JOC Article

Intramolecular Cyclization with Nitrenium Ions Generated by Treatment of *N*-Acylaminophthalimides with Hypervalent Iodine Compounds: Formation of Lactams and Spiro-Fused Lactams

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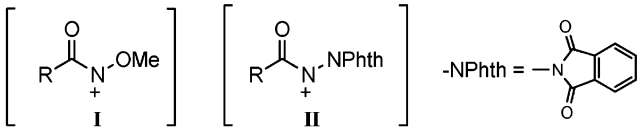
N-Phthalimido-*N*-acylnitrenium ions are generated from *N*-acylaminophthalimides, a new class of precursors, by treatment with hypervalent iodine compounds (PIFA and HTIB). In HFIP, the nitrenium ions undergo intramolecular electrophilic substitution reactions to afford *N*-aminonitrogen heterocycles in high yields. In TFEA, spirodienones bearing the 1-azaspiro[4.5]decane skeleton are obtained by treatment of *N*-phthalimido-3-(4-halogenophenyl)propanamides with HTIB as a result of ipso attack of the intermediate nitrenium ion. Similarly, using PIFA in TFEA, ipso cyclization of unactivated benzenoid compounds occurs to afford spirodiene derivatives. This involves loss of aromaticity despite the absence of other activating substituents on the phenyl group.

Introduction

Nitrenium ions are reactive intermediates that continue to attract attention from synthetic, theoretical, and biological perspectives.[1] However, despite much effort, synthetic applications of nitrenium ions remain limited, primarily because their existence as reaction intermediates is quite fleeting. Exceptions to this include synthetic applications of certain stabilized nitrenium ions. For example, arylnitrenium ions[2] and *N*-methoxy-*N*-acylnitrenium ions (**I**)[3] are stabilized by the neighboring aryl group and lone pair on oxygen, respectively, as shown by MNDO molecular orbital calculations and by reactions that involve them. In addition, the stabilization of nitrenium ions by other heteroatoms, such as nitrogen and sulfur, is also predicted.[4] These stabilized nitrenium ions are proving to be useful synthetic intermediates.



Previously, we have reported that **I** can be generated from the corresponding *N*-chloro-*N*-methoxyamides by the action of silver[5a−c] or zinc[6] ions or by direct oxidation of *N*-methoxyamides with phenyliodine(III) bis(trifluoroacetate)[5d] (PIFA). These nitrenium ions are stabilized by an electron-donating methoxy group attached to the nitrogen and are able to undergo inter- and intramolecular substitution reactions with a range of aromatic compounds. Since this report, several applications of these intermediates in the synthesis of biologically active compounds have been published.[7]

From our previous observations, we expected that replacing an oxygen atom by nitrogen in the precursor would also have an additional stabilizing influence on a generated nitrenium ion. We detail herein electrophilic reactions of *N*-phthalimodo-*N*-acylnitrenium ions (**II**), a new class of positive nitrogen ions, generated from **1**.

In our initial attempt, we studied the intramolecular cyclization of *N*-chloro-*N*-(3-phenylpropionyl)aminophthalimide synthesized from the corresponding amide (**1b**) by reaction with *t*-BuOCl. Cyclization with $Zn(OAc)_2$ following the literature procedure[6] produced *N*-phthalimido-3,4-dihydrocarbostyril (**2b**) in 85% yield. However, use of *t*-BuOCl is not recommended because of commercial inaccessibily in bulk quantities[8] and environmental problems related to disposal. Therefore, we have examined the reaction of **II** generated from **1** by the action of PIFA and [hydroxy(tosyloxy)iodo]benzene (HTIB), both of which reagents have low toxicity, are readily available, are easy to handle, and are environmentally

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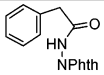
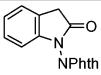
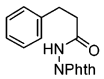
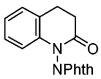
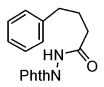
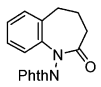
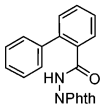
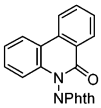
TABLE 1. Synthesis of Benzannulated Compounds from *N*-Acylaminophthalimides

entry	starting material	reagent[a]	solvent	time[b] (h)	product yield
1	 **1a**	A[c]	HFIP	1	 **2a**, 53%
2	**1a**	A[c]	TFEA	1	**2a**, 81%
3	 **1b**	A[d]	HFIP	17	 **2b**, 73%
4	 **1c**	A[d]	HFIP	17	 **2c**, 82%
5	 **1d**	A[d]	HFIP	3	 **2d**, 83%

[a] A: PIFA. [b] At room temperature. [c] 1.2 equiv. [d] 1.1 equiv.

