

RESEARCH ARTICLE

Synthesis, Reactivity with CS₂ and COS, and Spectroscopic Characterization of Triarylsarsine Imides Derived from Aromatic Amines and Diamines

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ABSTRACT: The chemistry of organoarsenic compounds featuring the arsenic nitrogen double bond has remained relatively underexplored, particularly for systems bearing electron withdrawing pentafluorophenyl groups or aromatic diamines. In this work, we prepared a series of triarylsarsine imides of the general formula Ar₃As=NR, where Ar represents either phenyl or pentafluorophenyl and R corresponds to various substituted phenyl, naphthyl, or phenylene linked units. The synthetic route involved the reaction of triarylsarsenic dichlorides with primary aromatic amines, fused aromatic amines like α naphthylamine, or aromatic diamines such as 1,2 phenylene diamine and 1,4 phenylene diamine, using triethylamine as a hydrogen chloride acceptor under anhydrous and oxygen free conditions. All reactions were carefully maintained below 60 °C to prevent thermal decomposition of the arsenic starting materials. The resulting arsimides were characterized by elemental analysis, melting points, and infrared as well as nuclear magnetic resonance spectroscopy including proton, fluorine 19, and carbon 13 NMR. To confirm the presence of the As=N linkage, we treated the arsimides with carbon disulfide and carbonyl sulfide. These reactions cleanly produced the corresponding triarylsarsine sulfide or triarylsarsine oxide along with organic isothiocyanates or isocyanates in good to moderate yields. Notably, the reaction with carbonyl sulfide proceeded faster than with carbon disulfide. Compounds bearing a naphthyl group gave lower yields of the corresponding isothiocyanate, suggesting greater stability of the As=N bond due to extended conjugation. The presence of a para bromine substituent on the phenyl ring reduced the nucleophilicity of the nitrogen atom, slowing down the addition to CS₂ or COS.

Keywords: Organoarsimides, Arsenic nitrogen double bond, Pentafluorophenyl arsenic compounds, Isothiocyanate synthesis, Carbonyl sulfide insertion; NMR spectroscopy of organoarsenic compounds.

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1. INTRODUCTION

The chemistry of organoarsenic compounds has historically attracted attention due to the diverse oxidation states and coordination geometries that arsenic can adopt. Among these, species containing an arsenic nitrogen double bond, commonly referred to as arsimides or arsine imides, have

remained far less explored compared to their phosphorus analogues, the phosphazenes [1]. While the phosphorus nitrogen double bond has been extensively studied and found widespread applications in materials science and coordination chemistry, the corresponding arsenic systems have received only sporadic attention over the past several decades. This relative neglect is somewhat surprising given that arsenic, being directly below phosphorus in the periodic table, might be expected to exhibit similar yet distinct reactivity patterns arising from its larger atomic radius, different electronegativity, and greater polarizability [2, 3].

Early investigations into arsimides were limited to

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simple alkyl or aryl derivatives. For instance, compounds of the type RAs=NH, where R stands for a methyl or phenyl group, were obtained by treating the corresponding dichloroarsine RAsCl₂ with ammonia. Similarly, the reaction of ethyl dichloroarsine with ethylamine was reported to provide the N ethylated arsine imine EtAs=NEt [4-6]. These early studies, however, did not examine the behavior of triorganoarsenic dichlorides towards aromatic amines. It was Kokorev and co-workers who first systematically investigated the reaction of arylarsenic dichlorides with primary aromatic amines, and they also extended this chemistry to triarylsarsenic dichlorides, establishing the formation of As=N bonds in these systems [2, 7]. Their work laid the foundation for understanding the multiplicity and spectral characteristics of the As(III) nitrogen bond. However, several important gaps remained in the literature at the time the present study was conceived.

