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Accounts

A New Aspect of Organobismuth Chemistry: Synthesis, Properties, and Reactions of Bismuthonium Compounds

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This article is intended to describe recent progress in the chemistry of bismuthonium compounds, represented by onium salts, ylides, and imides, that have long been left untouched within the frame of heteroatom chemistry mainly because of limited access. However, the recent development of methodologies for the preparation of bismuthonium compounds has enabled us to unveil their properties as well as their chemistry. The article is comprised of three sections that mainly deal with: *bismuthonium salts* synthesized from triphenylbismuth difluoride and organo-silanes or -stannanes; stabilized and moderately stabilized *bismuthonium ylides* synthesized from triphenylbismuth(V) compounds and bismuthonium salts; and *bismuthane imides* prepared by oxidative imination of bismuthanes and by reaction between triphenylbismuth(V) dihalides and sulfonamides. Synthesis, X-ray structures, and typical reaction modes of these bismuthonium compounds are delineated in the order in which they appear.

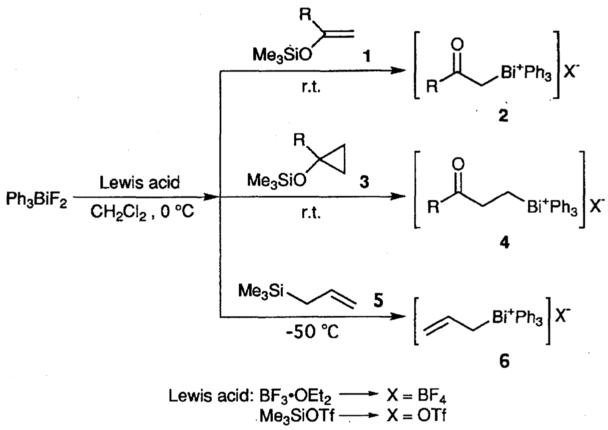
While the term onium compound is often used to mean *onium salt* in a narrow sense, it also covers in a wider sense *ylides* and *imides* that have a polarized formal double bond between a heteroatom and a carbon or nitrogen atom. Since the birth of the ylide chemistry in the middle of this century, enormous efforts have been devoted to the development of the chemistry of onium compounds that can be derived from typical elements, which include phosphorus, arsenic, antimony, sulfur, selenium, tellurium, bromine, and iodine. However, the chemistry of bismuthonium compounds is an exception; it has long been neglected within the frame of brilliant heteroatom chemistry mainly because of limited access to this type of compounds. Since bismuth possesses the largest orbital radius and the lowest electronegativity among these heteroatom elements, it forms relatively weak and polarized covalent bonds, as well as three-centered four electron hypervalent bonds with the first-row elements such as carbon, nitrogen or oxygen. This characteristic of bismuth as an element has often been manifested in molecular structures and chemical behaviors of bismuthonium compounds, which have been extensively investigated during the last decade in parallel with the development of methodologies for the preparation of this class of compounds.

In this paper, we overview recent progress of the chemistry of bismuthonium compounds, i.e., synthesis, properties and reactions of bismuthonium salts, bismuthonium ylides, and bismuthane imides. This article provides the only systematic source of information of its kind available at present.[1)]

Bismuthonium Salts

(1) Synthesis. Although several tetraphenylbismuthonium salts have been known for some years,[2)] only a few examples of alkylbismuthonium salts have been reported.[3)] There are two methodologies conceivable for the preparation of the latter class of bismuthonium compounds; one is the electrophilic alkylation of tertiary bismuthanes and the other is the nucleophilic alkylation of organobismuth(V) compounds. However, tertiary bismuthanes are generally so weak a nucleophile, due to the strong *s*-character of the unshared electrons, that the first methodology seems to be inadequate to construct the bismuthonium salts. In fact, most alkyl ligands to be introduced by using this methodology are limited to specific cases.[3a,3c)] On the other hand, the second methodology based on the use of triarylbismuth dihalides seems to be versatile enough to construct the bismuthonium salts, because the electrophilic bismuth center of this type of hypervalent compounds can undergo coupling with a wide range of *C*-nucleophiles under mild conditions to form the bismuth–carbon bond. Based on this reasoning, we have recently developed a novel convenient methodology for the preparation of alkyl-, alkenyl-, and aryl-triphenylbismuthonium salts.[4—8)]

Triphenylbismuth difluoride reacts smoothly with silyl enol ethers **1** in the presence of a Lewis acid such as $BF_3 \cdot OEt_2$ or Me_3SiOTf in CH_2Cl_2 to afford (2-oxoalkyl)triphenylbismuthonium salts **2** in good yield.[4)] Since volatile fluorotrimethylsilane is the sole by-product, the isolation of the final product is straightforward. In this reaction, a given Lewis acid plays a dual important role; it initially enhances the electrophilicity of the bismuth center through the coordinative interaction with the fluorine atom of triphenylbismuth difluoride and subsequently is transformed into a less nucleophilic counter anion to stabilize the resulting bismuthonium salt. In the absence of the Lewis acid, the starting materials are recovered unchanged. This methodology is quite efficient and general enough to be applicable to the preparation of other functionalized alkylbismuthonium salts. When siloxycyclopropanes **3** are used in place of silyl enolates, (3-oxoalkyl)triphenylbismuthonium salts **4** are obtained (Scheme 1).[5] The isolated yields of triflates **4** (X = OTf) are low to moderate, owing to their thermal instability in solution. Reaction of triphenylbismuth difluoride with allyltrimethylsilane **5** in the presence of $BF_3 \cdot OEt_2$ at low temperatures leads to the formation of allyltriphenylbismuthonium salt **6** as a reactive intermediate.[6]



Scheme 1.

