^+, 10), 204(100), 162(62), 119(10), 114(9), 105(16), 100(21), 72(68)
$Ph_2AsCH_2CONMe_2$	170—173(1.3×10^{-2})	86	60.51 (60.96)	5.88 (5.76)	4.32 (4.44)	315(M^+, 13), 238(43), 229(83), 227(67), 161(4), 86(14), 72(26), 44(100)
$Ph_2AsCH_2CONEt_2$	167—171(1.3×10^{-2})	89	63.28 (62.97)	6.68 (6.48)	3.91 (4.08)	343(M^+, 9), 243(6), 229(10), 227(13), 115(17), 100(9), 72)38), 58(100)
$Me_2SbCH_2CONMe_2$	71—72(26)	75	28.92 (30.29)	6.25 (5.93)	5.75 (5.58)	237(M^+, 2), 222(40), 207(5), 193(3), 165(10), 151(13), 86(3), 72(12), 44(100)
$Me_2SbCH_2CONEt_2$	81—86(4.0)	88	35.54 (36.12)	6.93 (6.82)	5.37 (5.27)	265(M^+, 3), 259(22), 208(18), 193(14), 165(11), 151(35), 115(13), 72(36), 43(100)

a) Masses refer to ^{121}Sb for the antimony compounds.

field compared with those of the corresponding *N,N*-dialkyl(dialkylmetal)acetamides, probably due to additional two electron-withdrawing $NCOCH_3$ groups. The α-methylene groups shift towards higher field with the central metal going from As to Sb and Bi, due to increasing electron density of the neighboring methylene groups in this order.

Diphenylketene, in which the methylene carbon is more sterically crowded than ketene, reacted slowly with aminoarsines and aminostibines, leading to the corresponding insertion products.

$$R_2M\text{-}NR'_2 + Ph_2C{=}C{=}O \longrightarrow R_2MCPh_2CONR'_2$$
$$M(NR'_2)_3 + 3Ph_2C{=}C{=}O \longrightarrow M(CPh_2CONR'_2)_3$$
$$(M = As, Sb;\ R = Me, Ph;\ R' = Me, Et)$$

Reaction of trimethoxyarsine with ketene proceeded very slowly in boiling benzene to give mono-insertion product, dimethoxy(methoxycarbonylmethyl)arsine, in quite low yield (24%), but ethoxy and higher alkoxyarsines did not react under the same conditions. On the other hand, tris(alkoxycarbonylmethyl)stibines were easily obtained in high yield by the reaction of ketene with trialkoxystibines in ether at room temperature, as reported by Lutsenko et al.[2a,b] Tris(ethylthio)stibine also reacted slowly with ketene to afford tris[(ethylthio)-carbonylmethyl)]stibine in 50% yield under refluxing benzene, whereas tris(ethylthio)arsine did not react under the analogous reaction conditions.

$$As(OMe)_3 + CH_2{=}C{=}O \longrightarrow (MeO)_2AsCH_2COOMe$$
$$Sb(OR)_3 + 3CH_2{=}C{=}O \longrightarrow Sb(CH_2COOR)_3$$
$$Sb(SEt)_3 + 3CH_2{=}C{=}O \longrightarrow Sb(CH_2COSEt)_3$$

Thus, the reactivity of tervalent group 5B compounds, =M-X, toward ketene increases in the order As<Sb<Bi for the metal (M), and SR<OR<NR_2 for the functional group(X). The highest reactivity of $Bi(NR_2)_3$ may be attributed to the enhanced nucleophilicity of the nitrogen caused by the weak and highly polar Bi-N bonds.

Experimental

Materials and General Procedures. The compounds Me_2AsNEt_2,[4] Ph_2AsNMe_2,[4] Ph_2AsNEt_2,[4] Me_2SbNMe_2,[5] Me_2SbNEt_2,[5] $As(NMe_2)_3$,[4] $As(NEt_2)_3$,[4] $Sb(NMe_2)_3$,[6] $Sb(NEt_2)_3$,[6] $Bi(NMe_2)_3$,[3c] $Bi(NEt_2)_3$,[3c] $As(OMe)_3$,[7] $Sb(OR)_3$ (R=Et, *n*-Pr, *i*-Pr, *n*-Bu),[7] and $Sb(SEt)_3$[7] were synthesized according to the published procedures. Ketene[8] was generated by the pyrolysis of diketene at 550 °C, and was purified through two traps cooled to −20 °C. Diphenylketene[9] was prepared by dehydrochlorination of diphenylacetyl chloride with triethylamine. All reactions were performed under an atmosphere of nitrogen or argon. ^1H (60 MHz) and ^{13}C (15.04 MHz) NMR spectra were measured in $CDCl_3$ with JEOL C-60 HL and JNM FX-60 FT instruments, respectively. IR spectra were recorded on a Shimadzu IR-430 spectrometer. Mass spectra (70 eV) were measured with a Hitachi RMU-6L spectrometer.