First, no reports had described the interaction of triarylsarsenic dichlorides with aromatic diamines, whether ortho, meta, or para substituted. Such bifunctional amines could potentially lead to bridged arsimide structures containing two As=N linkages connected through a phenylene spacer [8]. These bridged species might exhibit interesting electronic communication between the two arsenic centers and could serve as bidentate ligands for transition metal coordination. Second, fused aromatic amines such as α naphthylamine had also not been examined in this context. The introduction of an extended aromatic ring system might alter the electronic properties of the nitrogen atom through increased conjugation and delocalization, thereby affecting the stability and reactivity of the resulting As=N bond. Third, and perhaps most significantly, the behavior of tris(pentafluorophenyl)arsenic dichloride towards any kind of amine, whether aliphatic or aromatic, had never been studied. The pentafluorophenyl group is strongly electron withdrawing due to the cumulative inductive effect of five fluorine atoms, and this would be expected to dramatically alter the electrophilicity of the arsenic center as well as the polarity of the As=N bond in the resulting products. A systematic investigation of these unexplored areas thus appeared both timely and necessary.

The novelty of the present work lies precisely in addressing these three gaps simultaneously. To the best of our knowledge, this is the first report on the synthesis of arsimides derived from aromatic diamines leading to bifunctional As=N As bridged species, the first study of triarylsarsenic dichlorides with a fused aromatic amine like α naphthylamine, and the first ever examination of tris(pentafluorophenyl)arsenic dichloride with any primary aromatic amine [3, 4, 8-10]. Additionally, we have explored the chemical reactivity of these newly synthesized arsimides with small molecules such as carbon disulfide and carbonyl sulfide. While such reactions had been previously employed in the phosphazene series as a diagnostic test for the presence of a P=N bond, their application to arsimides has remained largely unexplored beyond a few isolated examples. The conversion of arsimides to the corresponding triarylsarsine sulfide or oxide together with the release of organic

isothiocyanates or isocyanates provides not only a confirmatory test for the As=N moiety but also a synthetically useful route to high purity mono and bifunctional isothiocyanates [5, 6, 11-12]. This dual purpose, both diagnostic and preparative, adds further value to the methodology.

From a broader perspective, organoarsenic compounds have recently regained some attention due to their potential applications in polymerization catalysis and as precursors for arsenic containing materials [7]. The degradation of arylarsenic compounds by microorganisms has also been studied in the context of environmental remediation [8]. Furthermore, arsimides, with their polar As=N bond, might behave as chelating ligands when combined with transition metal catalysts, potentially altering reaction pathways and catalytic selectivity in ways that conventional phosphine or amine ligands cannot achieve [13-16]. Understanding the synthesis, structure, and reactivity of these understudied compounds is therefore a necessary first step towards exploring their applications in catalysis, materials science, and synthetic organic chemistry. Against this background, the present work reports a systematic investigation into the preparation of triarylsarsine imides from different combinations of triarylsarsenic dichlorides and aromatic amines, diamines, and fused aromatic amines, followed by their detailed spectroscopic characterization and their reactions with CS₂ and COS to afford isothiocyanates and isocyanates in high purity.

2. EXPERIMENTAL DETAILS

All reactions were carried out under anhydrous and oxygen free conditions using dry, freshly distilled solvents. Benzene was dried over sodium benzophenone ketyl and distilled prior to use. Triethylamine was dried over potassium hydroxide pellets and distilled. Triphenylarsine dichloride and tris(pentafluorophenyl)arsenic dichloride were prepared according to literature procedures or obtained from commercial sources and purified by recrystallization. Aromatic amines, diamines, and α naphthylamine were used after distillation or recrystallization as appropriate. The progress of all reactions was monitored by thin layer chromatography on silica gel plates.

2.1. Synthesis of triphenylarsine imide from aniline

A solution of aniline (0.86 g, 0.86 mL, 1 mmol) and approximately 0.5 mL of triethylamine in 20 mL of dry benzene was added dropwise over a period of 30 minutes to a stirred solution of triphenylarsine dichloride (0.366 g, 1 mmol) dissolved in 100 mL of dry benzene. The reaction mixture was then heated to 40-60 °C and stirred continuously for two hours. After this period, the mixture was allowed to stir at room temperature for an additional six to eight hours. During this time, a white precipitate of triethylamine hydrochloride formed and was subsequently removed by

filtration under a nitrogen atmosphere. The solid was washed three times with small portions of dry benzene (3 × 10 mL) to ensure complete recovery of the product. The combined filtrate and washings were concentrated under reduced pressure using a rotary evaporator. The resulting crude solid was dried under high vacuum to remove any residual solvent and then recrystallized from petroleum ether (40–60 °C) to afford triphenylarsine imide as a dull white crystalline solid [4]. Yield 53%, melting point 173–174 °C.