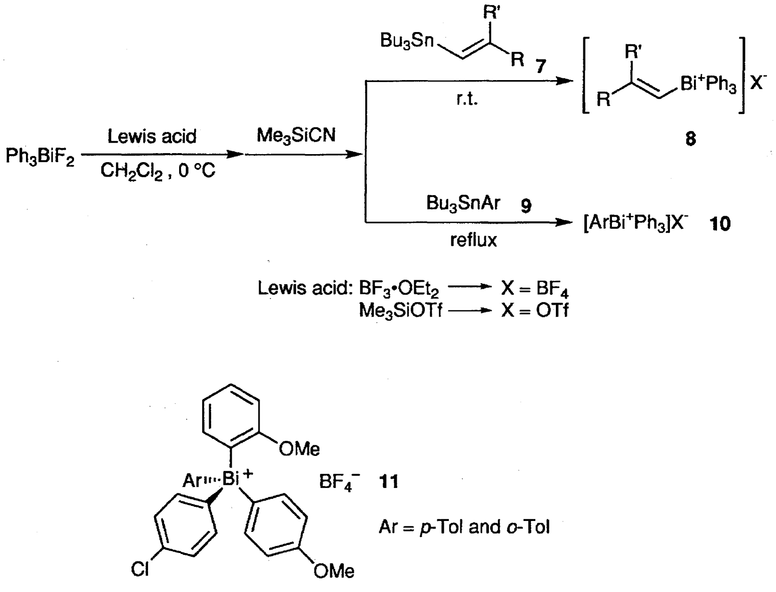
The use of alkenylstannanes **7** gives good results in the preparation of alkenylbismuthonium salts.[7] As shown in Scheme 2, successive treatment of triphenylbismuth difluoride with $BF_3 \cdot OEt_2$, cyanotrimethylsilane and the stannanes **7** gives the corresponding (1-alkenyl)triphenylbismuthonium salts **8** in good yield. In this reaction, the presence of the cyanosilane is essential to obtain the desired onium salts in a high state of purity.[9] This methodology has been successfully extended to the preparation of unsymmetrical aryltriphenylbismuthonium salts **10** by using arylstannanes **9** as an arylating agent (Scheme 2).[8] This has also enabled us to synthesize the first chiral bismuthonium salts **11** having four different aryl groups on the bismuth center.

An efficient synthesis of alkylbismuthonium salt from trialkylbismuthane has recently been reported by Wallenhauer and Seppelt.[10] They synthesized tetramethylbismuthonium triflate **12** by the reaction of trimethylbismuthane with methyl triflate in boiling acetonitrile (Scheme 3). In general, trialkyl compounds of 15 group elements show higher nucleophilicity than do the corresponding triaryl compounds. So this method is convenient for the synthesis of tetraalkylbismuthonium salts, in spite of the disadvantage that tertiary alkylbismuthanes tend to ignite in air.

(2) Properties. The stability of bismuthonium salts depends on both the counter anion and the ligand. In general, less nucleophilic counter anions form more stable bismuthonium salts. This has long been known for tetraphenylbismuthonium salts and now is found to hold true for alkylbismuthonium salts, too. Thus 2-oxoalkylbismuthonium tetrafluoroborates **2** ($X = BF_4$) are stable crystalline solids, but attempts to convert them into the corresponding bro-

$$\mathrm{Me_3Bi + MeOTf \xrightarrow[CH_3CN,\ reflux]{} \underset{\textbf{12}}{Me_4Bi^+\,OTf^-}}$$

Scheme 3.



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Scheme 2.

mides by metathetical reaction result in the quantitative formation of α-bromo ketones and bismuthane.[4] Both oxoalkylbismuthonium triflates **2** and **4** (X = OTf) are stable in crystalline form, but they slowly undergo reductive coupling in a chloroform solution to give the respective α- and β-substituted carbonyl compounds.[5] These decomposition reactions obey a pseudo-first-order kinetics, with $k = 3\times10^{-7}$ s^{-1} for salt **2** (R = OPr^i, X = OTf) and $k = 8\times10^{-6}$ s^{-1} for salt **4** (R = OPr^i, X = OTf). Salt **4** decomposes more rapidly than salt **2**, probably because the former salt has a less sterically hindered carbon atom adjacent to the bismuth center. Allylbismuthonium salts **6** are too unstable to be isolated under ambient conditions.[6]

