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IODOARENE-MEDIATED CYCLIZATION OF *N*-METHOXY-2-ARYLETHANESULFONAMIDES WITH OXONE

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Abstract - Iodoarene-mediated cyclization of *N*-methoxy-2-arylethane-sulfonamides with Oxone® was carried out to form the corresponding *N*-methoxy-3,4-dihydro-2,1-benzothiazine-2,2-dioxides in moderate to good yields in acetonitrile. In this reaction, reactive hypervalent iodine species, *i.e.,* [(hydroxy)(tosyloxy)iodo]arenes, were formed in situ and reacted with *N*-methoxy-2-arylethanesulfonamides to form the corresponding *N*-methoxy-3,4-dihydro-2,1-benzothiazine-2,2-dioxides in an electrophilic manner on the aromatic ring. Ion-supported PhI could be also used for the same cyclization of *N*-methoxy-2-arylethanesulfonamides with Oxone® to provide *N*-methoxy-3,4-dihydro-2,1-benzothiazine-2,2-dioxides in good to moderte yields. However, ion-supported PhI could not be reused for the same reaction. The same iodoarene-mediated cyclization of *N*-methoxy-3-phenylpropanamide and *N*-methoxy-4-phenylbutanamide with Oxone® was also carried out to form the corresponding *N*-methoxybenzolactams in moderate yields.

Dedicated to Professor Dr. A. Eschenmoser on the occasion of his 85th birthday

INTRODUCTION

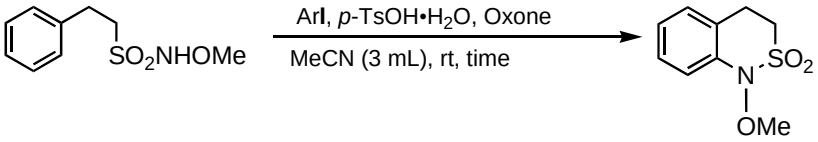
Sulfonamides possess potent biological activities.[1] In particular, cyclic sulfonamides (sultams) are important as therapeutic compounds[2] and chiral auxiliaries.[3] Especially, 3,4-dihydro-2,1-benzothiazine-2,2-dioxides (benzosultams) have potent biological activities, such as lipoxygenase inhibitory activity and are used as drugs for treating heart diseases.[4] Today, there are four established methods for the construction of the 3,4-dihydro-2,1-benzothiazine-2,2-dioxide skeleton, *i.e.*, cyclization of *N*-benzyl-*N*-methanesulfonyl-(*o*-chloromethyl)aniline with NaH,[5a] pyrolysis of 2-arylethanesulfonyl