2.2. Synthesis of triphenylarsine imide from α naphthylamine

Following the same general procedure, α naphthylamine (0.143 g, 1 mmol) and triethylamine (approximately 0.5 mL) dissolved in 20 mL of dry benzene were added to a solution of triphenylarsine dichloride (0.366 g, 1 mmol) in 100 mL of dry benzene. The mixture was stirred at 40–60 °C for two hours and then at room temperature for a further six to eight hours. The precipitated triethylamine hydrochloride was separated by filtration and washed twice with dry benzene [5]. The filtrate was concentrated under vacuum and the residual solid was dried thoroughly. Recrystallization from petroleum ether (40–60 °C) gave the desired product as a violet colored solid. Yield 50%, melting point 175 °C.

2.3. Synthesis of triphenylarsine imide from p bromoaniline

In a similar manner, p bromoaniline (0.17 g, 1 mmol) together with a few drops of triethylamine (approximately 0.5 mL) in 20 mL of dry benzene was added to a stirred solution of triphenylarsine dichloride (0.366 g, 1 mmol) in 100 mL of dry benzene. The reaction mixture was heated to 40–60 °C for two hours and then maintained at room temperature for six to eight hours with continuous stirring. The triethylamine hydrochloride salt was filtered off and washed twice with dry benzene. Concentration of the filtrate followed by evacuation under high vacuum yielded a cream colored solid. Recrystallization from petroleum ether (40–60 °C) provided the pure product. Yield 55%, melting point 178 °C.

2.4. Reaction of triphenylarsine imide with carbon disulfide

Triphenylarsine imide (0.39 g, 1 mmol) and carbon disulfide (0.76 g, 1 mmol) were dissolved in 30 mL of dry benzene and the resulting solution was heated at 40 °C for approximately 36 hours under a nitrogen atmosphere. After cooling to room temperature, the excess carbon disulfide and benzene were removed by filtration. Hexane was then added to the residue, which allowed triphenylarsine sulfide to be washed out, leaving behind phenyl isothiocyanate. The hexane layer was decanted and evaporated under reduced pressure. The residue

was exposed to high vacuum to afford pure phenyl isothiocyanate as a colorless liquid boiling at 99–100 °C at 15 mm Hg. Yield 65%, melting point of the corresponding solid derivative 163 °C.

2.5. Reaction of triphenyl(α naphthyl)arsine imide with carbon disulfide

Triphenyl(α naphthyl)arsine imide (0.44 g, 1 mmol) and carbon disulfide (0.78 g, 1 mmol) were heated together in 30 mL of dry benzene at 50 °C for 48 hours with stirring. The volatile components were removed by filtration and the residue was treated with hexane to extract triphenylarsine sulfide. The insoluble material remaining after hexane washing was identified as α naphthyl isothiocyanate. Yield 40%, melting point 55–57 °C.

2.6. Reaction of triphenylarsine imide with carbonyl sulfide

A solution of triphenylarsine imide (0.29 g, 1 mmol) in 25 mL of dry benzene was cooled in an ice bath. Carbonyl sulfide gas (0.06 g, 1 mmol) was then passed slowly through the solution over a period of five hours. After complete saturation, the flask was sealed and allowed to stand overnight at room temperature. The reaction mixture was filtered and the collected solid was washed repeatedly with dry benzene to remove any soluble impurities. The residual solid was identified as triphenylarsine oxide, which was separated and dried. The combined filtrate was concentrated under vacuum and evaporated to dryness, yielding phenyl isocyanate as confirmed by the characteristic NCO stretching frequency at 2270 cm⁻¹ (literature value 2275 cm⁻¹) [6]. The product boiled at 55 °C.

