Sulfonylimino Group Transfer Reaction Using Imino-\(\lambda^3\)-iodanes with I\(_2\) as Catalyst Under Metal-free Conditions

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Abstract: A new practical procedure of imination for sulfide has been developed. The treatment of (N-tosylimino)-phenyl-\(\lambda^3\)-iodane, PhINTs, with various sulfides in the presence of a catalytic amount of I\(_2\) under metal-free conditions affords the corresponding N-tosylsulfilimine compounds with moderate to good yields. This facile transfer procedure of the sulfonylimino group can also be applied to triphenylphosphine to produce the respective iminotriphenylphosphoranes in high yields. According to the reaction mechanism studies, the process of imination from (N-tosylimino)-phenyl-\(\lambda^3\)-iodane to sulfide under the conditions may involve radical steps within the reaction mechanism.

Keywords: iminoiodanes; imination; sulfide; sulfilimine; phosphine; iminophosphorane; amidyl radical; catalytic cycle; iodine

1. Introduction

Sulfur–carbon ylides and sulfur–heteroatom ylide compounds are widely used in many chemical reactions as important transformational reagents [1–5]. Numerous reactions employing sulfide ylides have been demonstrated in organic synthesis. In particular, sulfur–nitrogen ylides [6–8], N-sulfonyl sulfilimines, such as mono-aza analogues of sulfoxides, are common aziridination reagents [9], epoxidation reagents [10], or palladium metal ligands [11]. Sulfilimine compounds are also used as efficient synthons for sulfoximines, which can be easily prepared by the appropriate oxidants, and these compounds are used in medicinal or synthetic chemistry [12–15]. Synthetic methodologies for directly introducing N-sulfonylimino groups to sulfide atom using oxidants with nitrogen source have been developed [16–19].

Organohypervalent iodine compounds are known as efficient oxidative reagents for organic synthesis because of the exceptionally high leaving ability of the iodosobenzene group [20–24]. The versatile reactivity of hypervalent iodine(III) compounds allows for various bond formations, some of which are otherwise difficult reactions in the absence of iodine(III) reagents. Particularly, N-sulfonylimino-\(\lambda^3\)-iodanes represent an important class of hypervalent iodine(III) compounds,
which are commonly used as N-sulfonylimino group sources or selective oxidative reagents for various organic substrates [25–27]. For example, the reaction of sulfides with (N-tosylimino)-phenyl-λ³-iodane in the presence of Cu, Mn, or Fe metal catalyst gave the corresponding sulfoxime compounds (Scheme 1a) [28–33]. However, a metal-free condition for reactions is a significant goal in the development of eco-friendly reaction methodology. Recently, Lamar and Nicholas reported the C-H amidation reaction of saturated or unsaturated hydrocarbons using imino-λ³-iodanes in the presence of a catalytic amount of elemental iodine under transition metal-free conditions [34]. Lamar’s group also reported the amidation reaction of aldehydes under similar reaction conditions [35]. Metal-free aziridination reactions of styrenes using (N-tosylimino)-phenyl-λ³-iodane in the presence of I₂-tetrabutylammonium iodide combination have been developed by Minakata and co-worker [36]. To the best of our knowledge, however, I₂ mediated metal-free imination reactions of sulfides using imino-λ³-iodanes have not been developed. In this paper, we report the sulfonylimino group transfer reaction from imino-λ³-iodane to sulfide atom under metal-free conditions (Scheme 1b). Reaction mechanisms of this sulfonylimino group transfer reaction may involve the radical process under reaction conditions.

a) Metal-catalyzed imidation reaction of sulfides.

\[
R^1S^1R^2 + \text{PhlNTs} \xrightarrow{\text{Cu, Mn, or Fe catalyst}} \text{solvent, rt} \rightarrow \begin{array}{c}
\text{NTs} \\
R^1S^1R^2 
\end{array}
\]

b) Metal-free imidation reaction of sulfides. (this work)

\[
R^1S^1R^2 + \text{PhlNSO}_2R^3 \xrightarrow{\text{I}_2 \ (2 \text{ mol\%)}} \text{CH}_2\text{Cl}_2, \text{rt}, 24 \text{ h} \rightarrow \begin{array}{c}
\text{NSO}_2R^3 \\
R^1S^1R^2 
\end{array}
\]

Scheme 1. Transfer reaction of sulfonylimino groups from imino-λ³-iodane to sulfide atom.
(a) Metal-catalyzed imidation reaction of sulfides, (b) Metal-free imidation reaction of sulfides.