azides,[5b] cyclization of *N*-phenylsulfamoylacetic acid with PPA and subsequent reduction of the carbonyl group,[5c] and cyclization of 2-(*o*-aminophenyl)ethanesulfonic acid with $POCl_3$.[5d] However, those methods require quite acidic or basic conditions and many steps from commercially available materials, and the yields of the cyclized products are generally low. In our laboratory, novel methods for the preparation of heterocyclic compounds with hypervalent iodine reagents under photolytic conditions with a tungsten lamp have been studied to realize reactions that proceed under mild conditions with clean transformation and low toxicity.[6] Previously, we reported a new method for preparation of *N*-methyl-3,4-dihydro-2,1-benzothiazine-2,2-dioxide *via* a radical pathway using (diacetoxyiodo)arenes and molecular iodine under photochemical conditions.[7] However, the *N*-demethylation of *N*-methyl-3,4-dihydro-2,1-benzothiazine-2,2-dioxide to free NH group was impossible. On the other hand, the cyclization of *N*-methoxy-3-arylpropanamide with [bis(trifluoroacetoxy)iodo]benzene is known to provide benzolactams *via* *N*-acylnitrenium ions.[8] We have reported the preparation of *N*-methoxy-3,4-dihydro-2,1-benzothiazine-2,2-dioxides from *N*-methoxy-2-arylethanesulfonamides *via* an ionic pathway with [(hydroxy)(tosyloxy)iodo]arenes.[9] Here, the formed *N*-methoxy-3,4-dihydro-2,1-benzothiazine-2,2-dioxide could be smoothly converted into N-free 3,4-dihydro-2,1-benzothiazine-2,2-dioxides by reduction with SmI_2. On the other hand, recently, the PhI-catalyzed synthetic study with *m*-chloroperbenzoic acid (*m*CPBA) or peracetic acid,[10] Oxone®,[11] and H_2O_2[12] has become very popular. We have also reported the direct and efficient one-pot preparation of various [(hydroxy)(sulfonyloxy)iodo]arenes from iodoarenes with *m*CPBA and sulfonic acids at room temperature,[13] the PhI-catalyzed α-tosyloxylation of ketones with *m*CPBA and *p*-toluenesulfonic acid,[14] the efficient conversion of ketones into α-tosyloxyketones with *m*CPBA and *p*-toluenesulfonic acid in the presence of a catalytic amount of ion-supported PhI in [emim]OTs,[15] and the direct preparation of 2,5-disubstituted and 2,4,5-trisubstituted oxazoles by the reaction of alkyl aryl ketones with TfOH and *m*CPBA in the presence of iodoarene in acetonitrile, propionitrile, butyronitrile, and isobutyronitrile.[16] More recently, we have reported the PhI-catalyzed cyclization[17] and the ion-supported PhI-catalyzed cyclization[18] of *N*-methoxy-2-arylethanesulfonamides with *m*CPBA in 2,2,2-trifluoroethanol to form the corresponding *N*-methoxy-3,4-dihydro-2,1-benzothiazine-2,2-dioxides in moderate to good yields. However, in those reactions, expensive *m*CPBA is required. Here, as part of our study of the PhI-mediated organic synthesis with Oxone®,[19] we would like to report the PhI- and ion-supported PhI-mediated preparation of *N*-methoxy-3,4-dihydro-2,1-benzothiazine-2,2-dioxides from *N*-methoxy-2-arylethanesulfonamides with Oxone® in acetonitrile.

When Oxone® was added to *N*-methoxy-2-phenylethanesulfonamide in the presence of iodobenzene and *p*-toluenesulfonic acid monohydrate in acetonitrile under various reaction conditions, *N*-methoxy-3,4-dihydro-2,1-benzothiazine-2,2-dioxide was formed, as shown in Table 1 (entries 2~10). In the absence of iodobenzene and *p*-toluenesulfonic acid monohydrate, *N*-methoxy-3,4-dihydro-2,1-benzothiazine-2,2-dioxide was not formed at all and the starting material was recovered quantitatively (entry 1). As shown in entries 1~10, iodobenzene plays an important role and

[(hydroxy)(tosyloxy)iodo]benzene is formed in situ as a reactive hypervalent iodine species by the reaction of iodobenzene, *p*-toluenesulfonic acid monohydrate, and Oxone®.[19b] The best result was obtained when 1.0 eq. of iodobenzene, 3.0 eq. of *p*-TsOH•H_2O, 3.0 eq. of Oxone®, and 0.1 mL of 2,2,2-trifluoroethanol in acetonitrile (3 mL) were used (entry 4). However, iodobenzene could not be recovered efficiently probably due to the over-oxidation to PhI(V).[20] When the effects of iodoarenes, such as iodobenzene, 4-iodotoluene, 4-chloroiodobenzene, 4-iodoanisole, 4-iodobenzoic acid, and 3-trifluoromethyl-1-iodobenzene, were compared (entries 3, 11~15), iodobenzene showed the best reactivity, while 4-iodoanisole and 4-iodobenzoic acid did not work at all (entries 13, 14). Based on these results, *N*-methoxy-2-arylethanesulfonamides, *i.e.*, *p*-methyl, *p*-chloromethyl, *p*-fluoro, *p*-chloro, and *p*-bromo-substituted 2-phenylethanesulfonamides, were treated with Oxone® in the presence of iodobenzene and *p*-toluenesulfonic acid monohydrate in acetonitrile to provide

Table 1. Cyclization of *N*-Methoxy-2-phenylethanesulfonamides to Benzosultam Using Oxone

