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Hypervalent Iodine Nitrene Precursors Bearing *N*-Heterocyclic Rings

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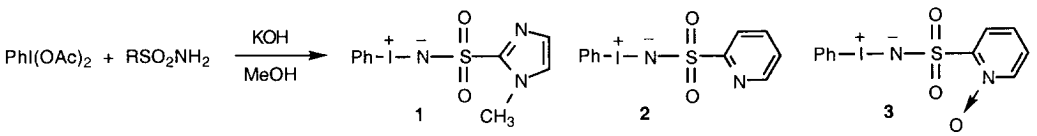
Abstract: *Novel nitrene precursors of the form $PhINSO_2R$ (R = 1-methylimidazolyl (**1**), pyridine (**2**), 2-pyridine N-oxide (**3**)) have been prepared that contain heterocyclic sulfonamide residues. These new iodinanes are evaluated as sources of the corresponding heterocycle-containing nitrenes in aziridination and sulfimidation reactions.*

Nitrogen transfer reactions are an important class of transformations in organic synthesis and the need for more general nitrenoid precursors is increasing. In particular, much recent attention has been focused on the Cu-catalyzed aziridination of olefins using PhINTs (Ts = *p*-toluenesulfonyl). Previous work has shown that PhINNs (Ns = *p*-nitrophenylsulfonyl) could offer increased yields in copper catalyzed aziridinations and rhodium catalyzed imination reactions.[1] Screening of iodinanes of the form $PhINSO_2Ar$ for nitrene transfer applications has shown that both chemical yields and enantioselectivities of aziridines can be influenced by choice of the nitrene precursor.[2] Despite efforts focused on modifying the arylsulfonyl group in $PhINSO_2Ar$, little work has been reported on classes of nitrogen sources that incorporate simple heterocyclic compounds. Recent application of *N*-chloro *N*-sodio salts of adenine derivatives (Chloramine-T analogues) as nitrenoid sources for the osmium-catalyzed aminohydroxylations of olefins illustrates the potential for other types of nitrogen transfer reagents.[3]

In the course of our study of hypervalent iodine based nitrene sources we have synthesized new imidazolyl- and pyridyl- derived (arylsulfonylimino)iodobenzenes **1-3** (Scheme 1). These materials are prepared

Scheme 1



as white to off-white solids in good yields by standard methods[4] with $TsNH_2$ being replaced by the appropriate sulfonamides.[5] Like PhINTs, these species are also insoluble in common unreactive solvents, and melt with explosive decomposition. The reactions of **1-3** with $PhSCH_2Ph$ and styrene under the influence of CuOTf catalysis were examined (Scheme 2). Sulfimidation of $PhSCH_2Ph$ using iodinanes **1** and **2** is slow and affords moderate yields of the new sulfimides **4** and **5**. Compounds **1-3** are interesting as primary nitrene sources for copper catalyzed nitrenoid transfer processes owing to the potential of the heterocyclic rings to offer copper binding sites and thus influence the nature of the transfer reactions. The moderate yields may reflect this feature of these systems, or the fact that the products **4** and **5** could also competitively chelate to Cu centers. Aziridinations of styrene using **1** and **2** were more effective and yielded the new aziridines **6** and **7**. Iodinane **3**, however, was totally ineffective as a nitrene precursor for both processes and extended reaction times yielded the sulfonamide as a product of hydrolysis. The new aziridines and sulfimides were isolated in high degree of purity and characterized by standard spectroscopic means.[6] The poor performance of iodinane **3** in the nitrene transfer