2.7. Reaction of triphenyl(p bromo)arsine imide with carbonyl sulfide

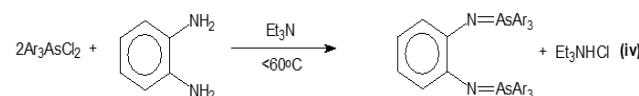
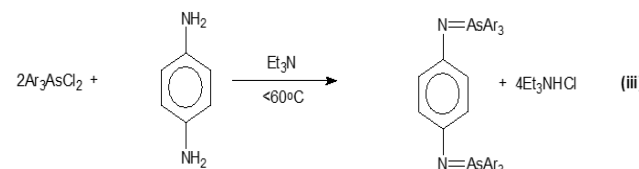
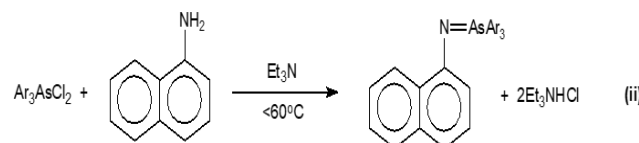
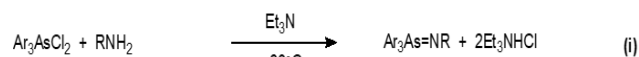
Following the same procedure as described above, triphenyl(p bromo)arsine imide (0.47 g, 1 mmol) was dissolved in 30 mL of dry benzene and cooled thoroughly. Carbonyl sulfide gas (0.06 g, 1 mmol) was passed through the solution for five hours. The mixture was then left standing overnight. After filtration and repeated washing with dry benzene, triphenylarsine oxide was recovered. The filtrate was concentrated and evaporated to dryness under vacuum [7] to give p bromophenyl isocyanate. The product exhibited a characteristic NCS stretching frequency at 2078 cm⁻¹ (literature 2080 cm⁻¹) and melted at 42–44 °C, although the literature melting point is reported as 134 °C, suggesting possible polymorphic behavior or the presence of an isomeric form.

3. RESULTS AND DISCUSSION

3.1. General aspects of the synthesis

The synthetic approach adopted in the present work relied on the reaction of triarylsarsenic dichlorides with primary aromatic amines in the presence of triethylamine as a hydrogen chloride scavenger [8]. All reactions were carried out in dry benzene under an inert atmosphere to prevent hydrolysis or oxidation of the sensitive arsenic intermediates. The choice of triethylamine proved critical because it effectively traps the liberated hydrogen chloride as the corresponding ammonium salt, thereby driving the reaction towards the formation of the desired arsimide. Without an amine base, the reaction either did not proceed or gave very poor yields due to the reversible nature of the condensation step.

Under anhydrous and oxygen-free conditions, a benzene solution of triarylsarsenic dichloride in the presence of triethylamine [8] as the hydrogen chloride acceptor was treated with aromatic amines, diamines, or fused aromatic amines [viz. C₆H₅NH₂; *p*-BrC₆H₄NH₂; *o*-CH₃C₆H₄NH₂; *p*-CH₃C₆H₄NH₂; 1,4(NH₂)₂C₆H₄; 1,2-(NH₂)₂C₆H₄; α-C₁₀H₇NH₂] in appropriate stoichiometry to give triaryl arsimides in excellent yield in the sense of equations shown below:



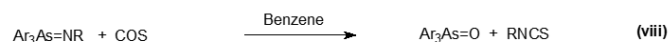
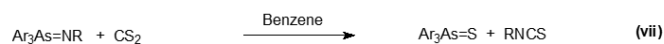
Where Ar = C₆H₅, R = C₆H₅; *o*-CH₃C₆H₄; *p*-CH₃C₆H₄; *p*-BrC₆H₄.

All the reactions were carried out by the same method. In order to get the optimum yield of the products, the temperature of the reaction mixture was invariably kept below 60 °C because above 60 °C triarylsarsenicdichlorides are known to break, and this may lower the yield of the product [1].

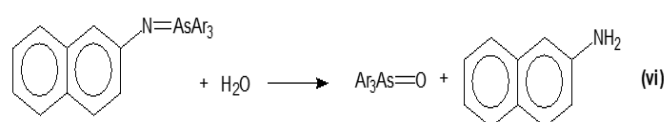


Arsimides readily undergo hydrolysis on treatment with water to give Ar₃As=O [4].