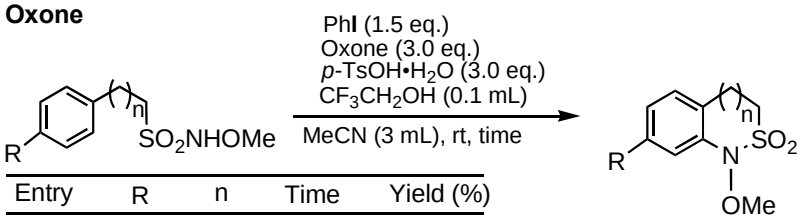


Entry	ArI (eq.)	*p*-TsOH•H_2O (eq.)	Oxone (eq.)	Time	Yield (%)
1	none	none	2.2	24 h	0 (94)[a]
2	PhI (0.1)	3.0	3.0	24 h	<1 (89)[a]
3	PhI (1.0)	3.0	3.0	8 h	75
4	PhI (1.0)	3.0	3.0	6 h[b]	82
5	PhI (1.0)	3.0	3.0	24 h	66
6	PhI (0.5)	3.0	3.0	8 h	48 (43)[a]
7	PhI (1.0)	1.5	1.5	8 h	47 (37)[a]
8	PhI (1.0)	1.5	3.0	8 h	44 (37)[a]
9	PhI (1.0)	3.0	1.5	8 h	51 (22)[a]
10	PhI (1.0)	5.0	5.0	8 h	65
11	4-MeC_6H_4I (1.0)	3.0	3.0	8 h	68 [22][c]
12	4-ClC_6H_4I (1.0)	3.0	3.0	8 h	59 [13][c]
13	4-$MeOC_6H_4$I (1.0)	3.0	3.0	8 h	0 (52)[a]
14	4-$HO_2CC_6H_4$I (1.0)	3.0	3.0	8 h	0 (76)[a]
15	3-$CF_3C_6H_4$I (1.0)	3.0	3.0	8 h	31 (57)[a]

[a] Yield of recovered sulfonamide.
[b] CF_3CH_2OH (0.1 mL) was added.
[c] Yield of recovered iodoarene.

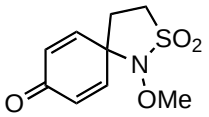
7-substituted *N*-methoxy-3,4-dihydro-2,1-benzothiazine-2,2-dioxides in good to moderate yields, as shown in Table 2 (entries 1~5). Meanwhile, *N*-methoxy-2-(4'-methoxyphenyl)ethanesulfonamide provided spiro compound **1** in good yield through the electrophilic cyclization at the ipso-position of the aromatic ring by the nitrogen atom

Table 2. Cyclization of *N*-Methoxy-2-arylethanesulfonamides to Benzosultams Using Oxone



Entry	R	n	Time	Yield (%)
1	Me	1	6 h	57
2	$ClCH_2$	1	6 h	79
3	F	1	24 h	36
4	Cl	1	6 h	49
5	Br	1	8 h	63
6	MeO	1	6 h	71[a]
7	H	0	24 h	28
8	H	0	8 h	31
9	H	2	24 h	0

[a] Yield of spiro compound **1**.

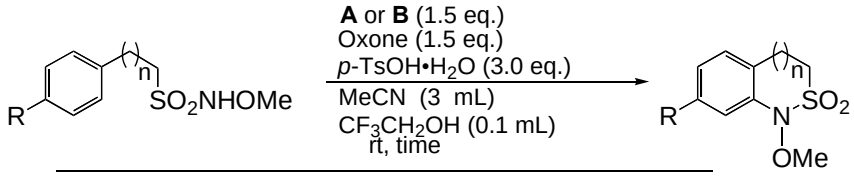


1

of the sulfonamide (entry 6). On the other hand, the same reaction with *N*-methoxy-phenylmethanesulfonamide gave the corresponding five-membered benzosultam in low yields, and the same treatment of *N*-methoxy-3-phenylpropanesulfonamide did not provide the corresponding seven-membered benzosultam at all, although the starting materials were consumed completely in these reactions (entries 7~9).

