



## Solubilization of the Primary Nitrene Sources (Tosyliminoiodo)arenes (ArINTs)

Dainius Macikenas, Bindu V. Meprathu, and John D. Protasiewicz\*

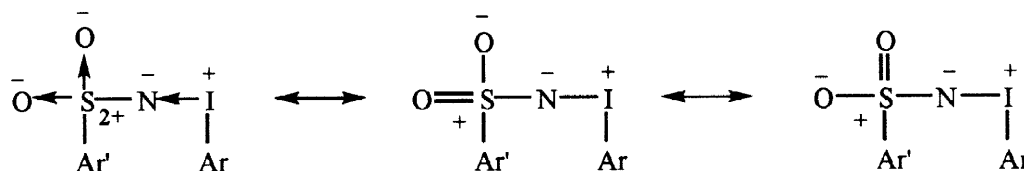
Department of Chemistry  
Case Western Reserve University  
Cleveland, Ohio 44106-7078

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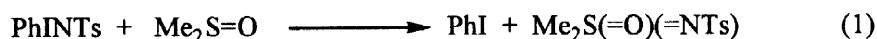
**Abstract:** The nitrene precursors ArINTs (Ts = *p*-toluenesulfonyl; Ar = phenyl (1), Ar = *o*-Tolyl (2), and Ar = Mesityl (3)) can be fully solubilized in organic media upon addition of organic *N*-oxides. <sup>1</sup>H-NMR spectroscopy of CDCl<sub>3</sub> solutions of PhINTs and excess Me<sub>3</sub>NO reveals rapid exchange of free and coordinated Me<sub>3</sub>NO to the hypervalent iodine species. The implications of this phenomenon on nitrene transfer processes are discussed.

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Many transition metal catalyzed processes employ PhINTs (Ts = *p*-toluenesulfonyl) as the primary nitrene source for nitrene insertion and addition reactions, and in particular, for aziridination reactions of olefins. This highly employed organoiodine(III) species is insoluble in common organic media in which it does not react, and thus its solution chemistry is rather ill-defined.<sup>1</sup> We and others have been studying how the nature of the aggregation of ArINSO<sub>2</sub>Ar' in the solid state is influenced by the character of the aryl groups.<sup>2-5</sup> A wide array of structural polymers have been identified, each utilizing various combinations of secondary I...O and I...N bonds. Secondary bonding of this type brings the atoms of opposite charge in close proximity to one another, and is exemplified by the resonance structures shown below for this class of materials.<sup>5</sup> While

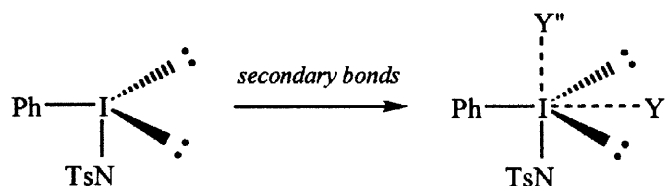


ArINSO<sub>2</sub>Ar' can be dissolved in DMSO and NMR spectra recorded, such solutions, however, rapidly yield the transylidation product shown in equation 1.<sup>6</sup> We reasoned that the ability of DMSO to accomplish this solubilization, albeit temporary, was due to the strong S→O dipole in DMSO. We also reasoned that materials containing related dipoles with strongly negatively charged oxygen atoms might break up secondary bonding between the I(III) centers and the sulfonyl oxygen atoms in ArINSO<sub>2</sub>Ar'. Tertiary amine *N*-oxides seemed

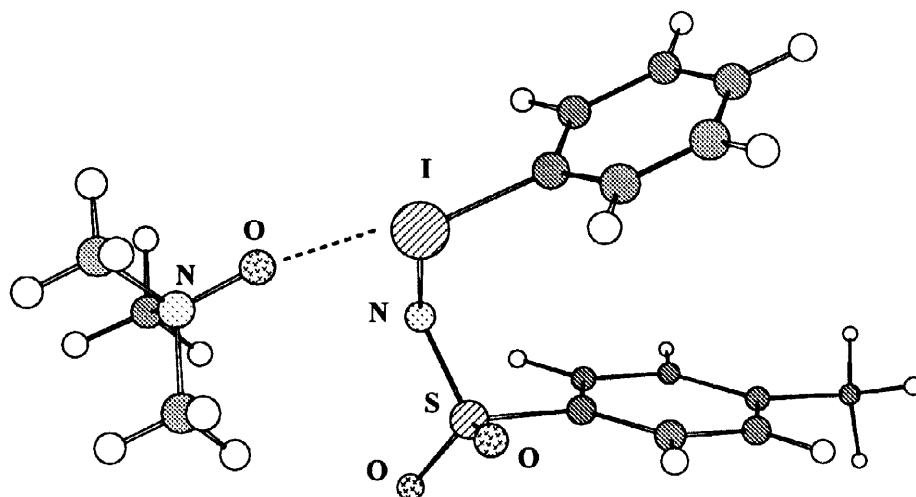


particularly attractive in this regard. Indeed, we have found that addition of either Me<sub>3</sub>NO or 4-methylmorpholine *N*-oxide will promote solubilization of ArINTs (Ar = Ph, *o*-Tolyl, Mesityl) in CH<sub>2</sub>Cl<sub>2</sub>,