The bismuthonium salts described here exhibit diagnostic spectral features. FAB mass spectra display a strong peak due to the M^+–X fragment in accord with the cationic nature of the quaternary bismuth center. IR spectra show strong absorptions characteristic of the counter ions; broad intense bands appear around 1150—950 cm^{-1} for tetrafluoroborates and around 1320—1100 cm^{-1} for triflates. Carbonyl stretching frequencies of salts **2** and **4** are observed at 1670—1695 cm^{-1} (for R = alkyl and aryl) and 1720—1725 cm^{-1} (for R = isopropoxy), most of which appear at slightly lower frequencies ($\Delta\nu$ = 10—25 cm^{-1}) as compared with those of parent ketones and esters. ^{1}H NMR spectra of alkylbismuthonium salts show a signal of the methylene protons adjacent to the bismuth atom in the range δ_H = 5.2—6.0 for **2**, δ_H = 3.7—4.5 for **4**, and δ_H = 4.8—4.9 for **6**. ^{13}C NMR signals of this methylene carbon are observed in the range δ_C = 54—59 for **2** and δ_C = 40—44 for **4**, respectively. The appearance of these signals at a relatively low field is in accord with the electron-withdrawing nature of the bismuthonium moiety. A diagnostic feature of the ^{13}C NMR spectra of 1-alkenylbismuthonium salts **8** is the resonance due to the olefinic carbon atoms, which appear at δ_C = 118—126 for the α-carbon and δ_C = 151—160 for the β-carbon. The low-field appearance of the β-carbon resonance shows that part of the positive charge on the bismuth atom is delocalized through the π-orbital of the carbon–carbon double bond.

X-Ray structure analyses of several bismuthonium salts have already been reported in the literature. They include tetramethylbismuthonium triflate,[10] tetraphenylbismuthonium perchlorate,[11] tosylate,[2g] and diphenylbis(trifluoroacetato)bismuthate,[2g] (3,3-dimethyl-2-oxobutyl)triphenylbismuthonium tetrafluoroborate[4] and triflate,[4] (2-isopropoxycarbonylethyl)triphenylbismuthonium triflate,[5] and (2-methyl-1-propenyl)triphenylbismuthonium tetrafluoroborate.[7] When the counter anion is so poor a nucleophile as the triflate, perchlorate or tetrafluoroborate, the central bismuth atom has a distorted tetrahedral geometry in accord with the onium nature of these compounds. Figure 1 illustrates the molecular structure of 2-oxoalkylbismuthonium salt **2** (R = Bu^t, X = OTf),[4] where the carbonyl oxygen atom is coordinated weakly toward the cationic bismuth atom (Bi–O distance is 2.93 Å). This type of coordinative interaction is also observed in the crystal structure of 3-oxoalkylbismuthonium triflate **4** (R = OPr^i, X = OTf), although it is apparently weaker than that of **2** (Fig. 2; Bi–O distance is 3.157 Å).[5] On the other hand, the bismuth center of tetraphenylbismuthonium tosylate has a distorted trigonal bipyramidal geometry with three phenyl groups at equatorial positions and one phenyl group and tosylate anion at apical positions, suggesting the hypervalent nature of the central bismuth atom.[2g] The origin of such different geometry among the above bismuthonium salts may well be attributed to the difference in nucleophilicity of the counter anions involved. The less nucleophilic triflate anion prefers a tetrahedral geometry, while the moderately nucleophilic tosylate anion prefers a trigonal bipyramidal geometry around the bismuth center.

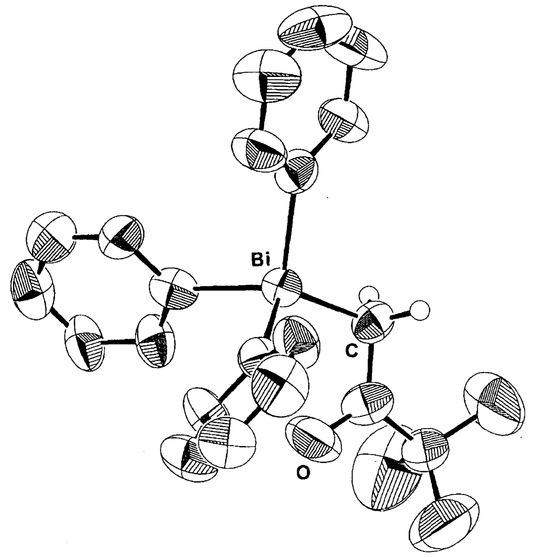


Fig. 1. ORTEP diagram for **2** (R = Bu^t, X = OTf). Triflate anion is omitted for clarity.

