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Articles

Periodic Terpolymerization of Cyclooligoarsine, Cyclooligostibine, and Acetylenic Compound

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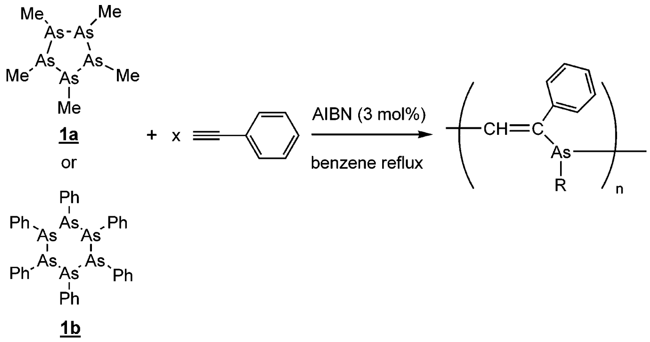
ABSTRACT: The ring-collapsed radical terpolymerization of pentamethylcyclopentaarsine (**1a**), hexaphenylcyclohexastibine (**2**), and dimethyl acetylenedicarboxylate (**3**) provided a periodic terpolymer containing both antimony atom and arsenic atom in the polymer chain. In the case of a 1:1:2 ratio of **1a**:**2**:**3**, the obtained polymer has 1:1:2 structure of arsine, stibine, and vinylene unit. Employing excess **1a** did not affect the periodic structure of the terpolymerization. On the other hand, employing excess **2** resulted in the terpolymer with more stibine units. The arsenic radical was more reactive toward **3** forming the vinyl radical, while the antimony radical was more reactive toward the vinyl radical forming the terpolymer. After the arsenic radicals were consumed, the antimony radical also reacted with **3** thereby affecting the periodic structure of the terpolymerization. Different reactivity of pnictogen radicals made it possible to construct the periodic vinylene−arsine−vinylene−stibine backbone.

Introduction

Polymers containing inorganic elements are one of the current interests due to their useful and interesting properties.[1,2] However, the synthesis of polymer with a wide variety of inorganic elements in the backbones is one of the challenging topics because the available synthetic methods are relatively limited. Among the various polymer syntheses, free radical polymerization is of greater advantage than any other method due to its nonionic character. Since radical polymerization is tolerant to a variety of polar functionalities, this technique is now widely used in industry and laboratory to synthesize a wide variety of polymers. Synthesis of an alternating copolymer by radical copolymerization have been achieved by using the combination of a donor monomer and an acceptor monomer in the most cases.[3] However, only a few examples of radical alternating copolymerization to obtain inorganic polymers have yet been reported.[4,5] A classical controlled radical terpolymerization provided random copolymer of (A−D_1) unit and (A−D_2) unit or (A_1−D) unit and (A_2−D) unit. A periodic terpolymerization (synthesis of A−B−C or A−B−A−C type polymer) has not yet been achieved by the radical terpolymerization. For the synthesis of the periodic terpolymer, precise control of propagating reactions is required. Developing the method for controlling the radical reactivity is necessary for constructing a finely designed inorganic polymer backbone.

Recently, we have developed a radical copolymerization of cyclooligoarsines (**1**) and phenylacetylenes[3] (Scheme 1). This copolymerization proceeds by the so-called ring-collapsed radical alternating copolymerization, RCRAC. In this system, the homolytic cleavage of **1** occurs followed by incorporation of the arsine units into the polymer backbones with no arsenic−arsenic bonds. This method produces polymers having a 1:1 alternating structure of the vinylene units and the arsenic elements in the backbone.

Scheme 1



The mechanism of RCRAC is as follows (Scheme 2).[5] First, AIBN cleaves the arsenic−arsenic bond of **1** to produce arsenic radicals (eq 1). The homolytic cleavage of the other arsenic−arsenic bonds proceeds spontaneously due to their instability by the destruction of the quite stable ring structure (eq 2). In competition with this reaction, the arsenic radical attacks the ethynyl group of the acetylenic compound to produce a vinyl radical (eq 3). Then, the vinyl radical reacts with the arsenic radical to produce a vinylene−arsine structure (eq 4).