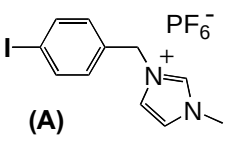
Then, to check whether or not PhI could be reused, the cyclization of *N*-methoxy-2-arylethane-sulfonamides with ion-supported PhI, 1-methyl-3-(4'-iodobenzyl)imidazolium phosphorushexafluoride (**A**) and (4-iodobenzyl)trimethylammonium trifluoromethanesulfonate (**B**), in acetonitrile was carried out and the corresponding 7-substituted 3,4-dihydro-2,1-benzothiazine-2,2-dioxides were produced in good to moderate yields.

Table 3. Cyclization of *N*-Methoxy-2-arylethanesulfonamides with Ion-supported PhI with Oxone

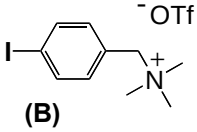


entry	R	n	Time (h)	Yields (%) A	Yields (%) B
1	H	1	12	84	72
2	$ClCH_2$		12	84	67
3	Me		15	53	54
4	Br		12	68	49
5	Cl		12	52	36
6	F		12	55	37
7	MeO		12	88[a]	12[a]
8	H	0	12	22	-
9	H	2	12	0	-

[a] Yield of spiro compound **1**.



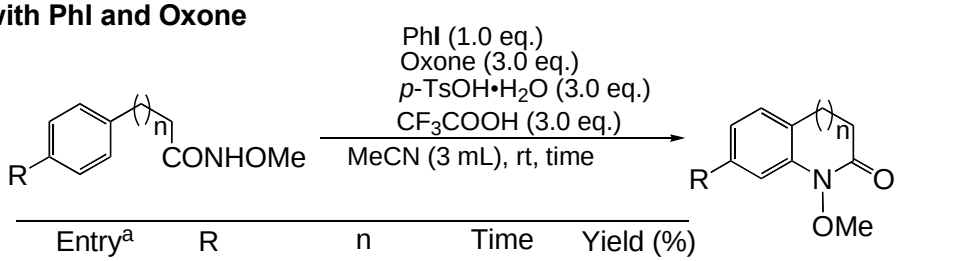
(A)



(B)

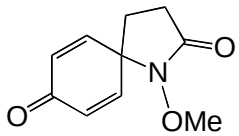
Here, ion-supported PhI (**A**) demonstrated better reactivity than (**B**), as shown in Table 3. When *N*-methoxy-2-(4'-methoxyphenyl)ethanesulfonamide was used under the same conditions, spiro compound **1** was obtained again in high yield (entry 7). However, after the extraction of the reaction mixture with ether, the precipitated ion-supported PhI (**A**) and (**B**) could not be reused, probably due to over-oxidation to inert ion-supported PhI(V) by Oxone®. Actually, 4-iodotoluene and 4-chloroiodobenzene were recovered in low yields in Table 1 (entries 11, 12).

Table 4. Cyclization of *N*-Methoxy-3-arypropanamides and *N*-Methoxy-4-arylbutanamide with PhI and Oxone



Entry[a]	R	n	Time	Yield (%)
1	H	0	8 h	15
2	H	1	8 h	45
3	H	2	24 h	32
4	OMe	1	8 h	50[a]

[a] Yield of spiro compound **2**.



2

When the present reaction was used for the same cyclization of *N*-methoxy-3-phenylpropanamide and *N*-methoxy-4-phenylbutanamides, the yields of the benzolactams were decreased, as shown in Table 4. Especially, the yield of five-membered benzolactam was extremely poor when *N*-methoxy-2-phenylethanamide was used as the strating material (entries 1~3). On the other hand, when *N*-methoxy-3-(4'-methoxyphenyl)propanamide was used under the same conditions, spiro compound **2** was obtained again in 50% yield (entry 4).[8b,10l] In these reactions, the starting materials were consumed completely.

