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Synthesis of diazafluorene- and diazafluorenone-*N*,*N*′-dioxides using HOF·CH_3CN

Tal Harel, Neta Shefer, Youlia Hagooly, Shlomo Rozen *

School of Chemistry, Tel-Aviv University, Tel-Aviv 69978, Israel

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A variety of diazafluorenes and diazafluorenones were oxidized using the HOF·CH_3CN complex to form the corresponding *N*,*N*′-dioxide derivatives under mild conditions. The products exhibit red-shift absorptions in the UV/visible spectrum relative to the parent compounds. Many such oxidations could not be achieved with any other oxygen-transfer agent.

1. Introduction

Recently, diazafluorene derivatives are receiving extensive attention as high performance electron transporting compounds, hole-blocking materials, good candidates for flat panel displays and more.[1,2] In order to succeed in these fields it is necessary, among other requirements, to introduce electron-withdrawing groups into the π-conjugated systems[3] and add electron deficient units such as oxadiazole.[4,5] Previous works showed that oxidation of the heteroatom in the relevant heterocycles narrowed the HOMO–LUMO gap significantly thus increasing their electron delocalization and affinity. Promising results were demonstrated when thiazoles were transferred to the respective *N*-oxides[6] and oligothiophenes to their *S*,*S*′-dioxides.[7,8] These results prompted us to explore the oxidation of the diazafluorene and diazafluorenone systems, by construction their respective *N*,*N*′-dioxide derivatives, which in many cases could not be achieved because of lack of suitable and powerful enough oxygen-transfer agents. We present here a novel route for the preparation of these bis-oxidized heterocycles by using the acetonitrile complex of the hypofluorous acid – HOF·CH_3CN. Indeed, the electron affinity of the aforementioned *N*,*N*′-dioxides was improved, as expected, and the HOMO–LUMO gap reduced.

The HOF·CH_3CN complex, easily prepared from diluted fluorine[9] and aqueous acetonitrile, was developed some years ago.[10] It has established itself as one of the best oxygen-transfer agents chemistry has in its arsenal. Earlier processes developed with the aid of this reagent are summarized in two reviews describing many first or difficult to achieve transformations.[11,12] Other unique reactions of this reagent involve synthesis of episulfones[13] and quinoxaline *N*,*N*′-dioxides,[14] transforming aldehydes to nitriles,[15] amino acids to α-alkyl ones[16] and oxidizing thiols and disulfides to either sulfonic or sulfinic acids at will.[17]

2. Results and discussion

Because of its potential importance, attempts to fully oxidize 4,5-diazafluoren-9-one (**1a**) have been made in the past including the use of concentrated H_2O_2/Na_2WO_4 system, but only partial oxidation was achieved and 4,5-diazafluoren-9-on-4-oxide (**1c**) was isolated in 7% yield only.[18] No traces of the target 4,5-diazafluoren-9-on-4,5-dioxide (**1b**) were found. In order to check if other oxygen-transfer agents are up to the challenge, we reacted **1a** with large excess of both dimethyl dioxirane (DMDO) and MCPBA, but even after prolonged reaction times only minute traces of the desired **1b** were formed. We turned our attention to HOF·CH_3CN, and when using stochiometric amount or small excess of this reagent only the starting material was recovered. However, using a large excess (10 mol equiv) changed the picture completely and the previously unknown **1b** was formed in almost quantitative yield in less then a minute (Scheme 1).

Another interesting substrate was 1,8-diazafluoren-9-one (DFO) (**2a**). This compound is used extensively for fingerprint visualization especially on paper. It seems that this compound is easier to oxidize than **1a**, and indeed it has been described once in the literature where it was reported that 1,8-diazafluoren-9-on-1,8-dioxide (**2b**) was formed in 47% yield after about 20 h heating with very large excess of hydrogen peroxide.[18] The facile formation of **2b**

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* Corresponding author. Tel.: +972 3 640 8378; fax: +972 3 640 9293; e-mail address: rozens@post.tau.ac.il.

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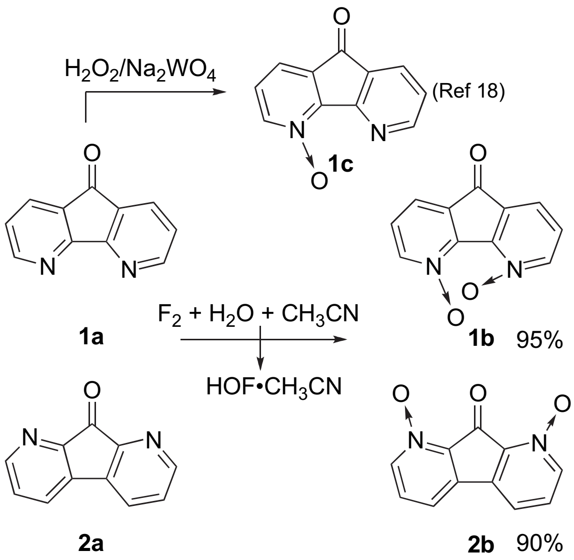
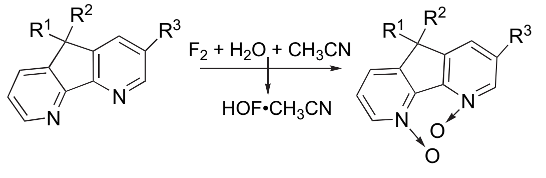


Scheme 1. Oxygenation of diazafluoren-9-ones.

relative to **1b** is also evident from its reaction with HOF·CH_3CN where only 3 mol equiv were needed to produce it practically instantaneously and in 90% yield (Scheme 1).