In RCRAC system, conjugated stabilization of the vinyl radical and electrostatic effect of the substituent on the acetylenic compound affect the addition rate of the arsenic radical to the acetylenic monomers.[6] The substituent effects promote or inhibit RCRAC, since the addition step of the pnictogen radical to the ethynyl group (eq 3) is the rate determinating step. We have also shown that RCRAC of a cyclooligostibine (**2**) and acetylenic compounds produced an organoantimony polymer, poly-

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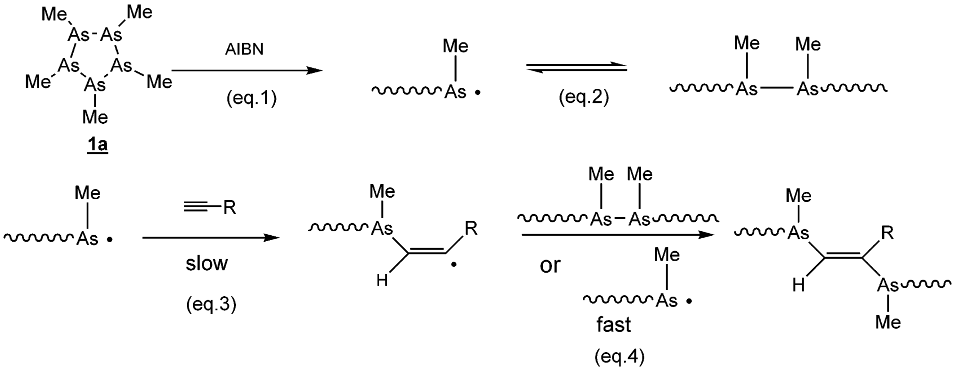
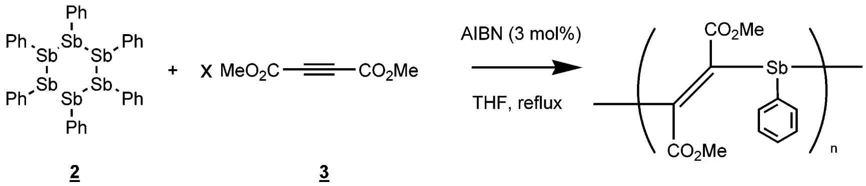
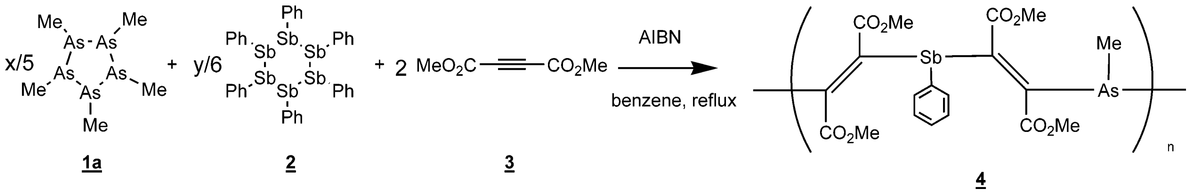
Scheme 2



Scheme 3



Scheme 4



(vinylene−stibine) (Scheme 3).[7] In that report, we found that the antimony radical was less reactive toward the ethynyl group, and was more reactive toward the vinyl radical than the arsenic radical. These findings motivated us to conduct the terpolymerization utilizing two kinds of pnictogen radicals for further consideration about RCRAC.

In this paper, we describe the terpolymerization of an acetylenic compound, a cyclooligoarsine and a cyclooligostibine. Different reactivity between the arsenic radical and the antimony radical made it possible to form poly(vinylene−arsine−vinylene−stibine) (Scheme 4). This terpolymerization will open a new area for construction of a controlled backbone structure in an easy way.

Results and Discussion

No polymer was obtained in RCRAC of pentamethylcyclopentaarsine (**1a**) with dimethyl acetylenedicarboxylate (**3**) after the reaction mixture was poured into *n*-hexane. According to a ^{1}H NMR analysis of the crude product from the filtrate, the starting materials were consumed to form oligomeric products. On the other hand, the corresponding poly(vinylene−stibine) was obtained in the case of hexaphenylcyclohexastibine (**2**) with **3**.[7] In the previous work, we have reported that acetylenic compounds were consumed faster in RCRAC since electron-withdrawing substitution and conjugative effect for the vinyl radical caused the rate-determining step faster.[6] These results support the higher reactivity of the antimony radical than that of the arsenic radical toward the vinyl radical.