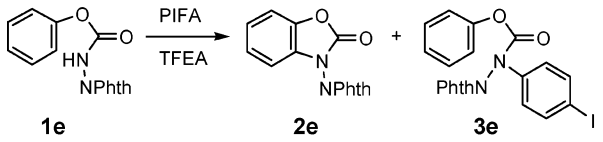
friendly. Herein, we report that nitrenium ions **II** possessing a pendant phenyl group undergo intramolecular cyclization reactions to give benzannulated or spiro benzannulated compounds.

Results and Discussion

Synthesis of Benzannulated Nitrogen Heterocycles. In preliminary studies, we examined the intramolecular cyclization reaction mediated by the reaction of *N*-phenylacetylaminophthalimide (**1a**) with PIFA in various solvents such as hexafluoroisopropyl alcohol (HFIP), 2,2,2-trifluoroethanol (TFEA), trifluoroacetic acid (TFA), acetic acid, chloroform, and dichloromethane. *N*-Phthalimido-2-indolinone (**2a**), the cyclization product, was obtained in 53% yield in HFIP and in 81% yield in TFEA after 1 h reaction. For the synthesis of other benzannulated compounds the use of HFIP afforded better results. Generally, reactions in poorly nucleophilic polar solvents gave good results, while use of other polar solvents such as dichloromethane, chloroform, acetic acid and TFA did not give satisfactory results. For the control experiment, we examined the cyclization reaction using 3-phenylpropionic acid *N*,*N*-dimethylhydrazide with PIFA in HFIP at room temperature overnight. This gave ambiguous results along with recovery of the starting compound in 30% yield. This confirms that the phthalimido group plays an important role for the stabilization of **II** and for promotion of further reaction. Several *N*-acylaminophthalimides (**1**) reacted in a similar way, and the results are presented in Table 1.

Very recently, the similar compounds were synthesized in moderate yields by intramolecular cyclization of aryl-substituted unsymmetrical azodicarbonyl compounds, generated from bishydrazides by oxidation, using $BF_3 \cdot Et_2O$.[9] However, the reaction is limited to highly electron-rich arenes bearing such substitutents as a methoxy or dimethoxy function. This limitation is consistent with the reported behavior of an intermolecular version of a similar reaction, in which highly electron-rich arenes alone can react with azodicarboxylates.[10]

SCHEME 1



The phthalimido group of *N*-phthalimido-3,4-dihydrocarbostyril (**2b**) was deprotected by the action of hydrazine hydrate as usual to give *N*-amino-3,4-dihydrocarbostyril in 95% yield. If desired, the *N*-amino group can be removed with Raney Ni (W-2) to give 3,4-dihydrocarbostyril in 91% yield or by the literature method ($NaNO_2$−HOAc).[9]

These *N*-amino compounds should be useful starting compounds for the synthesis of *N*,*N*′-linked bisazaheterocycles.[11] The oxidative rearrangement of *N*-amino-2-indolinone with lead tetraacetate and *t*-BuOCl gave 3(2*H*)-cinnoline.[12] *N*-Amino-2-indolinone also can be converted to the corresponding amino-nitrene by lead tetraacetate oxidation.[13]

Synthesis of 3*H*-Benzoxazol-2-ones and 4*H*-Benzo[1,4]oxazin-3-one. A valuable extension of this procedure would be its application to the synthesis of systems incorporating two heteroatoms in a ring. With this end in view, we have undertaken the synthesis of benzoxazolone derivatives (**2e**−**h**) using aryl *N*-phthaloylcarbamates (**1e**−**h**).

Treatment of **1e** with PIFA (1.1 molar equiv) in TFEA for 3 h at room temperature gave **2e** and the *p*-iodophenylated compound (**3e**) in 30% and in 20% yields, respectively (Scheme 1). It is evident that the oxygen function directly attached to the phenyl group unfavorably affected the cyclization reaction and the *p*-iodophenyl group of PIFA migrated to the amide nitrogen to afford **3e**.[14] As a strategy to retard this rearrangement, 4-chlorophenyliodine(III) bis(trifluoroacetate) (*p*-ClPIFA) was synthesized.[15] Reactions using *p*-ClPIFA were examined in solvents such as TFA, TFEA, HFIP, $CHCl_3$, and 1,2-dichloroethane. Use of *p*-ClPIFA in TFA improved the yield of **2e** to 74%. In the case of **1i**, polymerization occurred in TFA but the cyclizaton product **2i** could be obtained in 72% yield by changing the solvent from TFA to 1,2-dichloroethane. Several aryl carbamates (**1e**−**h**)