2. Results

2.1. Optimization of Reaction Conditions

Our approach to metal-free sulfonylimino group transfer reaction is based on previously reported reaction conditions such as (N-tosylimino)-phenyl-λ³-iodane in the presence of I₂ as a catalyst [34,36]. In the initial experiment, we investigated the reaction of thioanisole 1a (1 equiv.) with (N-tosylimino)-phenyl-λ³-iodane 2a (1.2 equiv.) in the presence of a catalytic amount of both I₂ and tetrabutylammonium iodide (TBAI) as an additive under various solvents at room temperature (Table 1, entries 1–9). We have found that dichloromethane is an efficient solvent for the metal-free imination reaction of thioanisole 1a using (N-tosylimino)-phenyl-λ³-iodane 2a. The presence of TBAI as an additive did not affect this reaction (entry 10). However, in the absence of I₂ as a catalyst, the reaction dramatically changed, resulting in a low yield of the formation of the desired N-tosyl sulfilimine 3a (entries 11 and 12). Extension of the reaction time was effective for the desired product 3a yield (entry 14). Decreasing the amount of I₂ catalyst from 10 mol% to 2 mol% increased the yield of N-tosyl sulfilimine 3a (entries 14–16). These results implied that the slow generation of the activated species was very important for this reaction because the species generated from (N-tosylimino)-phenyl-λ³-iodane 2a and I₂ were probably unstable in the reaction mixtures. Meanwhile, further reduction of the amount of I₂ catalyst and a longer reaction time led to a decreased amount of the desired product 3a (entries 17 and 18). Finally, performing the reaction under the dark conditions slightly suppressed the product yield, which supports a radical pathway in the reaction mixtures (entry 19) [36].
Table 1. Optimization of imination reaction of thioanisole 1a using \((N\text{-tosylimino})\)-phenyl-\(\lambda^3\)-iodane 2a 1.

| Entry | Time (h) | Solvent | \(I_2\) (mol%) | TBAI (mol%) | 3a Yield (%)
|-------|----------|---------|----------------|-------------|----------------|
| 1     | 3        | MeCN    | 20             | 10          | 81 (80)        |
| 2     | 3        | Hexane  | 20             | 10          | 15             |
| 3     | 3        | AcOEt   | 20             | 10          | 49             |
| 4     | 3        | MeOH    | 20             | 10          | 77             |
| 5     | 3        | THF     | 20             | 10          | 4              |
| 6     | 3        | Et\(_2\)O | 20           | 10      | Trace          |
| 7     | 3        | PhH     | 20             | 10          | 47             |
| 8     | 3        | CCl\(_4\) | 20          | 10      | 7              |
| 9     | 3        | CH\(_2\)Cl\(_2\) | 20        | 10      | 83 (83)        |
| 10    | 3        | CH\(_2\)Cl\(_2\) | 20        | none    | 84             |
| 11    | 3        | CH\(_2\)Cl\(_2\) | none       | 10      | 7              |
| 12    | 3        | CH\(_2\)Cl\(_2\) | none       | none    | 5              |
| 13    | 3        | CH\(_2\)Cl\(_2\) | 10         | none    | 72             |
| 14    | 24       | CH\(_2\)Cl\(_2\) | 10         | none    | 87             |
| 15    | 24       | CH\(_2\)Cl\(_2\) | 5          | none    | 91             |
| 16    | 24       | CH\(_2\)Cl\(_2\) | 2          | none    | 92 (88)        |
| 17    | 24       | CH\(_2\)Cl\(_2\) | 1          | none    | 68             |
| 18    | 48       | CH\(_2\)Cl\(_2\) | 1          | none    | 66             |
| 19\(^3\) | 24    | CH\(_2\)Cl\(_2\) | 2          | none    | 77             |

1 Reaction conditions: thioanisole 1a (0.20 mmol, 1 equiv.), iminoiodane 2a (0.24 mmol, 1.2 equiv.), and \(I_2\) (0–20 mol%) with TBAI (0–10 mol%) stirred in a solvent (2 mL) at room temperature for 3–48 h. 2 Yields of product 3a determined from \(^1\)H NMR spectra of reaction mixtures are shown (numbers in parentheses show isolated yield of 3a). 3 The reaction was performed under dark conditions.