Next, we performed the terpolymerization of **1a**, **2**, and **3**. A benzene solution of a catalytic amount of AIBN was added to a refluxing solution of these monomers. After stirring the reaction mixture for 15 h, the solution was poured into diethyl ether to yield polymer **4** of which the number-average molecular weight was 4800 with the yield of 15%. The lower yield is due to the removal of low molecular weight products during reprecipitation.

The ^{1}H NMR spectrum of the obtained polymer shows three peaks which correspond to the aromatic protons of the stibine unit, the methyl protons of the methoxycarbonyl unit, and the methyl protons of the arsine unit, respectively (Figure 1). Although no copolymerization of **1a** and **3** proceeded as described above, the terpolymer appeared to have the arsine unit in the main chain. From the integral ratio of the three peaks, we know that the terpolymer has 1:1:2 structure of the arsine, stibine and vinylene units. The peak attributed to the methoxycarbonyl group adjacent to the stibine unit (h1) should appear at 3.5−2.5 ppm due to the ring current effect of the benzene ring on the antimony atom.[7] The proton signal of the methoxycarbonyl group adjacent to the arsine unit (h2) should appear at around 4.0−3.5 ppm. The integral ratio of the peak area (h1 /h2) also supports the stibine unit and the arsine unit having 1 is to 1 ratio in the terpolymer. Therefore, the structure of the obtained polymer was predominantly proven to be a vinylene−arsine−vinylene−stibine unit in the backbone. A small peak appeared at around 3.1 ppm (h3) might be assignable to the methoxycarbonyl group in an alternating poly(vinylene−stibine) portion.

The ^{13}C NMR spectrum of **4** shows three peaks located around 170 ppm attributed to the carbonyl groups (Figure 2). Each of them is attributed to the methoxycarbonyl group adjacent to the stibine (e1) and the arsine (e2) units in the periodic terpolymer moiety, and to the methoxycarbonyl group adjacent to the stibine unit in the alternating poly(vinylene−stibine) portion (e3),[7] respectively. In this spectrum, the peaks of e1 and e2 clearly appeared and the peak of the methyl carbon of the arsenic unit, i, showed one sharp peak at around 10 ppm.

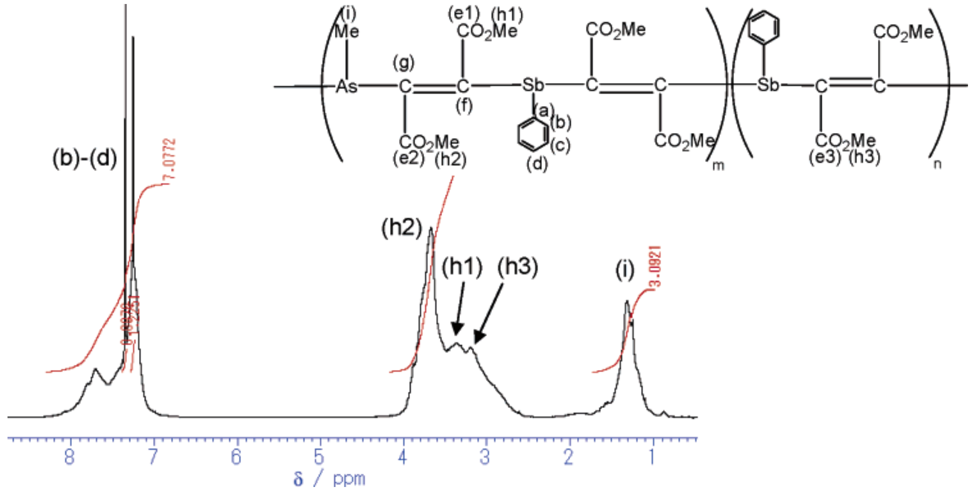


Figure 1. ^{1}H NMR spectrum of polymer **4** in CDCl$_3$.