Reaction of Dialkylaminodialkylarsines or -stibines with Ketene. An excess of ketene was passed through a stirred solution of diethylaminodimethylarsine (6.52 g, 36.8 mmol) in 20 ml of ether at about −20 °C during 10 min. Solvent removal under vacuum left a yellow liquid residue. From the residue, *N,N*-diethyl(dimethylarsino)acetamide (6.49 g, 81%) was obtained by fractional distillation as a yellowish liquid. In a similar way, reactions of ketene with dimethylaminodiphenylarsine at room temperature, with dimethyl aminodimethylstibine at −50 °C, and with diethylamino dimethylstibine at −50 °C gave the corresponding insertion products. Bp, yield, analytical, and mass spectral data of these products are shown in Table 1. The NMR and IR spectra of these metallated acetamides are summarized in Table 2.

Reaction of Tris(dialkylamino)arsines, -stibines, and -bismuthines with Ketene. Ketene was passed into an ethereal (20 ml) solution of tris(dimethylamino)arsine (3.89 g, 18.8 mmol) at room temperature. After removal of the solvent, the residue was dried under reduced pressure (ca. 10^{-2} Pa) for 4 h, leaving a reddish brown liquid (5.61 g), and whose ^1H and ^{13}C NMR and IR spectra were measured without further purification because of difficulties encountered during distillation or recrystallization: ^1H NMR δ=2.84 (s, 2H), 2.95 (s, 3H), and 3.11 (s, 3H); ^{13}C NMR δ=29.82, 35.22, 38.27, and 171.20; IR (neat) 1627 cm^{-1}. These spectra proved the product to be tris(dimethylcarbamoylmethyl)arsine (90%). A similar treatment of ketene with tris(diethylamino)-arsine at 0 °C, tris(dimethylamino)stibine at −20 °C, tris(diethylamino)stibine at −20 °C, tris(dimethylamino)bismuthine at −50 °C, or tris(diethylamino)bismuthine at −50 °C gave the corresponding insertion products. $As(CH_2CONEt_2)_3$: Red oil (84%); ^1H NMR δ=1.13, 1.19 (each t, 3H),

Table 2. NMR and IR Spectroscopic Data for the α-Metallated Acetamides, $R_2MCH_2CONR'_2$

Compound	^1H NMR(δ)			^{13}C NMR(δ)				IR
	R_2M	MCH_2	NR'_2	R_2M	MCH_2	CO	NR'_2	ν(CO) cm^{-1}
$Me_2AsCH_2CONEt_2$	1.09(s)	2.53(s)	3.39(q) 1.10(t) 3.50(q) 1.20(t)	9.55	30.99	170.16	38.89 13.38 42.82 14.42	1622
$Ph_2AsCH_2CONMe_2$	7.30(m)	3.05(s)	2.78(s) 2.83(s)	128.52 132.94 139.95	32.62	170.68	35.28 37.94	1630
$Ph_2AsCH_2CONEt_2$	7.27(m)	3.00(s)	3.09(q) 0.98(t) 3.25(q) 1.01(t)	128.52 133.65 140.28	32.88	169.84	40.22 13.06 42.82 14.36	1625
$Me_2SbCH_2CONMe_2$	0.88(s)	2.52(s)	2.94(s) 3.06(s)	−3.95	18.20	171.61	34.25 37.44	1620
$Me_2SbCH_2CONEt_2$	0.89(s)	2.52(s)	3.39(q) 1.11(t) 3.50(q) 1.19(t)	−2.79	18.91	171.53	39.83 13.71 43.01 14.42	1613

3.09 (s, 1H, $AsCH_2$), 3.29 and 3.39 (each q, 2H); ^{13}C NMR δ=13.25, 14.49, 30.08 (AsC), 40.22, 43.08, and 170.68; IR (neat) 1625 cm^{-1} (C=O). Sb $(CH_2CONMe_2)_3$: Red oil (98%); ^1H NMR δ=2.76 (s, 2H, $SbCH_2$), 2.95 (s, 3H), and 3.10 (s, 3H); ^{13}C NMR δ=22.16 (SbC), 35.35, 38.66, and 172.76; IR (neat) 1618 cm^{-1} (C=O). Sb $(CH_2CONEt_2)_3$: Red oil (100%); ^1H NMR δ=1.11, 1.20 (each t, 3H), 2.78 (s, 1H, $SbCH_2$), 3.40 (q, 2H); ^{13}C NMR δ=13.51, 14.49, 22.29 (SbC), 40.28, 43.40, and 172.05; IR (neat) 1610 cm^{-1}. Bi $(CH_2CONMe_2)_3$: Red solid (97%); ^1H NMR δ=2.03 (s, 2H, $BiCH_2$), 2.89 (s, 3H), and 2.99 (s, 3H); ^{13}C NMR δ=21.38(BiC), 34.89, 37.88, and 173.54; IR (nujol) 1640 cm^{-1} (C=O). Bi $(CH_2CONEt_2)_3$: Red oil (100%); ^1H NMR δ=1.12, 1.18 (each t, 3H), 2.08 (s, 1H, $BiCH_2$), 3.22, and 3.38 (each q, 2H); ^{13}C NMR δ=13.12, 14.23, 21.38 (BiC), 40.28, 43.60, and 172.94; IR (neat) 1640 cm^{-1} (C=O).