2.2. Scope of Reactions

According to the optimized conditions with 2 mol% \(I_2\), we have investigated the conversion of various substituted sulfides 1 to the corresponding sulfilimines 3. In general, the reactions of thioanisoles 1a–i with either electron-donating or electron-withdrawing substituents using \((N\text{-tosylimino})\)-phenyl-\(\lambda^3\)-iodane 2a in the presence of \(I_2\) as the catalyst gave the corresponding \(N\)-tosyl sulfilimine compounds 3a–i in moderate to good yields (Table 2, entries 1–9). In the reaction of the sterically hindered o-chlorothioanisole 1f or the strong electron-withdrawing substituted p-nitrothioanisole 1i, products 3 were obtained in 59–69% yields (entries 6 and 9). The reaction of diphenylsulfide 1j, benzyl phenyl sulfide 1k, and dibenzyl sulfide 1l gave the respective products 3j–k in moderate yields (entries 10–12). This reaction also worked for the acyclic 1 or cyclic aliphatic sulfides 1m–p to give the desired sulfilimines 3m–p in good yields (entries 13–16). However, the reaction with the most steric bulky sulfide, \(di\)-\(tert\)-butyl sulfide 1q, afforded the desired product 3q in only 8% (entry 17). As expected, the reaction of 1a using imino-\(\lambda^3\)-iodanes 2b–d with different substituents afforded the corresponding sulfilimines 3r–s in moderate to good yields (entries 18–20). This metal-free procedure gave comparable or higher yields of sulfilimines compared to the previously reported metal catalyst mediated \(N\)-tosyl sulfonylimino group transfer reaction to sulfide from \((N\text{-tosylimino})\)-phenyl-\(\lambda^3\)-iodane [28–33]. Particularly, the scaled up reaction of 1a (1 mmol) under optimized conditions gave the desired product 3a in 76%.
Table 2. Metal-free imination reaction of thioanisoles 1 with imino-\(\lambda^3\)-iodane 2 in the presence of I\(_2\) \(^1\).

| Entry | 1 R\(^1\), R\(^2\) | 2 R\(^3\) | 3 Yield(%) \(^2\) |
|-------|----------------|--------|-----------------|
| 1     | 1a Ph, Me      | 2ap-Tol | 3a 88% (76%) \(^3\) |
| 2     | 1bp-tol, Me    | 2ap-Tol | 3b 72%           |
| 3     | 1cp-MeOC\(_6\)H\(_4\), Me | 2ap-Tol | 3c 78%           |
| 4     | 1dp-ClC\(_6\)H\(_4\), Me | 2ap-Tol | 3d 79%           |
| 5     | 1em-ClC\(_6\)H\(_4\), Me | 2ap-Tol | 3e 80%           |
| 6     | 1fo-ClC\(_6\)H\(_4\), Me | 2ap-Tol | 3f 68%           |
| 7     | 1gp-BrC\(_6\)H\(_4\), Me | 2ap-Tol | 3g 86%           |
| 8     | 1hp-NCC\(_6\)H\(_4\), Me | 2ap-Tol | 3h 86%           |
| 9     | 1ip-NO\(_2\)C\(_6\)H\(_4\), Me | 2ap-Tol | 3i 59%           |
| 10    | 1j Ph, Ph      | 2ap-Tol | 3j 56%           |
| 11    | 1k Ph, Bn      | 2ap-Tol | 3k 65%           |
| 12    | 1l Bn, Bn      | 2ap-Tol | 3l 66%           |
| 13    | 1mmBu, tBu     | 2ap-Tol | 3m 79%           |
| 14    | 1mmOctyl, nOctyl | 2ap-Tol | 3n 90%           |
| 15    | 1o -(CH\(_2\))\(_3\)- | 2ap-Tol | 3o 97%           |
| 16    | 1p -(CH\(_2\))\(_4\)- | 2ap-Tol | 3p 76%           |
| 17    | 1qBu, tBu      | 2ap-Tol | 3q 8%            |
| 18    | 1a Ph, Me      | 2bp-NO\(_2\)C\(_6\)H\(_4\) | 3r 92%           |
| 19    | 1a Ph, Me      | 2co-NO\(_2\)C\(_6\)H\(_4\) | 3s 51%           |
| 20    | 1a Ph, Me      | 2d Ph   | 3t 67%           |

\(^1\) All reactions were performed using sulfide 1 (0.20 mmol, 1 equiv.) and imino-\(\lambda^3\)-iodane 2 (0.24 mmol, 1.2 equiv.) using I\(_2\) (2 mol%) in dichloromethane (2.0 mL) at room temperature for 24 h. \(^2\) Yields of isolated products. \(^3\) Large scale experiment: thioanisole 1a (1.0 mmol, 1 equiv.) and imino-\(\lambda^3\)-iodane 2 (1.2 mmol, 1.2 equiv.) using I\(_2\) (2 mol%) in the dichloromethane (10 mL) were stirred for 24 h at room temperature.