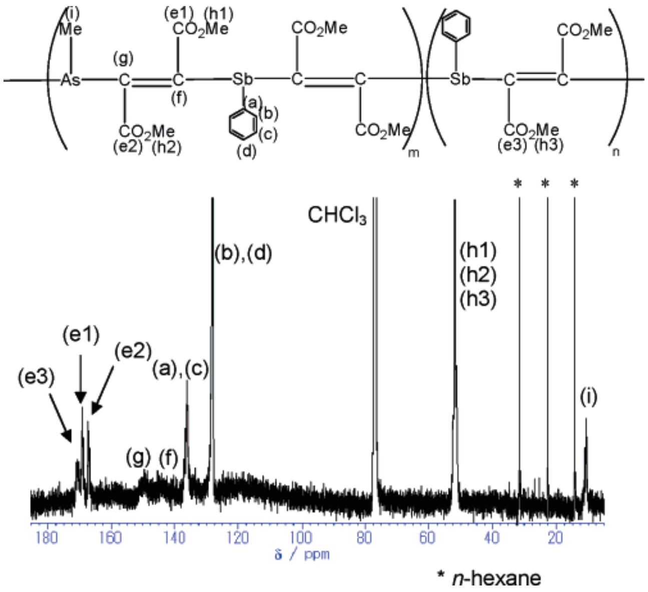


Figure 2. ^{13}C NMR spectrum of **4** in CDCl$_3$.

From the ^{1}H– and ^{13}C NMR spectra, it is fair to say that **4** has the periodic unit of the vinylene–arsine–vinylene–stibine with few alternating vinylene–stibine units.

When **2** was treated with a catalytic amount of AIBN in a refluxing benzene, a heterogeneous orange mixture became a dark brown dispersion within several minutes. The resulting dark brown solid is a polymerized form of the cyclooligostibine suggesting that the cleavage of the antimony–antimony bonds of **2** was promoted by AIBN.[8] The radical reaction of **1a**, **2**, and phenylacetylene gave no polymer after the reaction mixture was poured into *n*-hexane. This may be due to a lower reactivity of the vinyl radical toward the antimony–antimony bond or the antimony radical. This result suggests that the acetylenic compounds with the sufficient electron withdrawing group are preferred in the terpolymerization. The radical reaction of hexaphenylcyclohexaarsine (**1b**), **2**, and **3** also provided a corresponding terpolymer of which number-average molecular weight was 2700. The lower solubility and the lower reactivity of the phenyl substituted arsenic radical might decrease the molecular weight.[5]

We examined the terpolymerization of **1a**, **2**, and **3** in a different feed ratio of the monomers. From the integral ratios of the ^{1}H NMR spectra of the obtained polymers, the composition of the polymer chains was estimated. The results are summarized in Table 1. An excess amount of the cyclooligoarsine hardly affected the structure of the terpolymer (run 3), because excess arsenic radicals hardly reacted with the vinyl radical. On the other hand, an excess amount of the cyclooligostibine resulted in a higher molecular weight terpolymer with a lower ratio of the arsine units against the stibine units (run 1).

The ^{13}C NMR spectra of the terpolymers of all the runs in Table 1 are shown in Figure 3. In the carbonyl region at around 170 ppm, the spectra shows the peaks attributed to the carbonyl groups, e1, e2, and e3. In the case of the 1:2 feed ratio of the arsenic units and the antimony units (run 1a), the peak of the carbonyl groups in the vinylene–stibine alternating part (e3) strongly appears, as well as the clear peaks of the carbonyl groups of e1 and e2. This is because the antimony radical can react with both the vinyl radical and the ethynyl group to proceed the polymerization even after the arsenic radicals were consumed. In the case of the excess cyclooligoarsine (run 3c), the peak of e3 was hardly observed, which suggests that the formation of the terpolymer with a highly periodic backbone structure was obtained in run 3.

To proceed RCRAC, the pnictogen radicals should react with both the ethynyl group and the vinyl radical. Scheme 5 shows the mechanism of the terpolymer. As described in the introduction, the antimony radicals are less reactive to the ethynyl groups than the arsenic radicals. The antimony radicals are more reactive toward the vinyl radicals than the arsenic radicals. There are some similar reports about the reactivity of group 16 elements. Sulfur radicals attack unsaturated bonds faster than seleno radicals[9] and diselenides react with carbon radicals faster than disulfides.[10] According to Scheme 5, even in the presence of the antimony radicals, the arsenic radical preferentially adds to the ethynyl group. The resulting vinyl radical preferred to react with the antimony radical. Therefore, the terpolymerization of **1a**, **2**, and **3** provided the terpolymer with the high periodic structure of the vinylene–arsine–vinylene–stibine unit. In the case of **2** rich condition, the reaction continued with the formation of the vinylene–stibine unit since the antimony radical also reacted with **3** after the arsenic radicals were consumed.

