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PIFA-Mediated Oxidative Cyclization of 1-Carbamoyl-1-oximylcycloalkanes: Synthesis of Spiro-Fused Pyrazolin-5-one *N*-Oxides

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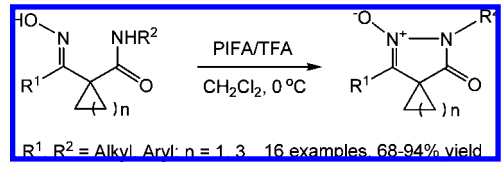
ABSTRACT



A convenient and efficient synthesis of spiro-fused pyrazolin-5-one *N*-oxides starting from readily available 1-carbamoyl-1-oximylcycloalkanes is developed. This general protocol features a novel and facile way for access to the five-membered azaheterocycles by formation of a new N−N single bond. The key cyclization step utilizes the formation of an *N*-oxonitrenium intermediate, mediated by the hypervalent iodine reagent PIFA, and its subsequent intramolecular trapping by the amide moiety under rather mild experimental conditions.

The pyrazolin-5-one ring makes up the core structure of numerous pharmaceutically active compounds, such as edaravone.[1,2] As an important class of aza-heterocycles, pyrazolin-5-ones and their heterocyclic fused analogues have found considerable utility as pharmaceutical agents,[3] synthetic scaffolds in combinatorial and medicinal chemistry,[4] photographic couplers,[5] chelating agents in coordination chemistry,[6] and agrochemical products.[7] The therapeutic importance of pyrazolin-5-one derivatives and their synthetic versatility as intermediates in organic chemistry have directed great research activity toward the construction of the skeleton of this kind of heterocycle. The most notable method for the synthesis of pyrazolin-5-ones involves the reactions

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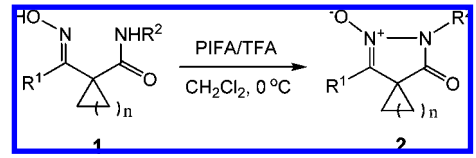
between β-oxo esters, or their derivatives, with hydrazines.[8] Other methods are reported by air oxidation of 1,2-hydrazinohydrazones,[9] palladium-catalyzed carbonylation of 1,2-diaza-1,3-buta-dienes,[10] or rearrangement of an oxadiazole derived from a 2-cyanoacetanilide.[11]

On the other hand, hypervalent iodine reagents have been extensively used as the oxidation reagents in synthetic organic chemistry.[12] One such reagent, phenyliodine(III)-bis(trifluoroacetate) (PIFA) has attracted considerable attention of research due to its ready availability, low toxicity, ease of handling, and reactivity similar to that of heavy metal reagents.[13] Its efficient utilization in metal-free transformations relies on both the extremely mild reaction conditions required and its ability to oxidize chemoselectively a wide range of functionalities such as phenols, amines, sulfides, and carbonyl compounds. Recently, Tellitu and co-workers developed novel metal-free approaches to the synthesis of nitrogen-containing heterocycles using properly substituted amides and amines as synthetic precursors via a PIFA-mediated oxidization process.[14]

During the course of our studies on the synthesis of carbo- and heterocycles based on β-oxo amide derivatives,[15] we successfully achieved efficient synthesis of substituted isothiazol-3(2*H*)-ones and pyrrolin-4-ones from readily available 1-carbamoyl ketene dithioacetals and enaminones, respectively, in the presence of PIFA, in which an intramolecular N−S or N−C bond is formed.[16] Very recently, we have reported a one-pot divergent synthesis of fully substituted 1*H*-pyrazoles and isoxazoles from 1-carbamyl-1-oximylcyclopropanes, in the presence of $POCl_3$/DMF (Vilsmeier reagent) and $POCl_3/CH_2Cl_2$, respectively.[17] Thus, in connection with these previous studies and following on from our research on the synthesis of highly valuable heterocycles through an oxidative processes, we have prepared a series of 1-carbamoyl-1-oximyl cycloalkanes from β-oxo amide derivatives and examined their reactivity toward the environmentally friendly reagent PIFA. As a result of these studies, we have developed a facile and efficient synthesis of spiro-fused cycloalkano-(C4)-pyrazolin-5-one *N*-oxides via PIFA-mediated intramolecular N−N bond formation.

The substrates, 1-carbamoyl-1-oximylcycloalkanes **1**, were prepared by the reaction of 1-acyl-1-carbamyl cycloalkanes with hydroxylamine (NH_2OH·HCl) in the presence of NaOAc in ethanol at room temperature in high yields (up to 95%).[18] We then selected cyclopropyl oxime **1a** from a series of substrates **1** (see Table 1) as the model compound to examine its reaction behavior in the presence of PIFA and trifluoroacetic acid (TFA).