Moreover, the reaction of triphenylphosphine 4 with (N-tosylimino)-phenyl-\(\lambda^3\)-iodane 2a under optimized conditions also allowed the transfer reaction of N-tosyl sulfonylimino group to give the (N-tosylimino)-triphenylphosphorane 5 in excellent yield (Scheme 2). The structure of 5 was confirmed by a single crystal X-ray crystallography (see Supplementary Materials) \(^37\). Compared to the previously reported preparation of 5 using imino-\(\lambda^3\)-iodanes, our reaction proceeds under very mild conditions and affords the product in higher yields \(^38,39\).

\[ \text{PPh}_3 + \text{PhINETS} \xrightarrow{\text{I}_2 (2 \text{ mol\%)}} \text{NTs} \]

Scheme 2. Transfer reaction of N-tosyl sulfonylimino groups to triphenylphosphine 4.

3. Discussion

3.1. Mechanistic Study

To clarify the mechanism of metal-free sulfonylimino group transfer reaction, we have performed several blank experiments (Scheme 3). Based on the previously reported experiment, a amidyl radical precursor like \(N,N\)-diiodotosylamide or a related species might be generated from (N-tosylimino)-phenyl-\(\lambda^3\)-iodane 2a with I\(_2\) \(^34-36,40\). A radical mechanism is plausible because
performing the reaction under dark conditions results in relatively low yields of product 3a (Table 1, entry 20). Therefore, the presence of a radical scavenger such as TEMPO or BHT in the reaction would be effective for identification of the reaction mechanism. In the case of both reactions, the desired sulfilimine 3a was detected in the reaction mixtures in low yields around 11% as compared to 88% without the radical scavenger, which implies that the amidyl radical species were involved under the reaction conditions. When benzene was added to the reaction instead of thioanisole 1a, azepine or N-phenyl-p-toluenesulphonamide was not detected and only p-toluenesulphonamide was recovered from the reaction mixtures. This result suggested that highly active nitrene species were not present under the reaction conditions.

3.2. Proposed Reaction Mechanism

From blank experiments and previously related results involving the amidyl radical species from imino-λ3-iodane 2a with I2 [34–36,40], we proposed the reaction mechanism of imination (Scheme 4). Initially, (N-tosylimino)-phenyl-λ3-iodane 2a reacted with I2 to produce N,N-diiodotosylamide 6 (or related species) followed by generation of the amidyl radical 7 and iodine radical under the reaction conditions. The generated amidyl radical 7 was trapped by thioanisole 1a to afford the intermediate compound 8, followed by loss of iodine radical to give the desired sulfilimine product 3a and reproduced I2. The regenerated I2 would continue the next catalytic cycle.

Scheme 4. Proposed reaction mechanism.
4. Materials and Methods

4.1. General Experimental Remarks

All reactions were performed under dry argon atmosphere with flame-dried glassware. All commercial reagents were ACS reagent grade and used without further purification. Dichloromethane was distilled from CaH₂ immediately prior to use. Melting points were determined in an open capillary tube with a Mel-temp II melting point apparatus. Infrared spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrophotometer, and peaks were reported in reciprocal centimeters (cm⁻¹). ¹H NMR spectra were recorded on a Varian Inova 500 and 300 MHz NMR spectrometer; °C NMR spectra were recorded on Varian Inova 500 and Varian 300 MHz NMR spectrometers at 125 and 75 MHz, respectively. Chemical shifts are reported in parts per million (ppm). ¹H and °C chemical shifts are referenced relative to tetramethylsilane. X-ray crystal analysis was performed by Rigaku RAPID II XRD Image Plate using graphite-monochromated MoKα radiation (λ = 0.71073 Å) at 173 K. (N-p-Tosylimino)phenyl-λ³-iodane 2a [41], (N-p-nosylimino)phenyl-λ³-iodane 2b [42], (N-o-nosylimino)phenyl-λ³-iodane 2c [43], and N-(phenylsulfonylimino)-phenyl-λ³-iodane 2d [44] were prepared according to the reported procedures.

