



Mixed arsonium–iodonium and sulfonium–iodonium ylides: synthesis and characteristics



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ABSTRACT

The preparation and properties of novel mixed arsonium–iodonium and sulfonium–iodonium ylides are reported. A series of substituted arsonium and sulfonium ylides was obtained by the nucleophilic substitution of iodonium groups in mixed ylides. A one-pot process, which included the nucleophilic substitution and silylation of arsonium–iodonium ylides with subsequent elimination of the silyl group and a Wittig olefination reaction, provided route to access Z- α,β -unsaturated haloketones.

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1. Introduction

Recently, a rapidly growing number of publications dedicated to the study of structural design, synthesis, and reactivity of ylides has appeared in the chemical literature. By definition, ylides are compounds, in which a neutral dipolar molecule containing a negatively charged carbon atom, directly attached to a positively charged heteroatom (usually nitrogen, phosphorus or sulfur), and in which both atoms have a full octet of electrons. Following Wittig's discovery in 1953 of the olefination reaction of carbonyl compounds by phosphorus ylides, the latter became a basis of development for ylide chemistry, leading to the discovery of new, unique types of transformations, rearrangements, and cyclizations and resulting in a great diversity of synthesized carbo- and heterocycles.

During the last decade, not only phosphorus ylides, but also ylides of sulfur, iodine, arsenic, etc., have found increasing utilization.¹ This is due to the fact that these ylides undergo various reactions, leading to the formation of new molecules that find diverse application.

Ylide structures containing two heteroatoms occupy a remarkable place in chemistry. Mixed phosphonium–iodonium ylides

stand out due to their synthetic availability as well as their unusual reactivity.^{2–8} We have discovered two new photochemical reactions of mixed phosphonium–iodonium ylides, one of which results in the synthesis of isoxazoles,⁹ while another leads to a synthesis of 5-phosphynolines.¹⁰

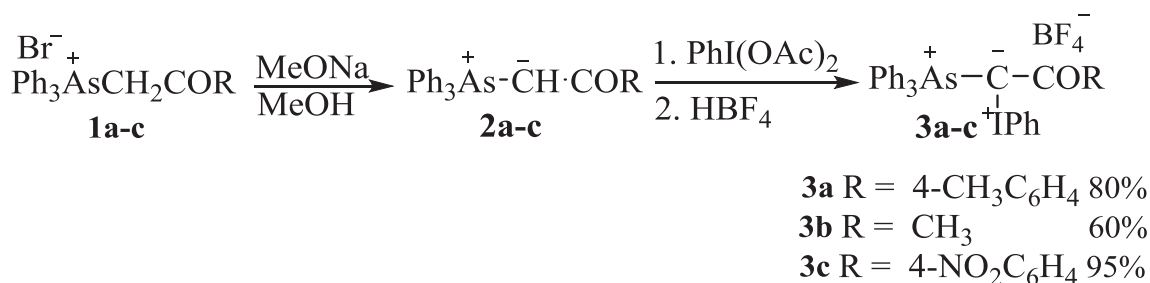
Thus, the synthesis of mixed sulfonium–iodonium and arsonium–iodonium ylides is a logical expansion of structural capabilities for these types of compounds, and we anticipate a corresponding broadening of their reactivity spectrum. It is also worth noting that while synthesis of arsonium–iodonium ylides has been demonstrated in three cases,^{4,5,11} the synthesis of mixed sulfonium–iodonium ylides has not been hitherto accomplished. In this light, the purpose of this research was the synthesis of sulfonium–iodonium and arsonium–iodonium ylides and study of their properties in reactions with nucleophilic reagents.

2. Results and discussion

2.1. Mixed ylide synthesis

To produce mixed sulfonium– and arsonium–iodonium ylides we used the method described earlier for their phosphonium analogues.^{6,7} From arsonium salts (**1a–c**) through the intermediary formation of arsonium ylides (**2a–c**) oxidized by (diacetoxyiodo) benzene, we obtained a series of new mixed arsonium–iodonium ylides (**3a–c**) (Scheme 1).