Summary

Radical reaction of cyclooligoarsine, cyclooligostibine, and dimethyl acetylenedicarboxylate provided terpolymer containing both the antimony atom and the arsenic atom in the backbone. In this reaction, the vinyl radical reacted with the antimony radical. While the ethynyl group reacted with the arsenic radical

Table 1. Results of Polymerization in Different Feed Ratios

run	[As−Me]:[Sb−Ph]:[**3**][a]	[As−Me]/[Sb−Ph][b]	yield (%)[c]	M_n[d]	M_w[d]	obsd [As−Me]/[Sb−Ph][e]
1	1:2:2	0.50	19	6400	8900	0.62
2	1:1:2	1.00	15	4800	7000	1.06
3	2:1:2	2.00	15	3300	5000	1.10

[a] [**3**] is constant in all runs. [b] As−Me and Sb−Ph represent methyl arsine (MeAs) and phenyl stibine (PhSb) units, respectively. [c] Isolated yields after reprecipitation into diethyl ether. [d] Estimated by GPC analysis in DMF on the basis of polystyrene standards. [e] Calculated from the integral ratio of the peaks in ^{1}H NMR spectrum.

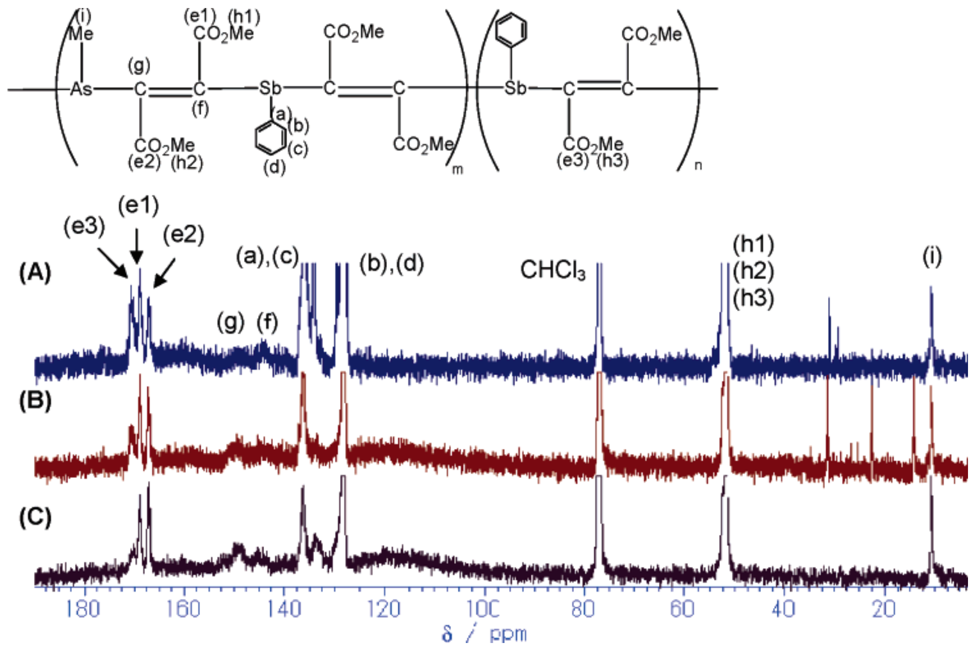
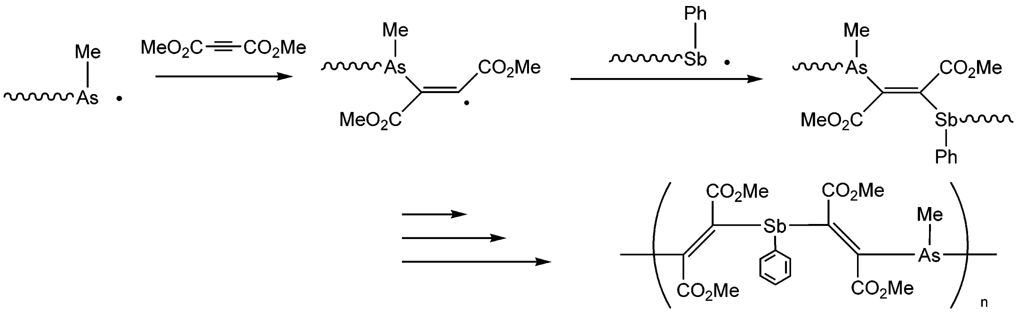


Figure 3. ^{13}C NMR spectra of polymer **4** in $CDCl_3$. Feed ratios of [As−Me]/[Sb−Ph] = 0.5 (A, run 1), 1.0 (B, run 2), and 2.0 (C, run 3).