4.2. General Procedure for Imination of Sulfides 1 with Imino-phenyl-λ³-iodane 2 in the Presence of I²

Imino-λ³-iodane 2 (0.12–0.24 mmol) was added at room temperature to a stirred mixture of sulfide 1 (0.10–0.20 mmol) and I² (0.002–0.004 mmol) in dichloromethane (1.0–2.0 mL). The reaction was stirred at room temperature for 24 h. After the reaction, 5% aqueous Na₂SO₃ (2.5–5.0 mL) was added to the mixture and the solution was extracted with ethyl acetate. The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was separated by column chromatography using the Hexane-EtOAc (1:1 to 0:100) to afford the pure product.

S-Methyl-S-phenyl-N-p-tosyl-sulfilimine 3a [45]. Reaction of thioanisole 1a (25 mg, 0.20 mmol) according to the general procedure afforded 52 mg (88%) of product 5a, isolated as a white solid: mp 129–130 °C (lit. [45]; mp 131.5–132 °C); ¹H NMR (500 MHz, CDCl₃): δ 7.73 (d, J = 8.5 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.56–7.46 (m, 3H), 7.16 (d, J = 8.5 Hz, 2H), 2.84 (s, 3H), 2.37 (s, 3H).

S-Methyl-S-(4-tolyl)-N-p-tosyl-sulfilimine 3b [29]. Reaction of methyl(4-tolyl)sulfide 1b (28 mg, 0.20 mmol) according to the general procedure afforded 44 mg (72%) of product 5b, isolated as a light brown oil; ¹H NMR (500 MHz, CDCl₃): δ 7.72 (d, J = 8.3 Hz, 2H), 7.57 (d, J = 8.5 Hz, 2H), 7.16 (d, J = 8.5 Hz, 2H), 2.82 (s, 3H), 2.39 (s, 3H), 2.35 (s, 3H).

S-Methyl-S-(4-methoxyphenyl)-N-p-tosyl-sulfilimine 3c [46]. Reaction of 4-methoxyphenyl(methyl)sulfide 1c (31 mg, 0.20 mmol) according to the general procedure afforded 51 mg (78%) of product 5c, isolated as a white solid: mp 147 °C (lit. [46]; mp 146–147 °C); ¹H NMR (500 MHz, CDCl₃): δ 7.68 (d, J = 7.3 Hz, 2H), 7.59 (d, J = 8.3 Hz, 2H), 7.13 (d, J = 7.3 Hz, 2H), 6.94 (d, J = 8.3 Hz, 2H), 3.81 (s, 3H), 2.80 (s, 3H), 2.33 (s, 3H).

S-Methyl-S-(4-chlorophenyl)-N-p-tosyl-sulfilimine 3d [46]. Reaction of 4-chlorophenyl(methyl)sulfide 1d (32 mg, 0.20 mmol) according to the general procedure afforded 52 mg (79%) of product 5d, isolated as a light yellow solid: mp 111–112 °C (lit. [46]; mp 112–113 °C); ¹H NMR (500 MHz, CDCl₃): δ 7.71 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 8.5 Hz, 2H), 7.45 (d, J = 8.5 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 2.84 (s, 3H), 2.36 (s, 3H).

S-Methyl-S-(3-chlorophenyl)-N-p-tosyl-sulfilimine 3e [47]. Reaction of 3-chlorophenyl(methyl)sulfide 1e (32 mg, 0.20 mmol) according to the general procedure afforded 53 mg (80%) of product 5e, isolated as a white solid: mp 137–138 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.68 (d, J = 8.0 Hz, 2H), 7.61 (s, 1H), 7.53 (d, J = 7.8 Hz, 1H), 7.44 (d, J = 7.8 Hz, 1H), 7.39 (t, J = 7.8 Hz, 1H), 7.15 (d, J = 8.0 Hz, 2H), 2.83 (s, 3H), 2.33 (s, 3H).