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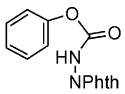
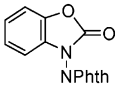
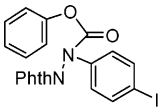
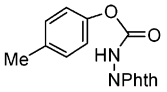
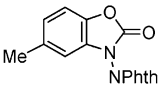
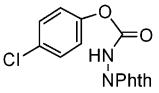
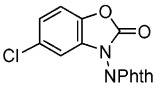
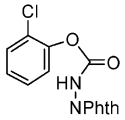
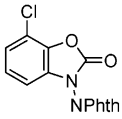
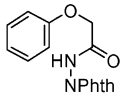
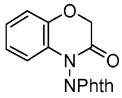
TABLE 2. Synthesis of Benzannulated Compounds from *N*-Acylaminophthalimides Bearing Phenoxy Function

entry	starting material	reagent[a]	solvent	time[b] (h)	product yield
1	 **1e**	A[c]	TFEA	3	 **2e**, 30%  **3e**, 20%
2	**1e**	B[d]	TFEA	6	**2e**, 61%
3	**1e**	B[d]	TFA	0.5[f]	**2e**, 74%
4	 **1f**	B[e]	TFA	0.5[f]	 **2f**, 62%
5	 **1g**	B[e]	TFA	0.5[f]	 **2g**, 66%
6	 **1h**	B[e]	TFA	0.5[f]	 **2h**, 30%
7	 **1i**	B[e]	CH_2Cl_2	17	 **2i**, 63%
8	**1i**	B[e]	$ClCH_2CH_2Cl$	5.5	**2i**, 72%

[a] A: PIFA. B: *p*-ClPIFA [4-$ClC_6H_4I(OCOCF_3)_2$]. [b] At room temperature. [c] 1.1 equiv. [d] 1.3 equiv. [e] 2.0 equiv. [f] At reflux.

and **1i** reacted in this way, and the results are presented in Table 2. *N*-Phthalimido-3*H*-benzoxazol-2-ones (**2e**−**g**) and 4*H*-benzo[1,4]oxazin-3-one (**2i**) were obtained in synthetically useful yields.

It is interesting to note that phenyl *N*-methoxycarbamate (the phthalimido group replaced with a methoxy group) failed to cyclize with PIFA, giving instead an unidentifiable product mixtures.[16]

Synthesis of Spirodienones. Spirodienones bearing the 1-azaspiro[4.5]decane skeleton have recently attracted considerable attention because of their presence in various natural products.[17] In our previouis work, we converted *N*-methoxy-3-phenylpropionamide and the corresponding *N*-chloro compound to 1-methoxy-1-azaspiro-[4.5]deca-6,9-diene-2,8-dione with PIFA[17] in 80% yield and with $Zn(OAc)_2$[6] in 83% yield, respectively. Very recently, it was reported that methyl N^2-(3-phenylpropionyl)carbazate was oxidized to 1-methoxycarbonylamino-1-azaspiro[4.5]deca-6,9-diene-2,8-dione with phenyliodine-(III) diacetate in 25% yield.[9a] We now have applied our present methodology to the synthesis of spirodienones. Thus, treatment of **1j** with PIFA in TFEA at room temperature for 3 h gave **4j** in 77% yield. The ipso position is activated by an electron-donating methoxy group and is attacked by the nitrenium ion to give the spiroannulated product. It is generally accepted that the spirodienones are the major or the exclusive products whenever the aromatic ring bears a methoxy group para to the alkyl side chain.[3,9] We have reported the similar formation of *N*-methoxyspirodienones by the ipso attack of *N*-methoxy-*N*-acylnitrenium ions generated from the *o*- and *p*-methoxyphenyl-*N*-methoxyamide derivatives.[5c]

In our earlier work,[18] we developed procedures for the synthesis of spirodienones from (4-halogenophenyl)-*N*-methoxyamides, more readily accessible compounds than the corresponding methoxy compounds, with HTIB in TFEA. We have applied this procedure to the synthesis of spirodienones bearing 1-azaspiro[4.5]decane skeleton using *N*-acylaminophthalimides bearing a pendant 4-halogenophenyl group (**1k**−**p**) with HTIB in TFEA. The results are presented in Table 3.

Two equivalents of HTIB to **1k**−**p** was needed to obtain a high yield of **4j**,**m**−**p**. Use of PIFA (2 molar equiv) instead of HTIB gave **4j** in low yield (Table 3, entry 2). Halogens have nonbonded electron pairs, which stabilize the cationic intermediate through their "back-donation" ability and promote further reaction.[19] The yields of spirodienones are directly related to the degree of "back-donation" and the best results are obtained with the 2,4-difluorophenyl compound (**1m**) (93%, Table 3, entry 5).