(3) Reactions. Tetraphenylbismuthonium compounds

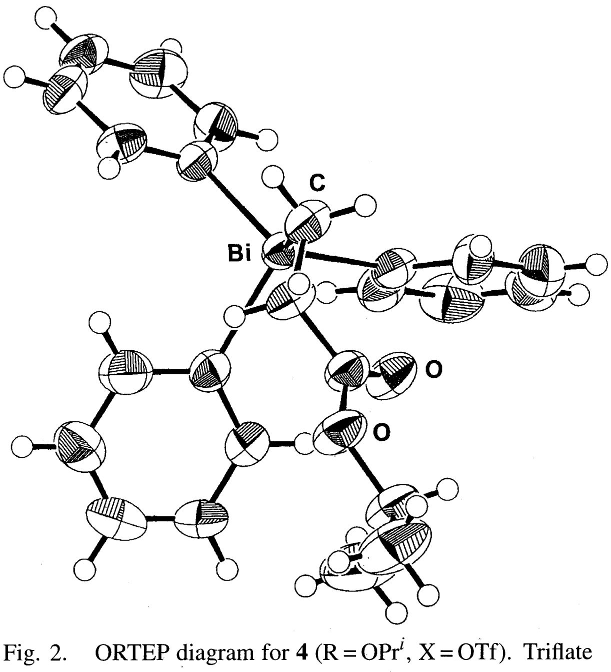
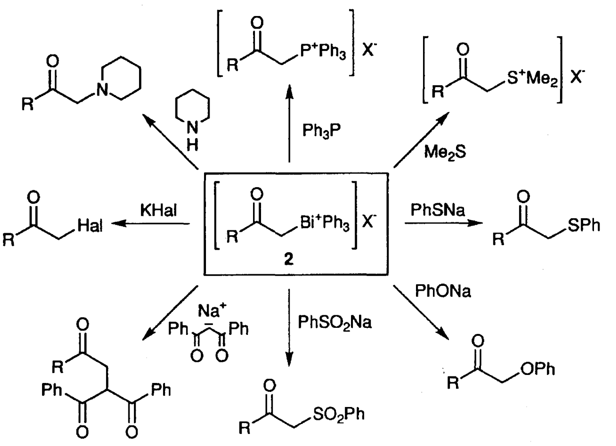


Fig. 2. ORTEP diagram for **4** (R = OPr^i, X = OTf). Triflate anion is omitted for clarity.

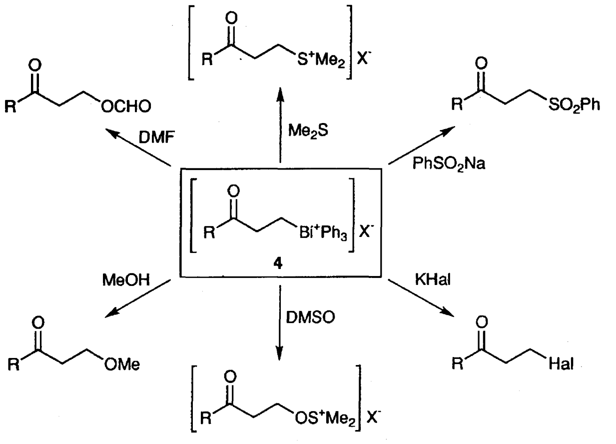
have been extensively used as the phenylating reagent for a wide variety of substrates, such as alcohols, enols, amines, phenols, indoles, thiols, sulfinates, nitro alkanes, and others.1d,12) The selectivity between *O*- and *C*-arylation of enolizable carbonyl compounds and phenols is highly dependent on the reaction conditions. They are also employed as the oxidizing agent for alcohols under basic conditions.1d,12)

(2-Oxoalkyl)triphenylbismuthonium salts **2** smoothly react with a variety of nucleophiles, such as piperidine, triphenylphosphane, dimethyl sulfide, sodium sulfinates, sodium thiolates, sodium phenoxides, sodium enolates, and potassium halides, to give the corresponding α-substituted carbonyl compounds in moderate to quantitative yields (Scheme 4).4) (3-Oxoalkyl)triphenylbismuthonium salts **4** also react with some of these nucleophiles, as well as some protic or aprotic solvents such as MeOH, DMSO and DMF, to afford the corresponding β-substituted carbonyl compounds.5) In the latter case, however, the β-elimination leading to α,β-unsaturated carbonyl compounds becomes prominent (Scheme 5). In both reactions, triphenylbismuthane is recovered quantitatively.

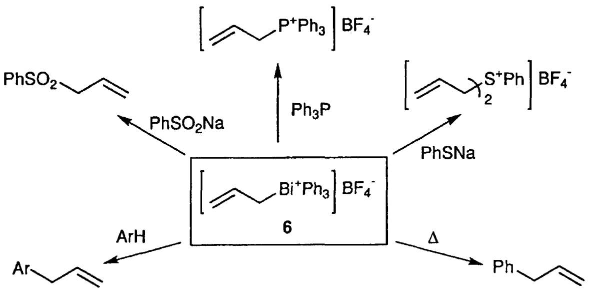
Allyltriphenylbismuthonium salt **6** generated in situ readily decomposes to form allylbenzene. In the presence of electron-rich arenes, it transfers the allyl moiety to the arenes.6) Some *S*-nucleophiles are allylated in good yield (Scheme 6).



Scheme 4.



Scheme 5.

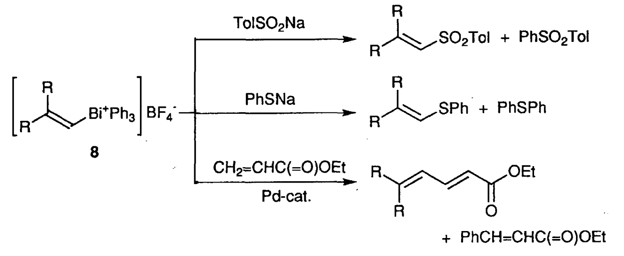


Scheme 6.