S-Methyl-S-(2-chlorophenyl)-N-p-tosyl-sulfilimine 3f [48]. Reaction of 2-chlorophenyl(methyl)sulfide 1f (32 mg, 0.20 mmol) according to the general procedure afforded 45 mg (68%) of product 5f, isolated as a white solid: mp 149–150 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.81 (d, J = 8.5 Hz, 2H), 7.73 (d, J = 8.0 Hz, 2H), 7.63 (s, 1H), 7.50 (d, J = 7.8 Hz, 1H), 7.44 (d, J = 7.8 Hz, 1H), 7.39 (t, J = 7.8 Hz, 1H), 7.17 (d, J = 7.8 Hz, 2H), 2.84 (s, 3H), 2.36 (s, 3H).
8.12 (d, J = 7.5 Hz, 1H), 7.71 (d, J = 8.3 Hz, 2H), 7.52–7.41 (m, 3H), 7.20 (d, J = 8.3 Hz, 2H), 2.87 (s, 3H), 2.36 (s, 3H).

\( S\)-Methyl-\( S\)-(4-bromophenyl)-\( N\)-p-tosyl-sulfilimine (3g) [49]. Reaction of 4-bromophenyl(methyl)sulfide 1g (41 mg, 0.20 mmol) according to the general procedure afforded 52 mg (70%) of product 3g, isolated as a white solid: mp 110–111 °C; \( ^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 7.70 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 9.0 Hz, 2H), 7.55 (d, J = 9.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 2.83 (s, 3H), 2.35 (s, 3H).

\( S\)-Methyl-\( S\)-(4-cyanophenyl)-\( N\)-p-tosyl-sulfilimine (3i) [50]. Reaction of 4-cyanophenyl(methyl)sulfide 1i (34 mg, 0.20 mmol) according to the general procedure afforded 40 mg (59%) of product 3i, isolated as a light brown solid: mp 159–160 °C; IR (neat) cm\(^{-1}\): 3096, 3035, 2929, 2856, 2234, 1400, 1144, 758; \( ^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 7.83 (d, J = 8.5 Hz, 2H), 7.74 (d, J = 8.5 Hz, 2H), 7.69 (d, J = 8.3 Hz, 2H), 7.17 (d, J = 8.3 Hz, 2H), 2.87 (s, 3H), 2.35 (s, 3H); \( ^{13}\)C NMR (75 MHz, CDCl\(_3\)): \( \delta \) 142.3, 141.6, 140.7, 133.5, 129.4, 126.6, 126.2, 117.1, 116.1, 38.8, 21.4; HRMS (ESI-TOF-positive mode): calcd for C\(_{15}\)H\(_{14}\)N\(_2\)NaO\(_2\)S\(_2\) ([M + Na]): 431.0394, found: 431.0382.

\( S\)-Methyl-\( S\)-(4-phenyl)-\( N\)-p-tosyl-sulfilimine (3j) [29]. Reaction of diphenylsulfide 1p (37 mg, 0.20 mmol) according to the general procedure afforded 40 mg (56%) of product 3j, isolated as a white solid: mp 108–109 °C (lit. [29]; mp 109.0–109.5 °C); \( ^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 7.74 (d, J = 9.0 Hz, 2H), 7.64–7.59 (m, 4H), 7.48–7.38 (m, 2H), 7.31–7.25 (m, 1H), 7.18 (t, J = 7.5 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 6.98 (d, J = 7.5 Hz, 2H), 4.34 (d, J = 12.8 Hz, 1H), 4.13 (d, J = 12.8 Hz, 1H), 2.32 (s, 3H).

\( S\)-Phenyl-\( S\)-benzyl-\( N\)-p-tosyl-sulfilimine (3k) [29]. Reaction of benzyl(phenyl)sulfide 1o (20 mg, 0.1 mmol) according to the general procedure afforded 24 mg (65%) of product 3k, isolated as a white solid: mp 149–150 °C (lit. [29]; mp 147–148 °C); \( ^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 7.62 (d, J = 8.0 Hz, 2H), 7.55–7.45 (m, 3H), 7.45–7.38 (m, 2H), 7.31–7.25 (m, 1H), 7.18 (t, J = 7.5 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 6.98 (d, J = 7.5 Hz, 2H), 4.34 (d, J = 12.8 Hz, 1H), 4.13 (d, J = 12.8 Hz, 1H), 2.32 (s, 3H).

\( S\)-S-Diphenyl-\( N\)-p-tosyl-sulfilimine (3l) [51]. Reaction of dibenzylsulfide 1l (43 mg, 0.20 mmol) according to the general procedure afforded 51 mg (66%) of product 3l isolated as a white solid: mp 187–189 °C (lit. [51]; mp 191–193 °C); \( ^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 7.43 (d, J = 8.0 Hz, 2H), 7.36–7.26 (m, 6H), 7.22 (d, J = 7.5 Hz, 4H), 6.97 (d, J = 8.0 Hz, 2H), 4.14 (d, J = 13.0 Hz, 2H), 4.06 (d, J = 13.0 Hz, 1H), 2.32 (s, 3H).