Reaction of Diphenylketene with Aminoarsines or Aminostibines. Diphenylketene (1.88 g, 9.68 mmol) was added dropwise to a solution of diethylaminodimethylarsine (1.71 g, 9.66 mmol) in 20 ml of ether at room temperature. The mixture was heated under reflux for 30 min. After removal of the solvent, the residue was distilled under vacuum to afford *N,N*-diethyl(dimethylarsino)diphenylacetamide (1.62 g, 45%) as an orange liquid, bp 180—187 °C/1.3×10^{-2} Pa: ^1H NMR δ=0.91 (s, 3H, CH_3As), 1.11, 1.12 (each t, 3H), 3.26, 3.38 (each q, 2H), and 7.22 (m, 5H); ^{13}C NMR δ=6.04 (CH_3As), 12.86, 14.62 (NCC), 40.67, 42.17 (NC), 54.58 (q-C), 126.89 (p), 128.45 (m), 129.04 (o), 140.02 (i), and 170.68 (CO); IR (neat) 1658 cm^{-1} (C=O); MS *m/z* (rel intensity) 371 (M^+; 8), 105 (100), 100 (82), 77 (88). Similarly, the following diphenylketene insertion products were obtained by the reaction of 3 molar equivalent of diphenylketene with dimethylaminodiphenylarsine, diethylaminodiphenylarsine, dimethylaminodimethylstibine, diethylaminodimethylstibine, tris(dimethylamino)arsine, tris(diethylamino)arsine, tris(dimethylamino)stibine, and tris(diethylamino)stibine. *N,N*-Dimethyl(diphenylarsino)diphenylacetamide: Yield 41%; bp 146—151 °C/5.3×10^{-3} Pa; ^1H NMR δ=2.94 (s, 3H), 2.98 (s, 3H), and 7.30 (m, 20H); ^{13}C NMR δ=36.13, 37.55, 54.90 126.96, 128.52, 129.04, 129.17, 131.05, 133.78, 139.63, 146.32, and 179.30; IR ($CHCl_3$) 1645 cm^{-1} (C=O). *N,N*-Diethyl(diphenylarsino)diphenylacetamide: Yield 68%, bp 140—150 °C/5.3×10^{-3} Pa; ^1H NMR δ=1.09, 1.10 (each t, 3H), 3.28, 3.39 (each q, 2H), and 7.27 (m, 10H); ^{13}C NMR δ=12.80, 14.62, 40.61, 42.10, 54.51, 126.83, 128.45, 128.97, 129.17, 130.99, 134.37, 139.95, 146.19, and 173.02; IR ($CHCl_3$) 1640 cm^{-1}. *N,N*-Dimethyl(dimethylstibino)diphenylacetamide: Yield 23%; bp 137—144 °C/1.3×10^{-2} Pa; ^1H NMR δ=0.97 (s, 6H), 2.94 (s, 3H), 2.97 (s, 3H), and 7.32 (m, 10H); ^{13}C NMR δ=4.09, 36.06, 37.55, 54.77, 126.89, 128.52, 129.04, 139.70, and 175.75; IR ($CHCl_3$) 1640 cm^{-1} (C=O). *N,N*-Diethyl(dimethylstibino)diphenylacetamide: Yield 25%; bp 110—111 °C/1.3×10^{-2} Pa; ^1H NMR δ=1.03 (s, 3H), 1.09 (t, 3H), 3.27, 3.39 (each q, 2H), and 7.28 (m, 5H); ^{13}C NMR δ=3.96, 12.86, 14.62, 40.67, 43.17, 54.51, 126.89, 128.26, 128.97, 138.85, and 172.49; IR (neat) 1656 cm^{-1} (C=O). Tris(dimethylcarbamoyldiphenylmethyl)arsine: Yield 41%; bp 114—126 °C/1.3×10^{-2} Pa; ^1H NMR δ=2.92 (s, 3H), 2.95 (s, 3H), and 7.26 (m, 10H); ^{13}C NMR δ=36.00, 37.49, 54.77, 126.89, 128.45, 128.97, 139.63, and 171.72; IR ($CHCl_3$) 1643 cm^{-1} (C=O). Tris(diethylcarbamoyldiphenylmethyl)arsine: Yield 56%; bp 136—141 °C/1.3×10^{-2} Pa; ^1H NMR δ=1.13 (t, 3H), 3.32, 3.44 (each q, 2H), and 7.33 (m, 5H); ^{13}C NMR δ=12.80, 14.62, 40.61, 42.17, 54.51, 126.89, 128.45, 128.97, 139.95, and 170.68; IR ($CHCl_3$) 1630 cm^{-1}. Tris(dimethylcarbamoyldiphenylmethyl)stibine: Yield 23%; bp 158—160 °C/1.3×10^{-2} Pa; ^1H NMR δ=2.98 (s, 3H), 3.00 (s, 3H), and 7.28 (m, 10H); ^{13}C NMR δ=36.06, 37.55, 54.84, 126.96, 128.52, 129.04, 139.63, and 171.72; IR ($CHCl_3$) 1639 cm^{-1} (C=O). Tris(diethylcarbamoyldiphenylmethyl)stibine: Yield 23%; bp 111—112 °C/1.3×10^{-2} Pa; ^1H NMR δ=1.07, 1.10 (each t, 3H), 3.28, 3.40 (each q, 2H), and 7.30 (m, 5H); ^{13}C NMR δ=12.80, 14.55, 40.61, 42.10, 54.44, 126.83, 128.38, 128.97, 139.95, and 170.68; IR ($CHCl_3$) 1625 cm^{-1} (C=O).