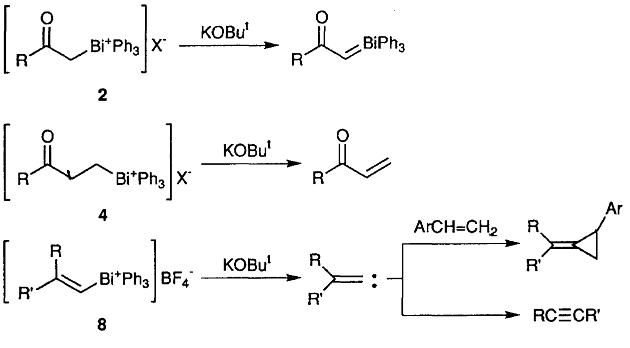
All alkyltriphenylbismuthonium salts described above can behave as an alkyl cation equivalent in the reaction with nucleophiles. A similar reactivity is not observed for the common alkylphosphonium salts. The enhanced reactivity of bismuthonium salts should arise largely from the good ability of triphenylbismuthonio group to leave as triphenylbismuthane.

The reactivity of (1-alkenyl)triphenylbismuthonium salts **8** towards nucleophiles is somewhat lower as compared with those of alkylbismuthonium salts (Scheme 7). They do not react with triphenylphosphane and dimethyl sulfide, but do react with sulfinate and thiolate anions to give the corresponding sulfones and sulfides, respectively.7) In these reactions, both the alkenyl and phenyl groups can be transferred, although the alkenyl-transfer is the more preferred reaction mode. When treated with ethyl acrylate in the presence of a palladium catalyst, (1-alkenyl)triphenylbismuthonium salt **8** effects the Heck-type vinylation and arylation competitively.

Bismuthonium salts **2**, **4**, and **8** react with a base in a characteristic manner depending on the structure of ligand molecules (Scheme 8). Thus, treatment of (2-oxoalkyl)triphenylbismuthonium salts **2** with a base in THF at low temperatures gives the triphenylbismuthonium 2-oxoalkyl-



Scheme 7.



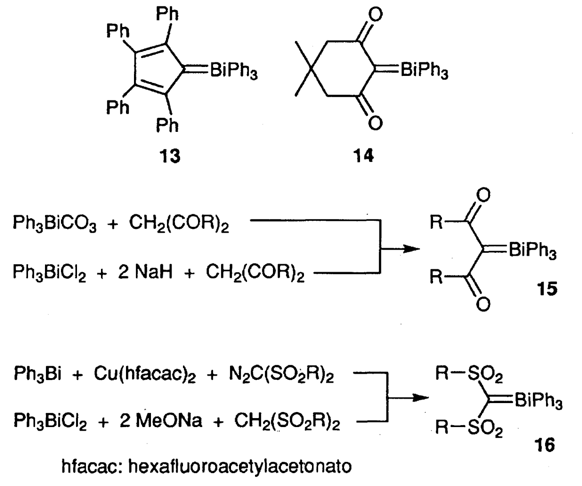
Scheme 8.

ides,[13] while a similar treatment of (3-oxoalkyl)triphenylbismuthonium salts **4** affords the α,β-unsaturated carbonyl compounds resulting from β-elimination.[5] Reaction of (1-alkenyl)triphenylbismuthonium salts **8** with a base generates 1-alken-1-ylidenes, which can be trapped efficiently by styrene derivatives to give the corresponding cyclopropanes on one hand, or undergo isomerization to form acetylenes quantitatively on the other.[7] Judging from a Hammett study of the cyclopropanation, the in situ generated reactive species is most likely to be a free 1-alken-1-ylidene. In these reactions, the high leaving ability of triphenylbismuthonio group would probably be the key factor to determine the reaction mode.

Bismuthonium Ylide

(1) Synthesis. The chemistry of bismuthonium ylides has received little attention until the late eighties. In 1967, Lloyd and Singer claimed the first synthesis of bismuthonium ylide **13** as a deep blue substance by heating a mixture of triphenylbismuthane and diazotetraphenylcyclopentadiene (Scheme 9).[14] The product obtained was, however, not well characterized. In 1986, Barton et al. were successful in obtaining a stable bismuthonium ylide **14** as a gummy substance from the reaction of triphenylbismuth carbonate and 5,5-dimethylcyclohexane-1,3-dione (dimedone).[15] Suzuki et al. isolated this ylide **14** as a crystalline solid and elucidated its structure by X-ray analysis.[16] They also synthesized several stabilized bismuthonium ylides **15** from triphenylbismuth dichloride and 1,3-dicarbonyl compounds and examined their chemistry.[17] Recently, Naumann et al. employed a similar methodology to obtain the stabilized ylides **16** having an acyclic α,α'-bis(perfluoroalkylsulfonyl) skeleton.[18] This type of ylides **16** had previously been synthesized by Lloyd et al. by the Cu(II)-catalyzed decomposition of disulfonyldiazomethane in the presence of triphenylbismuthane.[19] Interestingly, a weak nucleophile such as triphenylbismuthane can be efficiently trapped by a carbenoid species in the last case.

Deprotonation of onium salts by a suitable base is the best method for the in situ generation of moderately stabilized and non-stabilized ylides. Treatment of (2-oxoalkyl)triphenylbismuthonium salts **2** with a base at low temperatures generates the corresponding triphenylbismuthonium 2-oxoalkylides **17** as a thermally unstable and air-sensitive species,[13] which can be observed by ^{1}H and ^{13}C NMR at low temperatures (Scheme 10).