\( S\)-S-Dibutyl-\( N\)-p-tosyl-sulfilimine (3m) [49]. Reaction of dibutylsulfide 1m (29 mg, 0.20 mmol) according to the general procedure afforded 52 mg (79%) of product 3m, isolated as a white solid: mp 64–65 °C (lit. [49]; mp 77.5–78.5 °C); \( ^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 7.77 (d, J = 7.5 Hz, 2H), 7.23 (d, J = 7.5 Hz, 2H), 2.88–2.78 (m, 2H), 2.77–2.68 (m, 2H), 2.38 (s, 3H), 1.59–1.46 (m, 4H), 1.36–1.22 (m, 4H), 0.82 (t, J = 7.0 Hz, 6H).

\( S\)-S-Dioctyl-\( N\)-p-tosyl-sulfilimine (3n). Reaction of dioctylsulfide 1n (52 mg, 0.20 mmol) according to the general procedure afforded 77 mg (90%) of product 3n, isolated as a white solid: mp 82 °C; IR (neat) cm\(^{-1}\): 2918, 2858, 1534, 1439, 1313, 1268, 1223, 1171, 1161, 388, 21.4; HRMS (ESI-TOF-positive mode): calcd for C\(_{23}\)H\(_{42}\)NO\(_2\)S\(_2\) ([M + H]): 428.2657, found: 428.2665.

\( S\)-(\( S\)-Tosylimino)thietane (3o) [52]. Reaction of thietane 1o (15 mg, 0.20 mmol) according to the general procedure afforded 47 mg (97%) of product 3o, isolated as a white solid: mp 103–104 °C (lit. [52]; mp 98 °C); \( ^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 7.76 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 4.26–4.08 (m, 2H), 3.70–3.57 (m, 2H), 2.62–2.16 (m, 5H).

\( S\)-(\( S\)-Tosylimino)thiolane (3p) [53]. Reaction of tetrahydrothiophene 1p (18 mg, 0.20 mmol) according to the general procedure afforded 45 mg (76%) of product 3p, isolated as a white solid: mp
131–133 °C (lit. [53]); mp 132–134 °C; 1H NMR (300 MHz, CDCl₃): δ 7.79 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 3.19–3.00 (m, 4H), 2.58–2.42 (m, 2H), 2.40 (s, 3H), 2.11–1.93 (m, 2H); 13C NMR (75 MHz, CDCl₃): δ 143.6, 139.1, 129.5, 126.5, 54.5, 52.6, 25.6, 21.5.

S,S-Di-tert-buty1-N-p-tosyl-sulfilimine (3q) [54]. Reaction of di-tert-butylsulfide 1q (29 mg, 0.20 mmol) according to the general procedure afforded 5 mg (8%) of product 3q, isolated as a colorless oil; 1H NMR (500 MHz, CDCl₃): δ 7.86 (d, J = 8.8 Hz, 2H), 7.33 (d, J = 8.8 Hz, 2H), 2.46 (s, 3H), 1.43 (s, 18H); 13C NMR (75 MHz, CDCl₃): δ 144.5, 129.8, 129.5, 128.8, 49.6, 30.6, 30.9, 21.7.

S-Methyl-S-phenyl-N-p-nosyl-sulfilimine (3r) [55]. Reaction of thioanisole 1a (25 mg, 0.20 mmol) with imino-λ³-iodane 2b (97 mg, 0.24 mmol) according to the general procedure afforded 61 mg (92%) of product 3r, isolated as a white solid: mp 167 °C (lit. [55]; mp 164–165 °C); 1H NMR (300 MHz, CDCl₃): δ 8.20 (d, J = 8.7 Hz, 2H), 8.00 (d, J = 8.7 Hz, 2H), 7.70 (d, J = 8.1 Hz, 2H), 7.62–7.46 (m, 3H), 2.93 (s, 3H); 13C NMR (75 MHz, CDCl₃): δ 149.8, 149.2, 135.1, 133.1, 130.3, 127.4, 125.9, 124.0, 39.2.