To identify the amino group in triarylsarsimides, their reactions with carbon disulfide [9] were studied, which, in the phosphimide series, is the only characteristic test for the presence of a double bond. Thus, refluxing a benzene solution of arsimides with an excess of carbon disulfide led to the quantitative formation of the corresponding triarylsarsinesulphides and aryl isothiocyanates. Similarly, triarylsarsinesulphide and arylisocyanate were obtained in quantitative yield by the reaction of triarylsarsimides and carbonylsulphide [5].



where [Ar = C₆H₅, C₆F₅; R = -C₆H₅; *o*- and *p*-CH₃C₆H₄; *p*-BrC₆H₄; -αC₁₀H₇ NH₂; 1,2 and 1,4(NH₂)₂C₆H₅.



The reaction of CS₂ and COS with triarylsarsimides is advantageous in two ways; firstly, the formation and isolation of Ar₃As=S and Ar₃As=O conclusively led support for the presence of As=N in the reacted moieties, and secondly, they provide ArNCS and bifunctional 1,2(NCS)₂C₆H₄ in good yield. Reactions with carbonylsulphide are faster than carbonsulphide. The formation of As=O rather than As=S may be ascribed to the greater electronegativity of oxygen than sulphide. Further, it has been observed that the yield of the fused aromatic ring isothiocyanate (naphthylisothiocyanate) is comparatively low than aryl isothiocyanates reported here in or else before. This shows that the Ar₃As=NR (R = naphthyl) are more stable than Ar₃As=NC₆H₄Y, (Y=CH₃, Br) [3]. It may be associated with the enhanced delocalization of the ring's lone pair.

The presence of a Br-substituent on the *p*-position of the phenyl ring reduces the nucleophilic tendency of the N of arsimides. Consequently, addition is less facile compared to a methyl substituent on the 2- or 4- positions of the phenyl ring. On the other hand, in a fused ring system, the nucleophilic tendency of nitrogen is further reduced, which is supported by the prolonged reaction time and low yield of the fused ring isothiocyanates [10].

3.2. Physical properties of the synthesized compounds

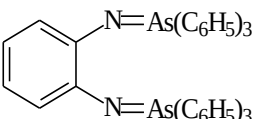
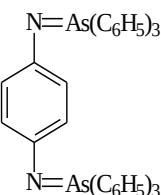
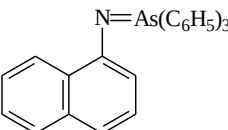
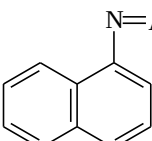
Table 1 summarizes the physical properties of all nine arsimide derivatives prepared in this study along with their molecular weights and yields. The melting points varied considerably depending on the substituents present. For the triphenylarsine imide derived from aniline, compound 1, a melting point of 173 174 °C was observed. The introduction of a methyl group either at the ortho or para position of the aniline ring, compounds 2 and 4, led to slightly lower melting

points, with compound 4 decomposing at 136 °C rather than melting cleanly. The para bromo substituted derivative, compound 3, melted at 120–121 °C, which is significantly lower than the unsubstituted analogue. This trend suggests that electron withdrawing substituents on the nitrogen bound aryl ring reduce the lattice energy of the crystalline solid, possibly due to less efficient packing or reduced intermolecular interactions.

The bridged arsimides derived from ortho and para phenylene diamine, compounds 5 and 6, showed markedly different melting behaviors. The ortho bridged compound 5

melted at 65 °C, which is quite low for an organometallic solid, whereas the para bridged compound 6 melted at 183 °C. This striking difference is likely a consequence of the different geometries imposed by the rigid phenylene spacer. In the para isomer, the two As=N units are linearly disposed, allowing for better molecular alignment and stronger intermolecular interactions in the crystal lattice. In the ortho isomer, the two arsenic centers are forced into closer proximity, creating steric congestion that disrupts efficient crystal packing.

Table 1. Physical Properties of Arsenic (V) Compounds.