In conclusion, the PhI-mediated preparation of *N*-methoxy-3,4-dihydro-2,1-benzothiazine-2,2-dioxides by the reaction of *N*-methoxy-2-arylethanesulfonamides with Oxone® in acetonitrile proceeded efficiently depending on the substituent of the aromatic ring. However, ion-supported PhI (**A**) and (**B**) could not be reused for the same reaction, in contrast to an PhI-*m*CPBA system.[18] When the reactivity and efficiency of an PhI-*m*CPBA system[18] and an PhI-Oxone® system (present reaction) in the cyclization of *N*-methoxy-2-arylethanesulfonamides were compared, the former system was found to be better than the latter one in view of the amounts of *p*-TsOH•H_2O and oxidant used. However, the advantages of PhI-mediated cyclization with Oxone® are that the oxidation reactions can be carried out under metal-free conditions and that Oxone® is an inorganic oxidant and is much less expensive than *m*CPBA.

EXPERIMENTAL

General: ^{1}H NMR and ^{13}C NMR spectra were obtained with JEOL-JNM-GSX-400, JEOL-JNM-LA-400, and JEOL-JNM-LA-500 spectrometers. Chemical shifts are expressed in ppm downfield from TMS in δ units. Mass spectra were recorded on JEOL-HX-110 and JEOL-JMS-AT Ⅱ 15 spectrometers. IR spectra were measured with a JASCO FT/IR-4100 spectrometer. Melting points were determined with a Yamato Melting Point Apparatus Model MP-21. Silica gel 60 (Kanto Kagaku Co.) was used for column chromatography and Wako-gel B-5F was used for preparative TLC.

General procedure for preparation of 1-methoxy-3,4-dihydro-2,1-benzothiazine 2,2-dioxides with PhI-Oxone® system:

To a solution of *N*-methoxy-2-phenylethanesulfonamide (0.5 mmol), PhI (0.5 mmol) *p*-TsOH·H_2O (1.5 mmol), and CF_3CH_2OH (0.1 mL) in MeCN (3 mL) was added Oxone® ($KHSO_5$ 45%, 1.5 mmol). The mixture was stirred for 6 h at rt under an argon atmosphere. After the reaction, the reaction mixture was poured into sat. aq Na_2SO_3 solution and extracted with acetonitrile (3 × 20 mL). The organic layer was dried over Na_2SO_4. After filtration and removal of the solvent under reduced pressure, the residue was purified by preparative TLC on silica gel (eluent: hexane-EtOAc = 3:1) to give 1-methoxy-3,4-dihydro-2,1-benzothiazine 2,2-dioxides in 82 % yield.

***N*-Methoxy-3,4-dihydro-2,1-benzothiazine-2,2-dioxide:** Mp 104.0-106.0 °C; IR (KBr) 3000, 2950, 2815, 1580, 1480, 1360, 1170 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.42 (t, J = 6.4 Hz, 2H), 3.50 (td, J = 6.4, 1.5 Hz, 2H), 4.08 (s, 3H), 7.20-7.23 (m, 1H), 7.31-7.34 (m, 2H), 7.36-7.40 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 27.9, 40.2, 65.6, 126.7, 127.9, 128.0, 128.9, 129.4, 141.9; MS (EI) M^+ 213. Anal. Calcd for $C_9H_{11}NO_3S$: C, 50.69; H, 5.20; N, 6.57. Found: C, 50.76; H, 5.32; N, 6.58%.

***N*-Methoxy-7-methyl-3,4-dihydro-2,1-benzothiazine-2,2-dioxide**: Mp 119.0-121.0 °C; IR (KBr) 3000, 2950, 2815, 1620, 1500, 1360, 1170 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.36 (s, 3H), 3.36 (t, J = 6.6 Hz, 2H), 3.47 (t, J = 6.6 Hz, 2H), 4.07 (s, 3H), 7.08 (d, J = 7.9 Hz, 1H), 7.12 (d, J = 7.9 Hz, 1H), 7.18 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.0, 27.6, 40.2, 65.7, 123.6, 128.3, 129.3, 130.1, 138.2, 141.6; MS (EI) M^+ 227. Anal. Calcd for $C_{10}H_{13}NO_3S$: C, 52.85; H, 5.77; N, 6.16. Found: C, 52.80; H, 5.69; N, 6.14%.