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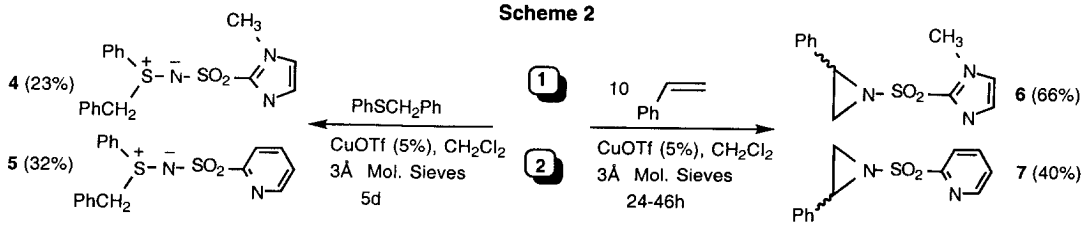
reactions follows the inhibitory effect of organic *N*-oxides in reactions using PhINTs.[7] In conclusion three new *N*-heterocycle containing nitrene sources have been prepared and two of these were shown to be effective in CuOTf catalyzed nitrene transfer reactions. These new heteroaromatic nitrene sources can potentially chelate to

Scheme 2



metal catalysts and perhaps be expected to exhibit substantially different reactivity than their non-heteroaromatic counterparts. It may be possible to exploit chelation in these reactive metal-bound nitrene intermediates in order to optimize chemo- and enantioselective heteroatom transfer processes.

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4) Following the procedure by Yamada, Y.; Yamamoto, T.; Okawara, M. *Chem. Lett.* **1975**, 361-362. **1**: 38%, Mp. 113°C (detonates), ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.87 (d, 2H, J = 7.1 Hz), 7.56 (t, 1H, J = 7.3 Hz), 7.45 (m, 2H), 7.11 (s, 1H), 6.83 (s, 1H), 3.63 (s, 3H). **2**: 54%, Mp. 148°C (det.), ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.54 (m, 1H), 7.89-7.97 (m, 3H), 7.75 (d, 1H, J = 7.8 Hz), 7.45-7.54 (m, 4H). **3**: 58%, Mp. 139-142°C (detonates), ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.45 (m, 1H), 8.05 (d, 2H, J = 7.1 Hz), 7.97 (m, 1H), 7.64-7.51 (m, 5H).

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6) (a) *N*-(Imidazol-1-methyl-2-sulfonyl)phenylbenzylsulfimide (**4**): ^{1}H NMR (200MHz, $CDCl_3$) δ 7.6-6.8 (m, 11H), 4.89 (d, 1H, J = 12.4 Hz), 4.39 (d, 1H, J = 12.4Hz), 3.90 (s, 3H). HRMS M^+ [$C_{17}H_{17}N_3O_2S_2^+$] calc. 359.07623 found 359.0763. *N*-(*o*-Pyridinesulfonyl)phenylbenzylsulfimide (**5**): ^{1}H NMR (300MHz, $CDCl_3$) δ 8.40 (m, 1H,), 7.98 (d, 1H, J = 8.1Hz), 7.79 (m, 1H), 7.6-6.9 (m, 11H), 4.61 (d, 1H, J= 12.4 Hz, -CH_2-), 4.24 (d, 1H, J= 12.4 Hz, -CH_2-). HRMS M^+ [$C_{18}H_{16}N_2O_2S_2^+$] calc. 356.0653 found 356.06507. (b) *N*-(Imidazol-1-methyl-2-sulfonyl)-2-phenylaziridine (**6**): ^{1}H NMR (300MHz, $CDCl_3$) δ 7.32-7.18 (m, 5H), 7.15 (s, 1H), 7.04 (s, 1H), 4.00 (s, 3H), 3.95 (dd, 1H, J = 7.2 Hz, J = 4.6 Hz), 3.16 (d, 1H, J = 7.2Hz), 2.50 (d, 1H, J = 4.6Hz). HRMS MH^+ [$C_{12}H_{13}N_3O_2SH^+$] calc. 264.08065 found 264.08058. *N*-(*o*-Pyridinesulfonyl)-2-phenylaziridine (**7**): ^{1}H NMR (200MHz, $CDCl_3$) δ 8.72 (m, 1H), 8.11 (m, 1H), 7.92 (m, 1H), 7.52 (m, 1H), 7.25 (m, 5H), 4.00 (dd, 1H, J = 7.2Hz, J = 4.7Hz), 3.20 (d, 1H, J = 7.3 Hz), 2.52 (d, 1H, J =4.7Hz). HRMS MH^+ [$C_{12}H_{11}N_2O_2S_2H^+$] calc. 261.0698 found 261.06956.

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