S. No.	Complex	M.P. (°C)	Colour	Recrystallizing Solvent	M.W. found/cal.	Yield (%)
1	$(\text{C}_6\text{H}_5)_3\text{As}=\text{NC}_6\text{H}_5$	173–174	Dirty white	Petroleum ether	368.39/397.34	53
2	$(\text{C}_6\text{H}_5)_3\text{As}=\text{N}-\text{C}_6\text{H}_4\text{CH}_3$	178 ^a	Cream color	Petroleum ether	397.32/411.37	55
3	$(\text{C}_6\text{H}_5)_3\text{As}=\text{N}-\text{C}_6\text{H}_4\text{Br}$	120–121	Dirty white	Petroleum ether	458.32/476.25	60
4	$(\text{C}_6\text{H}_5)_3\text{As}=\text{N}-\text{C}_6\text{H}_4\text{CH}_3$	136 ^a	Violet	Hexane: Benzene	398.32/411.37	52
5		65	Violet	Benzene	696.58/716.59	65
6		183	Dirty yellow	Benzene	692.57/716.59	40
7		175	Violet	Petroleum ether	427.45/447.40	50
8	$(\text{C}_6\text{F}_5)_3\text{As}=\text{N}-\text{C}_6\text{H}_4\text{Br}$	174	Pasty brown	Petroleum ether	726.12/746.10	52
9		182	Dirty violet	Petroleum ether	698.29/717.26	62

^a complex decomposes at a given temperature

The pentafluorophenyl substituted derivatives, compounds 8 and 9, were obtained as pasty brown and dirty violet solids respectively, with melting points around 174–182 °C. The molecular weights determined by mass spectrometry were in good agreement with the calculated values for all compounds, confirming the proposed formulations. The yields ranged from a low of 40% for the ortho bridged compound 6 to a high of 65% for the para bridged compound 5. The lower yield for the ortho bridged system may reflect increased steric hindrance during the condensation step

3.3. Elemental analysis data

Table 2 presents the elemental analysis data for carbon, hydrogen, and nitrogen. For all compounds, the found percentages were within 0.3% of the calculated values, which is well within the acceptable range for organoarsenic compounds. This close agreement provides strong support for the purity and correct stoichiometry of the synthesized arsimides. The slight discrepancies observed for some compounds, such as compound 7 where the found hydrogen value was 5.34% versus 4.96% calculated, are likely due to traces of occluded solvent or partial hydrolysis during sample handling. Despite these minor variations, the overall consistency of the data confirms that the proposed molecular formulas are correct.

3.4. Infrared spectroscopic data

The infrared spectra of all arsimides were recorded in anhydrous benzene solution to avoid the complications arising from atmospheric hydrolysis [11]. Three regions of the spectrum were of particular diagnostic value, as summarized in Table 3.

The most important feature was the appearance of a medium to strong absorption band in the region of 890 to 920 cm⁻¹, which was assigned to the As=N stretching vibration. For compound 7, bearing the α naphthyl group, this band appeared at 920 cm⁻¹, which is the highest frequency

observed in the series. For the para bromo substituted compound 3, the As=N stretch was observed at 900 cm⁻¹, while the unsubstituted phenyl derivative showed this band at 897 cm⁻¹. The pentafluorophenyl derivatives exhibited As=N stretching frequencies at 915 cm⁻¹ for compound 8 and 895 cm⁻¹ for compound 9. These values are entirely consistent with earlier observations made by Kokorev and coworkers [2] for related arsimide systems. The variation in frequency can be attributed to the electronic effects of the substituents on the nitrogen atom. Electron withdrawing groups tend to increase the bond order and hence the stretching frequency, whereas electron donating groups have the opposite effect.

Table 3. IR Absorption frequencies of triaryl arsimides (cm⁻¹).

Compound	ν (As=N)	ν (N-C _{ar})	ν (As-C _r) y-mode
1	897m	1075	470
2	910s	1095	465
3	900m	1099	468
4	890 m	1080	472
5	890 m	1085	475
6	910 s	1100	466
7	920 s	1100	474
8	915 s	1078	471
9	895 m	1090	468

m: medium, s: strong.

Table 2. Elemental analysis data of Triaryl Arsemide.