Table 1. Reactions of **1** with PIFA/TFA in CH_2Cl_2[a]



1 2

entry	1	n	R^1	R^2	2	yield[b] (%)
1	**1a**	1	Me	C_6H_5	**2a**	80
2	**1b**	1	Me	4-MeC_6H_4	**2b**	73
3	**1c**	1	Me	4-$MeOC_6H_4$	**2c**	71
4	**1d**	1	Me	4-ClC_6H_4	**2d**	68
5	**1e**	1	Me	2-MeC_6H_4	**2e**	75
6	**1f**	1	Me	2-$MeOC_6H_4$	**2f**	81
7	**1g**	1	Me	2,4-$Me_2C_6H_3$	**2g**	72
8	**1h**	3	Me	C_6H_5	**2h**	89
9	**1i**	3	Me	4-MeC_6H_4	**2i**	84
10	**1j**	3	Me	4-$MeOC_6H_4$	**2j**	85
11	**1k**	3	Me	4-ClC_6H_4	**2k**	83
12	**1l**	3	Me	2-MeC_6H_4	**2l**	91
13	**1m**	3	Me	2-$MeOC_6H_4$	**2m**	94
14	**1n**	3	Me	2,4-$Me_2C_6H_3$	**2n**	88
15	**1o**	3	C_6H_5	C_6H_5	**2o**	92
16	**1p**	3	Me	Me	**2p**	87

[a] Reagents and conditions: **1** (1.0 mmol), PIFA (1.1 mmol), TFA (3.0 mmol), CH_2Cl_2 (11 mL), 0 °C, 1.5−4.5 h. [b] Isolated yield.

Upon treatment of **1a** with 1.5 equiv of PIFA and 3.0 equiv of TFA in CH_2Cl_2 at room temperature for 1.5 h, the reaction proceeded smoothly as indicated by TLC and furnished a product after workup and purification by column chroma-

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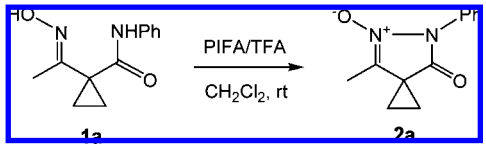
tography. From the spectral and analytical data, the product was characterized as 4-methyl-7-oxo-6-phenyl-5,6-diazaspiro-[2.4]hept-4-ene 5-oxide **2a**, a spiro-fused pyrazolin-5-one *N*-oxide (Scheme 1).[19] The reaction conditions, including

Scheme 1. Reaction of **1a** with PIFA/TFA



reaction temperature, the ratio of PIFA/TFA/**1a**, and the concentration of PIFA, were then investigated. A series of experiments revealed that 1.0 equiv of PIFA was sufficient for the synthesis of **2a**, and the optimal results were obtained when the reaction of **1a** was performed with PIFA (1.1 equiv, 0.1 M) and TFA (3.0 equiv) in CH_2Cl_2 at 0 °C for 2.0 h, whereby the yield of **2a** reached 80% (Table 1, entry 1).

Having established the optimal conditions for the cyclization process, we intended to determine its scope with respect to the amide motif. Thus, a series of cyclopropyl oximes **1b**−**g** were subjected to PIFA/TFA under conditions identical to those for **2a** in Table 1 (entry 1), and some of the results are summarized in Table 1. It was observed that all the reactions proceeded smoothly to afford the corresponding spiro-fused cyclopropano-(C4)-pyrazolin-5-one *N*-oxides **2b**−**g** in good yields (Table 1, entries 2−7).

We next extended the synthesis of spiro-fused pyrazolin-5-one *N*-oxides by subjecting cyclopentyl oximes **1h**−**p** to the above cyclization conditions. The versatility of the protocol proved to be suitable for **1h**−**o** bearing variable arylamide groups affording the corresponding spiro-fused cyclopentano-(C4)-pyrazolin-5-one *N*-oxides **2h**−**o** in high yields (Table 1, entries 8−15). To our delight, cyclopentyl oxime **1p** bearing an alkylamide group also rendered successfully the corresponding spiro-fused pyrazolin-5-one *N*-oxide **2p** in high yield (Table 1, entry 16). It is worth mentioning that the structure of **2l** was elucidated by means of the X-ray single crystal analysis (Figure 1) and further confirmed by NMR (^{1}H, ^{13}C) spectra.