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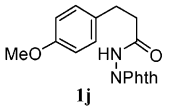
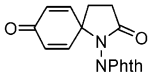
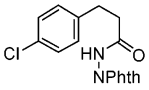
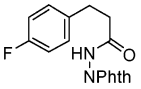
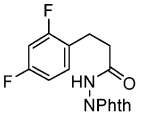
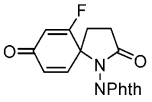
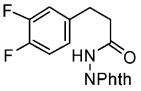
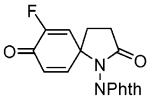
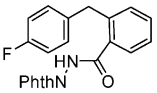
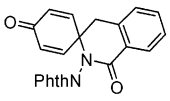
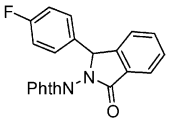
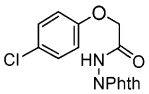
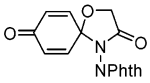
TABLE 3. Cyclization of *N*-Acylaminophthalimides with HIBT in TFEA

entry	starting material	reagent[a]	time[b] (h)	product yield
1	 **1j**	A[c]	3	 **4j**, 77%
2	 **1k**	A	1.5	**4j**, 56%
3	**1k**	C[d]	0.5	**4j**, 72%
4	 **1l**	C	0.5	**4j**, 79%
5	 **1m**	C	0.5	 **4m**, 93%
6	 **1n**	C	0.5	 **4n**, 66%
7	 **1o**	C	0.5	 **4o**, 70%  **5**, 29%
8	 **1p**	C	1.5	 **4p**, 45%

[a] A: PIFA (2.0 equiv). C: HIBT (2.0 equiv). [b] At room temperature. [c] 1.0 equiv. [d] 2.8 equiv.

These substances, themselves of potential synthetic interest, can be converted into quinolone derivatives by acid treatment.[9]

Synthesis of Spirodiene Compounds. The present reaction is influenced greatly by the choice of solvent. For example, in the reaction of **1b** with PIFA, the use of TFEA instead of HFIP resulted in unexpected attack of the nitrenium ion on the ipso position to give a spirodiene derivative (**6b**) in 76% yield along with the 3,4-dihydrocarbostyril derivative (**2b**) (17%). Similarly, reaction of *N*-(4-phenylbutyroyl)aminophthalimide (**1c**) under these conditions gave the corresponding spirobenzannulated compound (**6c**) and the benzannulated compound (**2c**) in 44% and 46% yields, respectively. From *o*-tolyl derivative (**1q**), the spirodiene compound (**6q**) was exclusively obtained (88%, Table 4, entry 4). Most reactions of unactivated monobenzenoid aromatics lead to substitution rather than addition. Formation of the spirodiene derivatives (**6**) by this ipso cyclization, which resulted in loss of aromaticity without any other substituents on the phenyl group, is an unusual result. Transformation of benzenoid compounds to nonbenzenoid compounds can provide valuable intermediates for the synthesis of a variety of organic compounds.[20] Several unactivated benzenoid compounds reacted similarly, and the results are presented in Table 4.

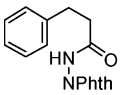
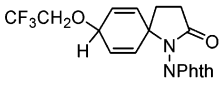
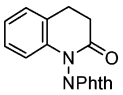
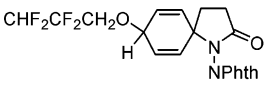
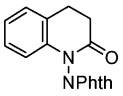
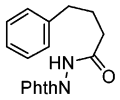
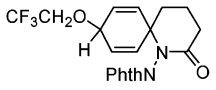
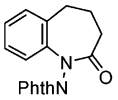
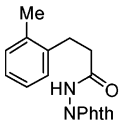
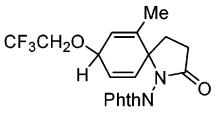
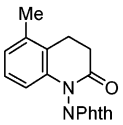
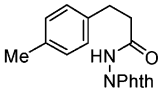
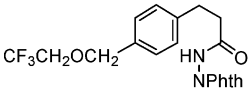
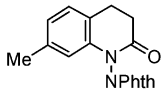
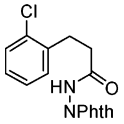
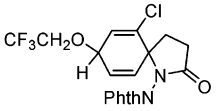
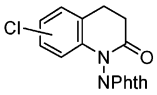
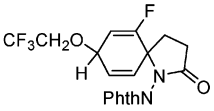
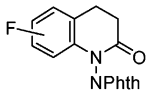
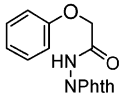
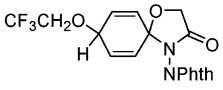
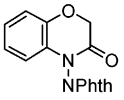
Illustrative of the procedure, stirring a mixture of **1b**, PIFA, and TFEA for 3 h at room temperature causes an intramolecular ipso attack of the electron-deficient hydrazide nitrogen with subsequent trapping of the cation with a trifluoroethoxide ion to give the spirodiene **6b**. The critical part of the process involves a coupled attack on the benzenoid ring by external nucleophilic trifluoroethanol and internal electrophilic acylnitrenium ion, the over-all results being 1,4-addition. In the case of **1r**, the trifluoroethoxy group of the transient spirodiene intermediate might be eliminated to afford the exo methylene compound and subsequent addition of TFEA to the