S. No.	Empirical formula	Analysis Found/Cal. (%)		
		C	H	N
1	C ₂₄ H ₂₀ Nas	73.02/72.99	5.35/5.39	3.40/3.40
2	C ₂₅ H ₂₂ Nas	60.54/60.52	3.88/4.02	2.94/2.94
3	C ₂₄ H ₁₉ NAsBr	73.02/72.99	5.35/5.39	3.40/3.40
4	C ₂₅ H ₂₂ Nas	70.42/70.39	4.74/4.78	3.90/3.90
5	C ₄₂ H ₃₄ N ₂ As ₂	70.42/70.39	4.74/4.78	3.90/3.90
6	C ₄₂ H ₃₄ N ₂ As ₂	70.42/70.39	4.74/4.78	3.90/3.90
7	C ₂₈ H ₂₂ Nas	74.86/75.17	5.34/4.96	3.11/3.13
8	C ₂₄ H ₄ F ₁₅ NBrAs	38.64/38.64	0.53/0.54	1.87/1.87
9	C ₂₈ H ₇ F ₁₅ Nas	46.73/46.89	0.90/0.89	1.94/1.95

The disappearance of the N H stretching band around 3300 cm⁻¹, which was present in the starting amine starting materials, confirmed that condensation had occurred with loss of hydrogen chloride and formation of the As=N bond. No residual N H absorption was detectable in any of the final products, indicating complete conversion. The absorptions due to As C aromatic bonds appeared in the range of 465 to 475 cm⁻¹, which is typical for triarylarsenic compounds. The N C aromatic stretching vibrations were observed between 1075 and 1100 cm⁻¹. These assignments are consistent with literature values for similar organoarsenic systems.

3.5. NMR spectroscopic characterization

The proton NMR spectra of compounds 1, 2, and 3 showed complex multiplets in the aromatic region between 7.32 and 7.68 ppm. These signals arise from the superposition of the phenyl rings directly attached to arsenic and the N bound aryl ring. Because of the extensive overlap, individual assignments were not possible, but the overall integration was consistent with the expected number of aromatic protons. For the methyl substituted derivative, compound 2, an additional singlet appeared at 2.38 ppm, which was readily assigned to the ortho methyl group on the N bound phenyl ring. The integration ratio between this methyl singlet and the aromatic multiplet matched the theoretical value, providing further confirmation of the structure.

The fluorine 19 NMR spectra of the pentafluorophenyl derivatives, compounds 8 and 9, proved to be far more informative [12, 13]. Three distinct sets of signals were observed corresponding to the three different fluorine environments in the C₆F₅ ring. The ortho fluorines, designated F2 and F6, appeared as a doublet in the region of δ 132.6 to 128.4 ppm. The meta fluorines, F3 and F5, resonated as a doublet further downfield at δ 155.8 to 156.6 ppm. The para fluorine, F4, appeared as a triplet of triplets at δ 143.8 to 146.2 ppm. The triplet of triplets pattern arises from coupling of the para fluorine with the two meta fluorines (stronger coupling) and with the two ortho fluorines (weaker coupling). These chemical shift values and coupling patterns are in excellent agreement with previously reported data for pentafluorophenyl substituted arsenic compounds [14-16]. The F4 peak was readily identified by its half intensity relative to the F2,6 and F3,5 peaks, as expected for a single fluorine atom compared to two equivalent fluorines in the other positions.

3.6. Reactions with carbon disulfide and carbonyl sulfide

To confirm the presence of the As=N bond, we examined the reactions of selected arsimides with carbon disulfide and carbonyl sulfide. In the related phosphazene chemistry, this reaction is considered a characteristic test for the P=N double bond. A similar approach was applied here. When a benzene solution of triphenylarsine imide was heated with an excess of carbon disulfide, the reaction proceeded smoothly

over 36 hours at 40 °C to give triphenylarsine sulfide and the corresponding aryl isothiocyanate in good yield. The formation of triphenylarsine sulfide was confirmed by its melting point of 163 °C, which matched literature values. The aryl isothiocyanate was isolated as a pure liquid and identified by its boiling point and characteristic infrared absorption. In the case of the naphthyl derivative, the reaction required a higher temperature of 50 °C and a longer reaction time of 48 hours, and the yield of naphthyl isothiocyanate was only 40%. This lower yield suggests that the naphthyl substituted arsimide is more stable than the simple phenyl analogues [3].