***N*-Methoxy-7-chloromethyl-3,4-dihydro-2,1-benzothiazine-2,2-dioxide**: Mp 120.0-122.5 °C; IR (Nujol) 1360, 1280, 1236, 1170 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.40 (t, J = 6.5 Hz, 2H), 3.49 (t, J = 6.5 Hz, 2H), 4.09 (s, 3H), 4.58 (s, 2H), 7.21 (d, J = 8.0 Hz, 1H), 7.34 (dd, J = 8.0, 1.9 Hz, 1H), 7.39 (d, J = 1.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 27.6, 40.1, 44.9, 65.7, 126.7, 127.4, 128.8, 129.8, 137.6, 141.9; MS (FAB) $(M+1)^+$ = 261. Anal. Calcd for $C_{10}H_{12}ClNO_3S \cdot 1/5H_2O$: C,45.44; H,4.69; N, 5.30. Found: C, 45.44; H, 4.62; N, 5.24%.

***N*-Methoxy-7-bromo-3,4-dihydro-2,1-benzothiazine-2,2-dioxide**: Mp 138.0-139.5 °C; IR (Nujol) 1360, 1292, 1167 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.35 (t, J = 6.6 Hz, 2H), 3.48 (t, J = 6.6 Hz, 2H), 4.08

(s, 3H), 7.08 (d, *J* = 8.4 Hz, 1H), 7.42 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.52 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 27.5, 40.2, 65.9, 120.9, 125.5, 130.0, 130.7, 131.7, 142.9; MS (FAB) $(M+1)^+$ = 291. Anal. Calcd for $C_9H_{10}BrNO_3S$: C, 37.00; H, 3.45; N, 4.79. Found: C, 36.87; H, 3.43; N, 4.75%.

***N*-Methoxy-7-chloro-3,4-dihydro-2,1-benzothiazine-2,2-dioxide**: Mp 123.0-125.0 ^oC; IR (KBr) 3000, 2950, 2815, 1600, 1480, 1360, 1160 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.37 (t, *J* = 6.5 Hz, 2H), 3.48 (t, *J* = 6.5 Hz, 2H), 4.08 (s, 3H), 7.14 (d, *J* = 8.2 Hz, 1H), 7.27 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.36 (d, *J* = 2.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *d* = 27.6, 40.4, 65.9, 125.1, 127.1, 128.9, 130.6, 133.5, 142.9; MS (EI) M^+ 247. Anal. Calcd for $C_9H_{10}ClNO_3S$: C, 43.64; H, 4.07; N, 5.65. Found: C, 43.39; H, 4.08; N, 5.52%.

***N*-Methoxy-7-fluoro-3,4-dihydro-2,1-benzothiazine-2,2-dioxide:** Mp 76.0-78.0 ^oC; IR (KBr) 3000, 2950, 2820, 1600, 1490, 1360, 1170 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.37 (t, *J* = 6.4 Hz, 2H), 3.47 (t, *J* = 6.4 Hz, 2H), 4.08 (s, 3H), 7.02 (td, *J* = 8.5, 2.7 Hz, 1H), 7.08 (dd, *J* = 8.9, 2.7 Hz, 1H), 7.17 (dd, *J* = 8.5, 5.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 27.2, 40.5, 65.8, 113.5 (t, $J_{C\text{-}F}$ = 23.8 Hz), 115.9 (t, $J_{C\text{-}F}$ = 22.1 Hz), 122.1 (q, $J_{C\text{-}F}$ = 4.2 Hz), 130.7 (t, $J_{C\text{-}F}$ = 8.2 Hz), 142.8 (q, $J_{C\text{-}F}$ = 9.8 Hz), 161.6 (q, $J_{C\text{-}F}$ = 247.5 Hz); MS (EI) M^+ 231. Anal. Calcd for $C_9H_{10}FNO_3S$: C, 46.75; H, 4.36; N, 6.06. Found: C, 46.94; H, 4.41; N, 5.89%.