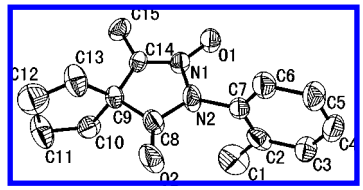


Figure 1. ORTEP drawing of **2l**.

The results shown above demonstrated the efficiency and synthetic value of the cyclization reaction with respect to oximes **1** bearing variable amide and cycloalkyl groups. Therefore, we provide a novel protocol for the synthesis of spiro-fused cycloalkano-(C4)-pyrazolin-5-one *N*-oxides **2**.

Actually, the reactions of oximes with hypervalent iodine reagents have been investigated by some other researchers. The deoximation reaction was observed when subjecting ketoximes to hypervalent iodine reagents, such as (diacetoxyiodo)benzene (DAIB),[20] (dichloroiodo)benzene (DCIB),[21] and [hydroxy(tosyloxy)iodo]benzene (HTIB).[22]In De's work on the reaction of oximes with HTIB, they obatined a new type of product, 8,12-dioxa-13-azatricyclo [8.3.1.0^{2,7}tetradeca-2(7),3,5,13-tetraen-14-ones] along with the deoximation product.[23] Aggarwal and co-workers achieved the synthesis of quinoxaline *N*-oxides via a oxidative cyclization of benzil-α-arylimino oximes mediated by iodobenzene diacetate (IBD).[24] The chemistry of heterocyclic *N*-oxides has raised widespread interest due to the exceptionally high bioactivity of these compounds.[25] Unfortunately, to the best of our knowledge, little is known regarding the synthesis and properties of pyrazolin-5-one *N*-oxides except that Goromaru and co-workers discovered two pyrazolin-5-one *N*-oxides from the metabolites of isopropylantipyrine by means of GC-MS.[26] In the present work, we described the first X-ray structure of one pyrazolin-5-one *N*-oxide.

It is well-known that nitrogen-containing compounds, such as amides and amines, can be conveniently oxidized by PIFA to the corresponding nitrenium ions, which are powerful electrophiles that easily undergo intramolecular heterocyclization reactions.[14d−h,27] However, synthetic applications of these electrophilic intermediates remain limited except when such nitrenium ions are stabilized by the electron-donating effect of a suitable neighboring group (aryl, alkoxy, or nitrogen-containing groups).[28] In these cases, the "stabilized" nitrenium ions can exhibit a long enough time to

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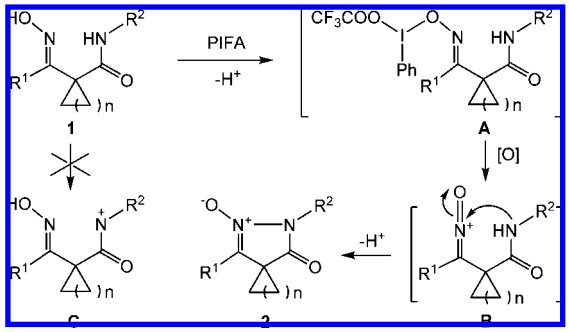
undergo further organic reactions.[29] On the basis of the obtained results and our previously reported work,[16] a plausible mechanism for the synthesis of pyrazolin-5-one *N*-oxides **2** is presented in Scheme 2. Oximyl cycloalkane **1**

Scheme 2. Plausible Mechanism for the Reaction of Cycloalkyl Oximes **1** with PIFA/TFA



initially reacts with PIFA to give intermediate **A**,[24,30] which is then transformed into *N*-oxonitrenium ion **B** via an oxidative process,[31] followed by an intramolecular cyclization reaction to yield pyrazolin-5-one *N*-oxide **2**.

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In summary, a facile and efficient synthesis of spiro-fused cycloalkano-(C4)-pyrazolin-5-one *N*-oxides **2** has been developed from readily available 1-carbamoyl-1-oximylcycloalkanes **1**, which involves the formation of a *N*-oxonitrenium intermediate, mediated by PIFA, and the succeeding intramolecular trapping by the amide moiety to form a new N−N single bond. This protocol is associated with readily available starting materials, mild conditions, good to high yields, and a broad range of synthetic potential of the products. Further work on the utilization and extension of the scope of the protocol and the examination of biological activity of the novel products are currently under investigation in our laboratory.

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Supporting Information Available: Experimental details, spectral data for compounds **1** and **2**, and CIF data for **2l**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(31) The format ion of *N*-oxonitrenium ion **B**, instead of *N*-acylnitrenium ion **C**, is based on the fact that the presented process can be extended to certain alkyl amides (Table 1, entry 16), and the nitrenium ion in **B** can be stabilized by its adjacent oxygen atom.