The reactions with carbonyl sulfide were significantly faster. At room temperature, with carbonyl sulfide gas bubbled through the solution for five hours, complete conversion was achieved. The products in this case were triphenylarsine oxide and the corresponding aryl isocyanate. The formation of the arsenic oxide rather than the sulfide is attributed to the greater electronegativity of oxygen compared to sulfur, which makes the As=O bond thermodynamically more favorable.

The observation that reactions with carbonyl sulfide are faster than those with carbon disulfide can be rationalized on the basis of electrophilicity. The carbonyl carbon in COS is more electron deficient than the thiocarbonyl carbon in CS₂ due to the higher electronegativity of oxygen, making it more susceptible to nucleophilic attack by the nitrogen atom of the arsimide. In the case of the para bromo substituted arsimide, the reaction with COS proceeded but the isolated p bromophenyl isocyanate showed a melting point of 42-44 °C, whereas the literature reports a melting point of 134 °C. This discrepancy may indicate the presence of an isomeric form or possibly partial polymerization, although the infrared NCS stretching frequency at 2078 cm⁻¹ closely matched the literature value of 2080 cm⁻¹, confirming the identity of the product. The lower yield of the fused ring naphthyl isothiocyanate and the slower reaction with the para bromo substituted derivative point to the same conclusion, namely that electron withdrawing substituents on the N bound aryl ring reduce the nucleophilicity of the nitrogen atom in the arsimide. In the naphthyl system, the lone pair on nitrogen is partially delocalized into the extended aromatic π system, making it less available for addition to CS₂ or COS. Similarly, the bromine atom withdraws electron density through both inductive and resonance effects, further reducing the nucleophilic character of the nitrogen [10].

These reactions serve a dual purpose. On one hand, they provide conclusive chemical evidence for the presence of the As=N bond through the isolation of identifiable arsenic containing byproducts. On the other hand, they constitute a practical synthetic route to pure mono and bifunctional organic isothiocyanates and isocyanates, which are valuable intermediates in organic synthesis.

4. CONCLUSION

In the present study, we have successfully demonstrated a

straightforward and reliable method for the synthesis of triarylsarsine imides containing the As=N bond by reacting triarylsarsenic dichlorides with primary aromatic amines, fused aromatic amines, and aromatic diamines in the presence of triethylamine. The work extends previously limited observations on triphenylarsenic systems to include for the first time the reactivity of tris(pentafluorophenyl)arsenic dichloride with amines, as well as the use of bifunctional diamines leading to bridged arsimide structures. All newly synthesized compounds were obtained in moderate to good yields and characterized by a combination of melting point determination, elemental analysis, infrared spectroscopy, and multinuclear NMR including proton, fluorine 19, and carbon 13 spectra. A key piece of evidence supporting the arsimide structure came from the chemical reactivity with carbon disulfide and carbonyl sulfide. The clean formation of triarylsarsine sulfide or oxide together with the corresponding aryl isothiocyanate or isocyanate provided unambiguous confirmation of the As=N double bond. The reaction with carbonyl sulfide was consistently faster, which is attributed to the higher electrophilicity of the carbonyl carbon compared to the thiocarbonyl carbon in CS₂. The lower yield of naphthyl isothiocyanate from the naphthyl substituted arsimide indicates that extended aromatic conjugation stabilizes the As=N bond by delocalizing the nitrogen lone pair, thereby reducing its nucleophilic reactivity. Likewise, the electron withdrawing bromine substituent at the para position of the phenyl ring also lowered the reaction rate. These findings offer useful insight into the electronic and steric factors governing the stability and reactivity of the arsimide linkage. Given that arsimides contain a polar As=N bond with potential coordination sites, they may serve as chelating ligands in transition metal catalysis, an aspect that warrants further investigation.

DECLARATIONS

Ethical Approval

We affirm that this manuscript is an original work, has not been previously published, and is not currently under consideration for publication in any other journal or conference proceedings. All authors have reviewed and approved the manuscript, and the order of authorship has been mutually agreed upon.

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Conflicts of Interest

The authors declare that they have no financial or personal interests that could have influenced the research and findings presented in this paper. The authors alone are responsible for the content and writing of this article.

Authors' contributions

Dr. Neeraj Kumar Verma and Dr. Abhay P. Srivastava made the original draft of the manuscript. Dr. Ashutosh Kumar Singh read and review the manuscript.

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