***N*-Methoxy-3,4-dihydroquinolin-2(1*H*)-one:** Oil. IR (neat): 2936, 1697, 1354, 1332, 1267, 1192, 1065 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS): ™ = 2.71 (t, *J* = 7.5 Hz, 2 H), 2.92 (t, *J* = 7.4.Hz, 2 H), 3.93 (s, 3 H), 7.05 (td, *J* = 7.3, 1.4 Hz, 1 H), 7.15-7.32 (m, 3 H); ^{13}C NMR ($CDCl_3$, TMS): ™ = 165.7, 137.8, 127.7, 124.3, 123.6, 112.3, 62.5, 31.5, 24.8. HRMS (FAB): *m*/*z* calcd for $C_{10}H_{11}NO_2$ (M): 177.0790; found: 177.0785.

***N*-Methoxy-4,5-dihydro-1*H*-benzo[*b*]azepin-2(3*H*)-one:** Oil. IR (neat): 2935, 1690, 1457, 1358, 1329, 1244, 1038 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS): ™ = 2.17-2.34 (m, 4 H), 2.78 (t, *J* = 7.1 Hz, 2 H), 3.79 (s, 3 H), 7.21-7.25 (m, 2 H), 7.31-7.39 (m, 1 H). 7.44 (d, *J* = 7.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, TMS): ™ = 168.5, 139.3, 134.2, 129.2, 127.7, 127.2, 121.9, 62.1, 32.7, 30.2, 28.5. HRMS (FAB): *m*/*z* calcd for $C_{11}H_{14}NO_2$ (M+H): 192.1025; found: 192.1012.

***N*-Methoxy-1,3-dihydrobenzisothiazole 2,2-dioxide**: Oil. IR (neat) 3000, 2940, 2820, 1500, 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS) δ = 4.14 (s, 3H), 4.34 (s, 2H), 7.12-7.32 (m, 2H), 7.34-7.41 (m, 2H); ^{13}C NMR ($CDCl_3$, TMS) δ = 49.9, 65.9, 120.0, 125.7, 126.2, 128.8, 129.8, 142.4. HRMS (FAB): *m*/*z* calcd for $C_8H_9NO_3S$: 199.0303; found: 199.0288.

***N*-Methoxy-2,2-dioxo-2l^6-thia-1-azaspiro[4.5]deca-6,9-dien-8-one:** Mp 133.0-135.0 °C. IR (KBr) 2980, 2950, 2830, 1680, 1610, 1400, 1330, 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS): ™ = 2.44 (t, *J* = 7.9 Hz, 2H), 3.44 (t, *J* = 7.9 Hz, 2H), 3.81 (s, 3H), 6.39 (d, *J* = 10.4 Hz, 2H), 7.05 (d, *J* = 10.4 Hz, 2H); Anal. Calcd for $C_9H_{11}NO_4S$: C, 47.15; H, 4.84; N, 6.11. Found: C, 47.16; H, 4.68; N, 6.07%.

1-Methyl-3-(4'-iodobenzyl)imidazolium Phosphorushexafluoride (A)

Mp 99-100 °C. IR (Nujol): 1440, 1380, 1160, 840, 820, 750, 560 cm^{-1}; ^{1}H NMR (400 MHz, Acetone-d_6):

™ = 3.95 (s, 3 H), 5.45 (s, 2 H), 7.19 (d, *J* = 8.5 Hz 2 H), 7.63 (d, *J* = 3.4 Hz, 1 H), 7.66 (d, *J* = 3.4 Hz, 1 H), 7.70 (d, *J* = 8.5 Hz, 2 H), 9.00 (s, 1 H). Anal. Calcd for Calcd for $C_{11}H_{12}F_6IN_2P$: C, 29.75; H, 2.72; N, 6.31. Found: C, 29.88; H, 2.49; N, 6.28%.

(4-Iodobenzyl)trimethylammonium Trifluoromethanesulfonate (B)

Mp 138.5-143.0 °C. IR (Nujol): 3034, 1479, 1464, 1261, 1230, 1150, 1034, 645, 517 cm^{-1}; ^1H NMR ($CDCl_3$, TMS): ™ = 3.16 (s, 9 H), 4.60 (s, 2 H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.80 (d, *J* = 8.2 Hz, 2 H). Anal. Calcd for $C_{11}H_{15}F_3INO_3S \cdot 1/20CF_3SO_3Ag$: C, 30.30; H, 3.45; N, 3.20. Found: C, 30.37; H, 3.15; N, 3.19%.

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