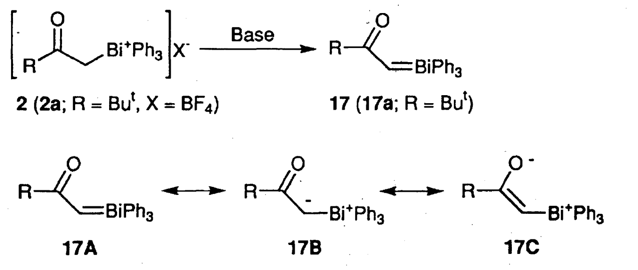
hfacac: hexafluoroacetylacetonato

Scheme 9.

(2) Properties. All reported bismuthonium ylides having a cyclic α,α'-dicarbonyl skeleton such as **14** are stable solids and can be handled in air without decomposition. However, the ylides having an acyclic α,α'-dicarbonyl or α,α'-disulfonyl skeleton tend to decompose when left in air or during chromatographic treatment, although they are all thermally stable. Different moisture-sensitivity of these stabilized bismuthonium ylides may in part be attributed to the difference in molecular rigidity around the carbonyl and sulfonyl functions attached to the alkylidene moiety.

The ylides with one carbonyl group at α-position are generally regarded as stabilized ylides because the negative charge on the ylidic carbon is spread over the carbonyl function through resonance, but bismuthonium 2-oxoalkylides **17** are highly reactive and readily decompose under ambient conditions. Therefore, the ylide **17** is better classified as a moderately stabilized ylide in spite of the presence of an oxo group at α-position.

The most characteristic spectral feature of the bismuthonium ylides is shown in their NMR spectra. The ylidic carbon of the stabilized ylides **14** and **15** appears in the range $\delta_C = 100$—113.[16,17] The moderately stabilized bismuthonium ylide **17a** ($R = Bu^t$) shows signals due to the α-proton, ylidic and carbonyl carbons at $\delta_H = 5.84$, $\delta_C = 86.4$ and 187.9, respectively.[13] The appearance of the ylidic carbon at lower field as compared to the corresponding α-carbon ($\delta_C = 59.6$) of the parent onium salt **2a** ($R = Bu^t$, $X = BF_4$) is in accord with the change in orbital hybridization mode of the carbon atom from sp^3 to sp^2. A large value for the C–H coupling constant of the ylide **17a** ($J = 186$ Hz) as compared with the salt **2a** ($J = 147$ Hz) is also a reflection of the increased *s* character of the ylidic C–H bond. Furthermore, the ^{13}C signal of the carbonyl carbon of the ylide **17a** is observed at higher field $\delta_C = 187.9$ than that of the parent onium salt **2a** $\delta_C = 213.2$. This is an indication of a relatively large electron density localized on the relevant carbon atom. Judging from these spectral features, the ylide **17** may well be represented as a hybrid of the canonical forms **17A**, **17B**, and **17C**, in which the roles of the latter two would be more important.



Scheme 10.

Figure 3 shows the simplified molecular structure of the bismuthonium ylide **14**, which is the only example structurally characterized by X-ray diffraction analysis.[20] The bismuth center has a distorted tetrahedral geometry with the Bi–C_{Ph} bond lengths [2.21(1)—2.22(1) Å] and the C–Bi–C bond angles [101.6(4)—119.6(4)°]. The Bi–C_{ylide} bond [2.156(11) Å] is slightly shortened as compared with the Bi–C_{Ph} single bond, suggesting that the former bonding is polar and that there is little double bond character between the bismuth and ylidic carbon atoms. This interpretation is also supported by an observation that the bismuth atom is weakly coordinated by one of the carbonyl oxygen atoms.

(3) Reactions. The low electronegativity and the large 6p orbital of the bismuth give rise to the unique reactivity of the bismuthonium ylides, which would not be expected from simple analogy with the behavior of analogous ylides of other 15 group elements.

Suzuki et al. have examined the reaction of the stabilized bismuthonium ylide **14** and congeners **15** with a variety of substrates (Scheme 11). In boiling CH_2Cl_2 or benzene, the ylide **14** reacts with aromatic aldehydes to afford several coupling products.[21] The initial stage of this reaction is the Wittig-type olefination and the resulting α,β-unsaturated diketones undergoes the Corey-type cyclopropanation with another ylide molecule to yield tetraacylcyclopropane and its descendants. Reaction of the ylide **14** with a sulfene, generated in situ from methanesulfonyl chloride and triethylamine, gives rise to five-membered heterocyclic compounds.[17] In the presence of a copper salt as catalyst, the ylide **14** undergoes a coupling reaction with phenyl isothiocyanate,[16] triphenylphosphane,[22] triphenylarsane,[22] and terminal acetylenes[23] to give 1,3-oxathiole, phosphonium ylide, arsonium ylide, and furan derivatives, respectively. In the last reaction, the copper(I) salt is assumed to catalyze the generation of a triplet carbene as an intermediate.