Scheme 5



faster than the antimony radical. Utilizing different reactivity of the pnictogen radicals, we were able to obtain the polymer in which the backbone consists of the periodic vinylene−arsine unit and vinylene−stibine unit. This is the first example to provide A−B−A−C type polymer by a simple radical reaction to open a new area employing novel method to make polymers with periodic backbones.

Experimental Section

Materials. Dehydrated benzene (water <30 ppm, Wako Pure Chemical Industries, Ltd.) was bubbled with a stream of nitrogen before use. Dehydrated *n*-hexane was used without further purification. 2, 2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. Diethyl ether was dried over Na and distilled before use. Dimethyl acetylenedicarboxylate (**2**) was distilled before use. Hexaphenylcyclohexaarsine (**1b**),[11] and pentamethylcyclopentaarsine (**1a**)[12] were synthesized using literature procedures.

Hexaphenylcyclohexastibine (2).[13] **2** was synthesized using a literature procedure.[14] A solution of 1.0 g (5.29 mmol) of cobaltcene in 50 mL of THF was added dropwise in the dark to the solution of 2.14 g (7.93 mmol) of dichlorophenylstibine in 50 mL of THF. Stirring the mixture for 0.5 h resulted in the formation of a red solution and a yellow solid. The solution was separated by decantation and cooled to −50 °C After several days, 0.18 g of **2** was formed as an orange solid (yield 17.7%). Calcd for $C_{36}H_{30}Sb_6$: C, 36.2; H, 2.5. Anal. Found: C, 36.0; H, 2.5.

Equipments. ^{1}H and ^{13}C NMR spectra were obtained using a JEOL JNM-EX270 instrument (270 and 67.5 MHz, respectively) for solutions in $CDCl_3$ and were referenced to $SiMe_4$ (TMS). Gel permeation chlomatography (GPC) analysis was carried out on a Tosoh 8020 instrument with an *N*,*N*-dimethylformamide solution containing 10 mM LiBr as an eluent at 40 °C after calibration with standard polystyrene samples.

Terpolymerization of 1a, 2, and 3. A typical experimental procedure (run 2) is as follows. Under an argon atmosphere, a benzene solution of AIBN (0.0025 g, 0.0015 mmol) was added to a refluxing benzene solution (2 mL) of **1a** (0.054 g, 0.054 mmol), **2** (0.054 g, 0.045 mmol), and **3** (0.077 g, 0.54 mmol). After being stirred for 15 h, the reaction mixture was filtered and poured into diethyl ether to precipitate the product, which was purified three times by reprecipitation from benzene to diethyl ether. After freezedrying, the corresponding product was obtained as a yellow powder.

4 (in Run 2 of Table 1). ^{1}H NMR (δ in $CDCl_3$, ppm): 8.0−6.7 (Ar-*H*), 4.0−3.5 (As−C−$CO_2C\mathit{H}_3$) 3.5−2.0 (Sb−C−$CO_2C\mathit{H}_3$), 1.5−0.9 (As−CH_3). ^{13}C NMR (δ in $CDCl_3$, ppm): 171−169 ($\mathit{C}O_2$-CH_3 in the sequential vinylene−stibine unit), 169−168 (Sb−C-$\mathit{C}O_2CH_3$), 167−166 (As−C-$\mathit{C}O_2CH_3$) 155−148 (As−*C*═C), 148−143 (As−C═*C*), 137−132 (C_{Ar}−Sb, *m*-C_{Ar}−Sb), 130−127 (*o*,*p*-C_{Ar}−Sb) 145−142 (C_{Ar}−Sb), 137−132 (*m*-C_{Ar}−Sb), 130−127 (*o*,*p*-C_{Ar}−Sb), 53−50 ($CO_2\mathit{C}H_3$), 12−9 (As−$\mathit{C}H_3$). Calcd for $C_{19}H_{20}O_8AsSb$: C, 39.8; H, 3.5. Anal. Found: C, 39.6; H, 3.8.

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