It is worth noting that, when **1b** was qualitatively compared to **2a** in regard to their affinity toward amino acids, in particular alanine (i.e., a preliminary test for the efficiency of fingerprint detection), no substantial differences were noticed.[19] This indicates that further studies on **1b** should be conducted in order to evaluate its possible role in this field.

Very few 4,5-diazafluorene *N*,*N*-dioxide derivatives such as 9,9-dimethyl-4,5-diazafluoren-4,5-dioxide (**3b**) were synthesized in the past with orthodox oxygen-transfer agents.[20] They were used as precursors for building oligomeric diazafluorenes and published mainly as patents. However, a prerequisite for a success in the oxidation of diazafluorenes is the presence of electron donating groups at C-9. Obviously, HOF·CH_3CN could transfer oxygen to the nucleophilic sites of such compounds as well, as seen, for example, when 9,9-dimethyl-4,5-diazafluorene (**3a**) was converted to the appropriate *N*,*N*′-dioxide (**3b**) in a few seconds and in 90% yield. Similarly, 9,9-bis(4-methoxyphenyl)-4,5-diazafluorene (**4a**)[1] was oxidized to provide the new 9,9-bis(4-methoxyphenyl)-4,5-diazafluoren-4,5-dioxide (**4b**) using 3 equiv of HOF·CH_3CN in 95% yield. The situation, however, was radically different when electron-withdrawing groups are located at the 9-position. We have chosen to demonstrate this point by using the previously unknown 9,9-difluoro-4,5-diazafluorene (**5a**) (Scheme 2).



3a $R^1 = R^2 = Me; R^3 = H$ **3b** 90%

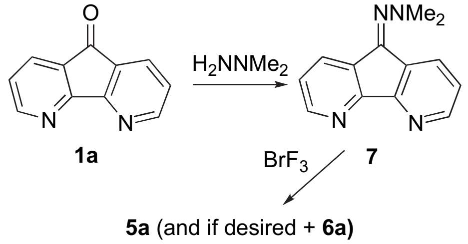
4a $R^1 = R^2 = 4\text{-}MeOC_6H_4; R^3 = H$ **4b** 95%

5a $R^1 = R^2 = F; R^3 = H$ **5b** 90%

6a $R^1 = R^2 = F; R^3 = Br$ **6b** 95%

Scheme 2. Oxygenation of 4,5 diazafluorenes.

The preparation of **5a** seemed to be a worthy challenge since, in addition to the fluorine's electron withdrawing ability, in many cases it also contributes to the molecular stability, an important issue in organic electronic devices.[21] In several cases we have used bromine trifluoride (BrF_3) as an efficient tool for converting carbonyls to the CF_2 group.[22] Thus, we have prepared the corresponding 9-dimethyl-hydrazone-4,5-diazafluorene (**7**)[23] from **1a** and reacted it with 2.5 mol equiv of BrF_3. In a few seconds the difluoro derivative **5a** was obtained in higher than 95% yield and 60% conversion. If an excess of BrF_3 (3.5 mol equiv) was applied, a full conversion was achieved and the yield of **5a** reached 70%, but was also accompanied by 30% of the unknown 2-bromo-9,9-difluoro-4,5-diazafluorene (**6a**), a typical result of aromatic brominations with BrF_3 (Scheme 3).[24]



Scheme 3. Preparation of 9,9-difluoro diazafluorenes.

Indeed, the HOF·CH_3CN complex demonstrated its unique oxygen transfer abilities when reacted with both electron deficient **5a** and **6a**. Applying 5 mol equiv of the reagent at room temperature on **5a** gave the unknown 9,9-difluoro-4,5-diazaflouren-4,5-dioxide (**5b**) in 90% yield in a few seconds. The same procedure was repeated with **6a** and the new 2-bromo-9,9-difluoro-4,5-diazafluoren-4,5-dioxide (**6b**) was formed quantitatively in 10 s (Scheme 2). For comparison, we have reacted both **5a** and **6a** with large excess of either DMDO or MCPBA for several hours, but this gave mostly the starting materials with less then 5% of the desired products.

The spectral UV/vis properties of these easily obtained diazafluorenes and diazafluorenones *N*,*N*′-dioxides are summarized in Table 1. One can clearly see that a substantial narrowing of the HOMO–LUMO energy gap, relative to the starting materials (ΔE_g), did take place.

Table 1
Absorption (λ_{max}, nm) and HOMO–LUMO energy gap (ΔE_g, eV) from UV/vis, HOMO–LUMO energy gap change ($\Delta\Delta E_g$, eV) from UV/vis

Compd	λ_{max} [nm]	ΔE_g[eV]	$\Delta\Delta E_g$[eV]
1a	303	4.10	0.27
1b	324	3.83	
2a	380	3.27	0.38
2b	430	2.89	
3a	309	4.02	0.26
3b	330	3.76	
4a	310	4.00	0.12
4b	320	3.88	
5a	309	4.02	0.37
5b	340	3.65	
6a	309	4.02	0.13
6b	319	3.89	

ΔE_g(HOMO–LUMO gap)$=h\nu/\lambda$.
$\Delta\Delta E_g=\Delta E_g$(starting material)$-\Delta E_g$(product).

3. Conclusion

All the above-mentioned results show initial promising characteristics suitable for compounds serving as electron transporting, hole blocking and electroluminescent devices, and in all cases