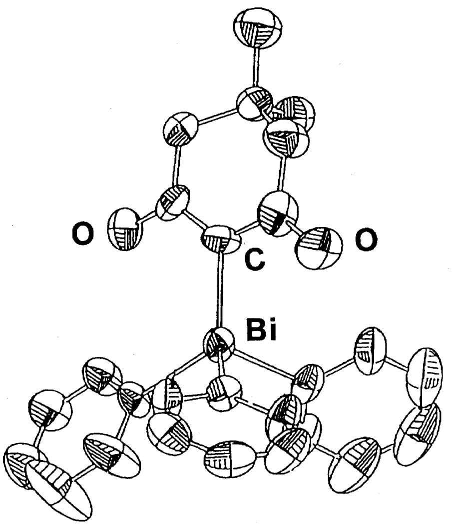
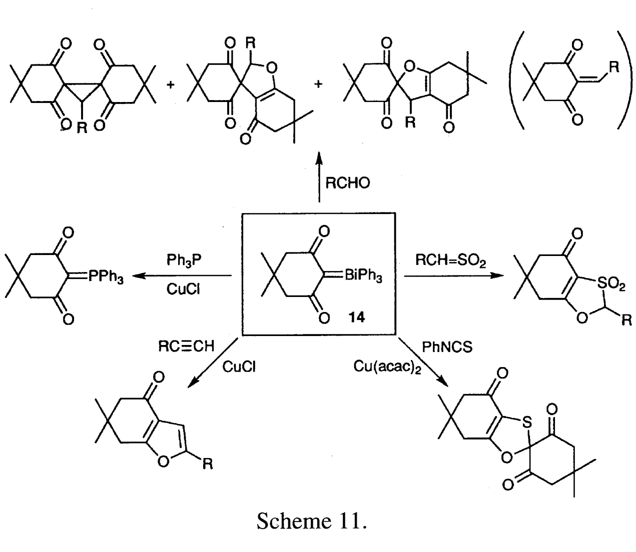


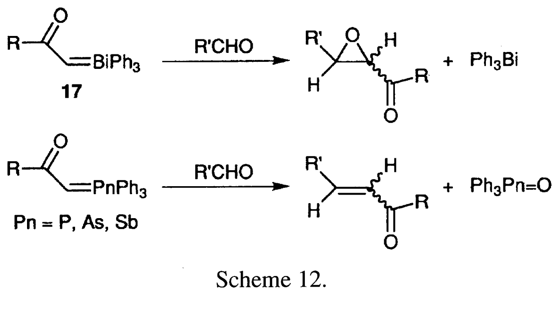
Fig. 3. ORTEP diagram for **14**.



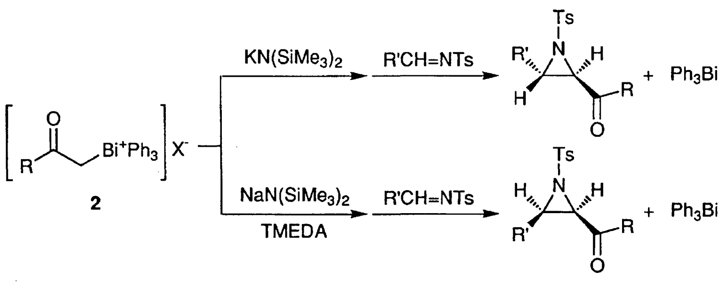
Scheme 11.

The moderately stabilized bismuthonium 2-oxoalkylides **17** readily react with aldehydes at low temperatures to give α,β-epoxyketones as a sole coupling product (Scheme 12).[13] This is in marked contrast to the behaviors of analogous phosphonium, arsonium, and stibonium ylides, which undergo the Wittig-type reaction with aldehydes to give α,β-unsaturated carbonyl compounds and the corresponding oxides. The unique reaction mode of triphenylbismuthonium 2-oxoalkylides **17** probably arises from the high nucleophilicity of the ylidic carbon as well as the large fugative tendency of the triphenylbismuthonio moiety to escape as triphenylbismuthane. A marked contrast in reaction mode, as illustrated in Scheme 12, is compatible with the results of the theoretical calculation about the reaction between $H_3Pn{=}CH_2$ and $H_2C{=}O$, where Pn denotes a member of the 15 group element family.[24] The diastereoselectivity would be determined by the extent of mutual interaction between the ylide and aldehyde functions during the C–C bond forming process. The preference seems to line up the ylide and aldehyde functions in such a way as to give the *trans* isomer ultimately, avoiding the steric congestion between the substituents in the transition state.

Although the bismuthonium 2-oxoalkylides **17** failed to react with ketones and *N*-alkylimines, they readily couple with *N*-sulfonylimines to afford α,β-iminoketones in good yield (Scheme 13).[25] Interestingly enough, the *cis/trans* geometry of the aziridine moiety can be controlled by a proper choice of a base and an additive. When potassium *t*-butoxide or bis(trimethylsilyl)amide is used as a base, the major isomer obtained is *trans*. In contrast, when sodium bis(trimethylsilyl)amide is used as a base in the presence of HMPA or TMEDA, the major isomer is *cis*. It is not clear at present how the cation and additives can work on the *cis/trans* stereo-



Scheme 12.