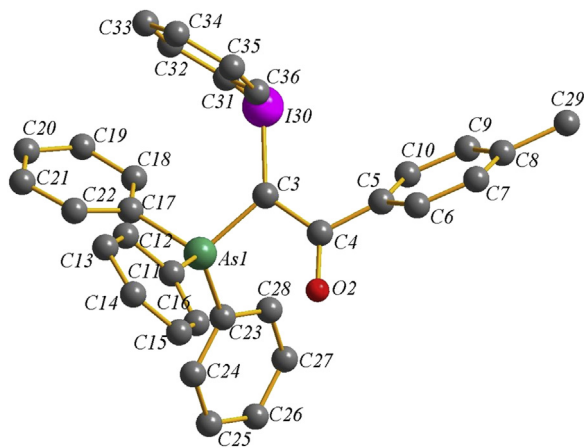
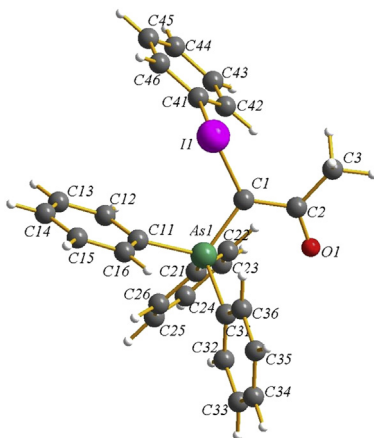
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Scheme 1.

We verified the structure of the obtained compounds **3a–c** with NMR (¹H, ¹³C), IR spectra and composition with mass spectrometry.

Additionally, for mixed ylides **3a** (Fig. 1) and **3b** (Fig. 2), we verified the structure using X-ray crystallography. For ylide **3b**, we were able to grow single crystal, while ylide **3a** was attained in the form of a fine crystalline substance and its structure was determined using X-ray powder diffraction data.¹²

Fig. 1. Structure of ylide **3a**.Fig. 2. Structure of ylide **3b**.

Atoms of As, I, the ylide carbon atom and carbonyl group form a flat conjugated system in both structures. The As1–C1 bond for ylide **3b** is equal to 1.865(10) Å and may be considered as intermediate between single and double bonds (average As–C bond lengths are equal to 1.81 Å and 1.96 Å for double and single bonds,

respectively).¹³ Partial double connectivity between the C1 and C2 atoms (C1–C2–1.438(15) Å) and a small elongation of the C=O bond (C2–O1–1.222(14) Å) are observed. Probably, such changes occurred due to partial redistribution of electron density from the ylide carbon atom to the π*-orbital of the C=O bond. The positioning of the As1, C3, C4 and O2 atoms of ylide **3a** in one plane is similar to ylide **3b** and indicates partial double connectivity between arsenic and carbon atoms (As1–C3–1.87(4) Å). The chemical bond between the ylide and carbonyl group carbon atoms is equal to 1.49(4) Å, which is somewhat shorter than the single C–C bond. On the contrary, the C=O bond is slightly longer (1.49(4) Å), than that of ketones.

From there, we moved on to the study of the synthesis of sulfonium–iodonium ylides. We accomplished the synthesis of sulfonium ylides in a manner analogous to the synthesis of arsonium ylides by producing sulfonium salts **4a–c** (tetrahydrothiophene derivatives), followed by their deprotonation using an appropriate base. In this manner, we obtained a series of ylides **5a–c** in high yields.

The oxidation of sulfonium ylide **5a**, containing a strong electron withdrawing substituent, produced a mixed sulfonium–iodonium ylide **6a** (Scheme 2).

The structure of this compound was verified by low-temperature NMR spectroscopy, since this mixed sulfonium–iodonium ylide **6a** is unstable at temperatures above –10 °C. The composition of the ylide **6a** was verified by HRMS spectroscopy. However, oxidation of sulfonium ylides **5b** and **5c** resulted in formation of less stable compounds, which we were not able to characterize.

Expecting to obtain more stable compounds, we performed a similar sequence with diphenylsulfide derivatives (Scheme 3).

As a result, we obtained a mixed ylide **6d** with a low melting point (–20 °C); its composition was verified by high resolution mass spectrometry, while its structure was verified using NMR spectroscopy. Nevertheless, this mixed ylide was also a rather unstable compound, thus we used all mixed sulfonium–iodonium ylides without isolation for all subsequent transformations.

2.2. Nucleophilic substitution of the iodonium moiety

We then studied the behaviour of the obtained mixed ylides in nucleophilic substitution reactions. The presence of a good leaving group (iodonium group) in the structure of mixed ylide molecules led us to believe that mixed ylides of arsenic and sulfur may react with nucleophiles with substitution of the iodonium moiety. The interaction of ylides **3a–c** with ammonium thiocyanate, which is the S-nucleophile, in acetonitrile solution at room temperature led to the formation of the corresponding thiocyanate substituted arsonium ylides **7a–c** in 60–70% yields. The sulfonium–iodonium ylides **6a,d** react similarly, producing the corresponding thiocyanates **8a,b** with yields of 75% and 65%, respectively (Scheme 4).

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