(20) (a) Gassman, P. G.; Campbell, G. A. *J. Chem. Soc., Chem. Commun.* **1970**, 427. (b) Corey, E. J.; Barcza, S.; Klotmann, G. *J. Am. Chem. Soc.* **1969**, *91*, 4782.

(21) Winters, G.; Odasso, G.; Conti, M.; Tarzia, G.; Galliani, G. *Eur. J. Med. Chem.* **1984**, *19*, 215.

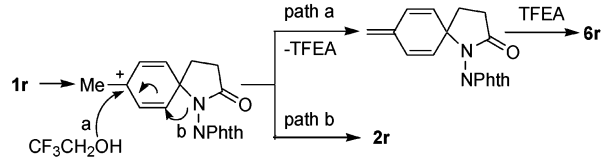
(22) Blout, E. R.; Silverman, D. C. *J. Am. Chem. Soc.* **1944**, *66*, 1442.

TABLE 4. Cyclization of *N*-Acylaminophthalimides with PIFA in TFEA

entry	starting material	reagent[a]	time[b] (h)	product yield	
1	 **1b**	A	3	 **6b**, 76%	 **2b**, 17%
2[c]	**1b**	A	17	 **6b'**, 67%	 **2b**, 15%
3	 **1c**	A	17	 **6c**, 44%	 **2c**, 46%
4	 **1q**	A	4	 **6q**, 88%	 **2q**, 5%
5	 **1r**	A	17	 **6r**, 60%	 **2r**, 5%
6	 **1s**	A	1	 **6s**, 77%	 **2s**, 7%[d]
7	 **1t**	A	0.5	 **6t**, 88%	 **2t**, 6%[d]
8	 **1i**	A	17	 **6i**, 31%	 **2i**, 26%

[a] A: PIFA (1.0 equiv). [b] At room temperature. [c] 2,2,3,3-Tetrafluoro-1-propanol was used for solvent. [d] Small amounts of a mixture of benzannulated regioisomers were obtained.

SCHEME 2



methylene group gave **6r** (Scheme 2, path a). Compound **2r** might be formed through direct ortho attack or through ipso attack followed by C−N bond migration (Scheme 2, path b).[9]

It is noteworthy that in the fluorine-containing primary alcohol, 2,2,3,3-tetrafluoro-1-propanol, the corresponding spirodiene compound (**6b′**) having a 2,2,3,3-tetrafluoro-1-propanoxy group was formed (Table 4, entry 2). However, in HFIP, a secondary alcohol, the benzannulated product was formed without formation of the spirodiene compound. This is probably due to steric hindrance and the low nucleophilicity of this solvent (Table 1). Transformation of benzenoid compounds to nonbenzenoid compounds provides an attractive strategy for the synthesis of a variety of functionalized six-membered ring compounds.[20] Conversion of **1** to spirodienones (**4**) and spirodienes (**6**) bearing the nitrogen atom bound to the spiro carbon should offer valuable intermediates for the synthesis of a variety of organic compounds.

Conclusions

In summary, we have generated a new class of reactive nitrenium ions **II** by the reaction of **1** with hypervalent

iodine compounds. The phthalimido group is a good protecting group and also effectively stabilizes **II** to promote further reactions. The interesting transformations that derive form **II** can be summarized as follows. PIFA reacts with the amide nitrogen in HFIP to form an intermediate, which presumably is decomposed to generate an electron deficient nitrogen. This, in turn, undergoes intramolecular electrophilic aromatic substitution reactions to afford *N*-aminonitrogen heterocycles in high yield. In TFEA, ipso attack of the nitrenium ion is observed to give spirodienone and spirodiene derivatives. The latter involves loss of aromaticity in the absence of other activating substituents on the phenyl group, a process that is very unusual.

Supporting Information Available: Experimental procedures and characterization data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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