Reaction of Trimethoxyarsine and Trialkoxystibines with Ketene. A large excess ketene was bublled into a solution of trimethoxyarsine (4.66 g, 27.7 mmol) in boiling benzene (10 ml). After removal of the solvent, dimethoxy(methoxycarbonylmethyl)arsine (1.37 g, 24%) was obtained by distillation: Bp 58—59 °C/5.3 Pa; ^1H NMR δ=3.13 (s, 2H), 3.55 (s, 6H), and 3.74 (s, 3H); ^{13}C NMR δ=37.88 (AsC), 48.93 (MeOAs), 52.63 (COOMe), and 168.41; IR (neat) 1718 cm^{-1}. Reaction of trialkoxystibines with ketene was carried out in ether at room temperature. The following tris(alkoxycarbonylmethyl)stibines were obtained. $Sb(CH_2COOR)_3$: R=Et (yield 77%): Bp 134—138 °C/0.47 Pa; ^1H NMR δ=1.26 (t, 3H), 2.53 (s, 2H), 4.08 (q, 2H); ^{13}C NMR δ=14.42, 21.77 (SbC), 60.49, and 172.24; IR (neat) 1710 cm^{-1} (C=O). R=*n*-Pr (85%): Bp 150—151 °C/1.3×10^{-2} Pa; ^1H NMR δ=0.95 (t, 3H), 1.66 (m, 2H), 2.52 (s, 2H), and 3.98 (t, 2H); ^{13}C NMR δ=10.46, 21.83 (SbC), 22.16, 66.14 and 172.24; IR (neat) 1709 cm^{-1} (C=O). R=*i*-Pr (85%): Bp 122—123 °C/6.7×10^{-2} Pa; ^1H NMR δ=1.23 (d, 6H), 2.50 (s, 2H), and 4.91 (m, 1H); ^{13}C NMR δ=21.50 (SbC), 22.03, 67.12, and 171.72; IR (neat) 1708 cm^{-1} (C=O). R=*n*-Bu (74%): Bp 161—162 °C/1.2×10^{-2} Pa; ^1H NMR δ=0.95 (t, 3H), 1.13—1.78 (m, 4H), 2.50 (s, 2H), and 4.05 (t, 2H); ^{13}C NMR δ=13.71, 19.17, 21.83 (SbC), 30.86, 64.58, and 172.37; IR (neat) 1700 cm^{-1} (C=O).

Reaction of Tris(ethylthio)stibine with Ketene. Ketene was bubbled through a boiling benzene (20 ml) solution of tris(ethylthio)stibine (3.70 g, 12.2 mmol). Distillation afforded tris[(ethylthio)carbonylmethyl]stibine (2.80 g, 53%) as a yellow liquid: Bp 150—154 °C/1.3×10^{-1} Pa; ^1H NMR δ=1.26 (t, 3H), 2.90 (q, 2H), and 3.06 (s, 2H); ^{13}C NMR δ=19.17, 21.05 (SbC), 24.69, and 178.29; IR (neat) 1662 cm^{-1} (C=O).

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