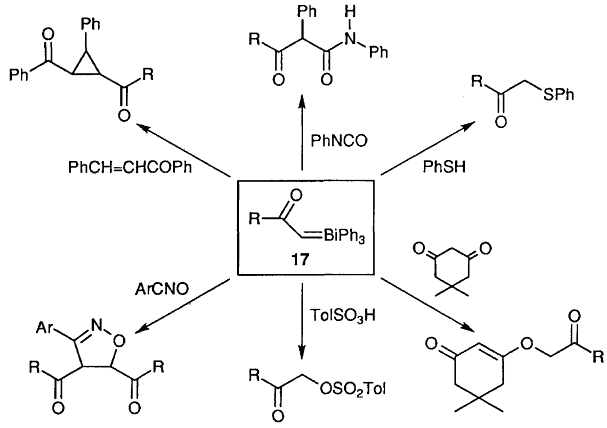
Scheme 13.

selection of the products. Since a similar phenomenon is not observed in the reactions with parent aldehydes, the sulfonyl function of the activated imine substrates might exert influence on the geometry of the transition state leading to the ring compound.

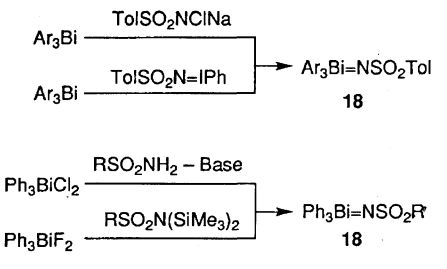
Other typical reaction modes of triphenylbismuthonium 2-oxoalkylides **17** are summarized in Scheme 14, from which the high ability of triphenylbismuthonio group to leave as triphenylbismuthane can be easily understood.[13]

Bismuthane Imides

(1) Synthesis. In contrast to extensive studies on imides of other 15 group elements, only little attention has been paid to the chemistry of bismuthane imides to date. In 1964 Wittig et al. reported the first synthesis of (*N*-sulfonyl)triphenylbismuthane imide **18** (Ar = Ph) by the reaction of triphenylbismuthane with dried Chloramine-T® in acetonitrile (Scheme 15).[26] This methodology has been used to synthesize related triarylbismuthane imides **18**.[27] A similar oxidative imination of triarylbismuthanes can be accomplished by using phenyl-*N*-tosylimino-λ^3-iodane as an oxidant.[28] Recently, Naumann et al. reported alternative synthesis of (*N*-sulfonyl)triphenylbismuthane imides **18** by the base-promoted reaction of triphenylbismuth dichloride with sulfonamides and also by the defluorosilylation of triphenylbismuth difluoride with *N*,*N*-bis(trimethylsilyl)sulfonamides (Scheme 15).[29]



Scheme 14.



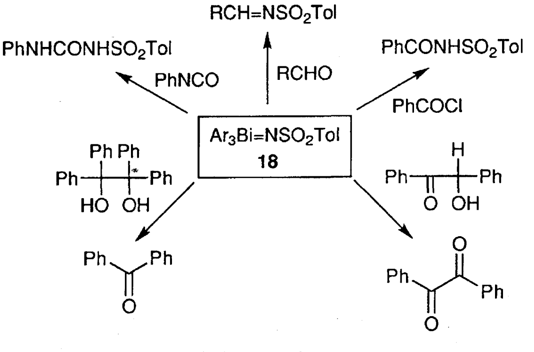
Scheme 15.

(2) Properties. Most of the reported (*N*-sulfonyl)triphenylbismuthane imides **18** are sensitive to moisture, but they are thermally stable owing to the high electron-withdrawing ability of *N*-sulfonyl function. In IR spectra, the sulfonyl absorptions of the imides **18** appear at around 1325—1335 cm^{-1} and 1155—1160 cm^{-1}. There is no report of X-ray structure analysis for bismuthane imides as yet.

(3) Reactions. Scheme 16 summarizes the typical reaction modes of (*N*-sulfonyl)triphenylbismuthane imides **18**. The imide **18** transfers its imino moiety to electrophiles such as aldehydes, phenyl isocyanate, and benzoyl chloride, affording the corresponding imides, urea derivative, and amide in moderate yields.[27] The imide **18** possesses a mild oxidizing ability to convert alcohols to carbonyl compounds via two different reaction pathways.[28] This contrasts to the analogous imides of other 15 group elements which do not show this type of oxidizing ability.

Conclusion

In the last decade, bismuthonium compounds have been receiving increasing attention in the synthetic, structural, and theoretical fields of heteroatom chemistry. As have been illustrated in this article, bismuthonium salts, ylides, and imides now enjoy the many-sided unique chemistry considerably different from that of other 15 group element analogs. Better understanding of this class of compounds, therefore, would no doubt provide a sound basis for the future development of heavy heteroatom chemistry.



Scheme 16.

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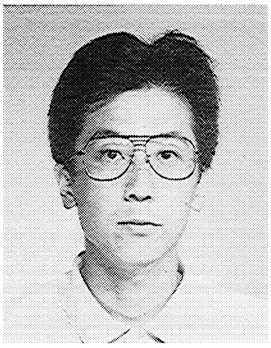

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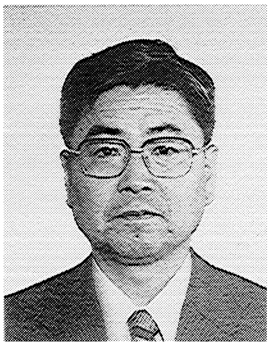

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