CHCl<sub>3</sub> and MeCN. The minimal ratios for complete solubilization of PhINTs by Me<sub>3</sub>NO in CH<sub>2</sub>Cl<sub>2</sub> is 1:1, for *o*-TolylINTs is 1:1.3, for MesINTs is 1:0.6. Complete solubilization of PhINTs by Me<sub>3</sub>NO in CHCl<sub>3</sub> requires more Me<sub>3</sub>NO (minimal ratio ~1:1.7). Fairly concentrated solutions of PhINTs•Me<sub>3</sub>NO can be prepared in CH<sub>2</sub>Cl<sub>2</sub> (ca ~0.2 M) which retain their oxidizing ability (as ascertained by iodometric titrations) for a limited amount of time. Pyridine *N*-oxide, being less basic than Me<sub>3</sub>NO, required about 5 equivalents to fully dissolve PhINTs in CH<sub>2</sub>Cl<sub>2</sub>. Triphenylphosphine oxide was even less effective. Such ArINTs•Me<sub>3</sub>NO solutions retain the strong yellow color characteristic of ArINTs, but decay to form ArI and H<sub>2</sub>NTs (rate of decomposition depends on the dryness of the solvent). Analysis of freshly prepared solutions by <sup>1</sup>H NMR (CDCl<sub>3</sub>) shows resonances attributable to PhINTs and a contact shifted resonance for the methyl groups of Me<sub>3</sub>NO.<sup>7</sup> Ratios greater than unity for Me<sub>3</sub>NO:ArINTs show only a single broadened resonance for the methyl groups of Me<sub>3</sub>NO, indicating rapid exchange of free and “coordinated” Me<sub>3</sub>NO. The solid state aggregation of ArINTs reveal the shortest I...O secondary bonds in such structures are located approximately *trans* to the nitrogen atom to complete a pseudo trigonal bipyramidal ( $\psi$ -TBP) geometry for the iodine atom.<sup>5</sup>



Crystals of such an adduct have not yet been obtained, but molecular modeling of a PhINTs•Me<sub>3</sub>NO adduct (MNDO/d) yielded a minimized structure having a T-shaped geometry by the iodine atom (Figure 1).<sup>8-11</sup> Unexpectedly, the lowest energy structure contained the N-O dipole directed at the Y' site ( $d_{I...O} = 2.41$  Å),



**Figure 1.** MNDO/d minimized structure for PhINTs•Me<sub>3</sub>NO adduct.

rather than being trans to the most electronegative ligand of the iodonium species. The structure having secondary bonding at the Y'' position was 3.3 kcal/mole higher in energy ( $d_{I...O} = 2.65 \text{ \AA}$ ). A structure of a carbene adduct of organoiodine(III),  $\text{PhIC}(\text{SO}_2\text{CF}_3)_2$ , has appeared in which the iodine atom binds to a dimethylsulfoxide in the Y'' site at a distance of  $2.564(4) \text{ \AA}$ .<sup>12</sup> This particular ylid displays enhanced stability relative to ArINTs, requiring 2 months for transylidation to dimethylsulfoxide to occur.

Catalytic systems using PhINTs are performed in a heterogeneous manner as a result of the high insolubility of PhINTs. For systems that utilize chiral metal complexes for enantioselective aziridination, homogeneous conditions may offer chances for increased enantioselectivities and turnover numbers, especially if reactions can be carried out at lower temperatures.<sup>13</sup> Additionally, reactions which are performed in dichloromethane are often plagued by metal catalyzed hydrolysis of PhINTs to PhIO and  $\text{H}_2\text{NTs}$ , and often necessitate the use of molecular sieves in the reaction mixtures to maintain anhydrous conditions.<sup>14,15</sup> Solubilization may provide more reactive nitrene precursors for interaction with metal centers, thus the influence of *N*-oxides on nitrene transfer was investigated. Reaction of PhINTs with PhSMe, PhSCH<sub>2</sub>Ph, and *p*-TolylSMe in  $\text{CH}_2\text{Cl}_2$  led to the corresponding sulfilimines  $\text{ArS}(=\text{NTs})\text{R}$  in 50-60% isolated yields.<sup>16</sup> In the presence of 1.5 equivalents of  $\text{Me}_3\text{NO}$ , however, no sulfilimines are formed and the sulfides could be recovered. The inhibitory effects are less dramatic for either pyridine *N*-oxide or  $\text{Ph}_3\text{PO}$ , with reduced yields of 31% and 20% being realized for reaction of PhSCH<sub>2</sub>Ph with PhINTs, respectively. Attempts to induce asymmetric nitrene transfer to ArSR by solubilization with nicotine-*N,N'*-dioxide<sup>17</sup> resulted in recovery of unreacted ArSR. Parallel studies on the influence of these *N*-oxides ( $\text{Me}_3\text{NO}$ , pyridine *N*-oxide, nicotine-*N,N'*-dioxide) upon the aziridination of styrene by PhINTs catalyzed by  $[\text{Mn}(\text{salen})\text{OAc}]$  complex (salen = *N,N'*-bis(salicyldine)-1,2-phenylenediamine) determined that aziridination is completely inhibited by these materials.<sup>18</sup> By contrast, pyridine *N*-oxide and 4-phenylpyridine *N*-oxide have been found to improve manganese(salen) catalyzed chiral aziridinations using PhINTs.<sup>19,20</sup> More recently substantial beneficial effects of adding 5% sulfolane to rhodium catalyzed nitrene transfers from PhINNs (Ns = *p*-nitrophenylsulfonyl) have been reported.<sup>21</sup> Related beneficial effects of *N*-oxides for manganese(salen) catalyzed olefin epoxidations have long been used to advantage, and explained by either modifying the nature of the catalysts or by acting as a phase transfer catalyst.<sup>22,23</sup> We have found that addition of  $\text{Me}_3\text{NO}$  to PhIO, however, can not bring about complete solubilization of PhIO in  $\text{CH}_2\text{Cl}_2$  as found for ArINTs. The data presented here offers yet another potential influence of *N*-oxides in reactions using organoiodine(III) reagents as primary nitrene or oxo sources.

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