S-Methyl-S-phenyl-N-o-nosyl-sulfilimine (3s). Reaction of thioanisole 1a (25 mg, 0.20 mmol) with imino-λ³-iodane 2d (86 mg, 0.24 mmol) according to the general procedure afforded 38 mg (67%) of product 3s, isolated as a colorless oil; IR (neat) cm⁻¹: 3096, 3065, 3023, 2926, 1540, 1370, 1305, 1149, 1124, 852, 766; 1H NMR (300 MHz, CDCl₃): δ 8.16 (d, J = 6.0 Hz, 1H), 7.79 (d, J = 8.1 Hz, 2H), 7.66–7.49 (m, 6H), 2.95 (s, 3H); 13C NMR (75 MHz, CDCl₃): δ 147.5, 137.1, 136.2, 132.2, 131.8, 130.3, 130.1, 125.8, 123.7, 39.1; HRMS (ESI-TOF-positive mode): calcd for C₁₃H₁₃N₂O₄S₂ ([M + H]+): 325.0317, found: 325.0319.

S-Methyl-S-phenyl-sulfansylnyl-sulfilimine (3t) [56]. Reaction of thioanisole 1a (25 mg, 0.20 mmol) with imino-λ³-iodane 2d (86 mg, 0.24 mmol) according to the general procedure afforded 38 mg (67%) of product 3t, isolated as a white solid: mp 89–90 °C; 1H NMR (300 MHz, CDCl₃): δ 7.85 (d, J = 7.8 Hz, 2H), 7.68 (d, J = 8.1 Hz, 2H), 7.57–7.32 (m, 6H), 2.85 (s, 3H).

4.3. Large Scale Reaction of 1a

Imino-λ³-iodane 2a (448 mg, 1.20 mmol) was added at room temperature to a stirred mixture of thioanisole 1a (124 mg, 1.00 mmol) and I₂ (5 mg, 0.02 mmol) in dichloromethane (10.0 mL). The reaction was stirred at room temperature for 24 h. After reaction, 5% aqueous Na₂S₂O₅ (25 mL) was added to the mixture and the solution was extracted with ethyl acetate. The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was separated by column chromatography using the Hexane-EtOAc (1:1) to afford the pure product 3a in 76% (223 mg).

4.4. Reaction of Triphenylphosphine 4

Imino-λ³-iodane 2a (90 mg, 0.24 mmol) was added at room temperature to a stirred mixture of triphenylphosphine 4 (52 mg, 0.20 mmol) and I₂ (1 mg, 0.004 mmol) in dichloromethane (2.0 mL). The reaction was stirred at room temperature for 24 h. After reaction, 5% aqueous Na₂S₂O₅ (2.5 mL) was added to the mixture and the solution was extracted with ethyl acetate. The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was separated by preparative TLC using the Hexane-EtOAc (1:1) to afford the pure product 5 in 98% (84 mg).

N-(p-Tosyl)iminotriphenylphosphorane (5) [39]. Isolated as a white solid: mp 190 °C (lit. [39]; mp 185.5–186.2 °C); 1H NMR (500 MHz, CDCl₃): δ 7.44 (dd, J = 12.3 Hz, 7.8 Hz, 2H), 7.57 (t, J = 7.8 Hz, 3H), 7.50 (d, J = 7.8 Hz, 2H), 7.46 (dt, J = 7.8 Hz, 3.0 Hz, 6H), 7.00 (d, J = 7.8 Hz, 2H), 2.23 (s, 3H).

Single crystals of product 5 suitable for X-ray crystallographic analysis were obtained by slow crystallization from dichloromethane solution. X-ray diffraction data for 5 were identical to the previously reported compound [37].

5. Conclusions

In conclusion, we have developed the metal-free methodology of the sulfonyl group transfer reaction of sulfides 1 or triphenylphosphine 4 using imino-λ³-iodanes 2 in the presence of a catalytic amount of I₂. The novel procedure gives the corresponding (N-sulfonyl)-sulfilimines
3 or (N-tosylimino)-triphenylphosphorane 5 in moderate to good yields. According to the blank experiment study, the reaction mechanism most likely involved the amidyl radical species, which are generated from imino-λ3-iodanes 2 and I2.

**Supplementary Materials:** The following are available online. The 1H and 13C NMR spectra of 3a–t, 5, and X-ray structure data of 5 can be found in the SI.

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**Sample Availability:** Samples of the compounds 2a and 3a are available from the authors.

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