STRUCTURE AND REDOX REACTIONS OF TRICYCLIC PYRIDINIUM *N*-IMINES[†]

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Abstract - X-Ray structural analysis of tricyclic pyridinium *N*-imine (**1a**), which is a novel *N*-alkylated pyridinium *N*-imine, revealed characteristics of the structure. Studies on the redox reactions demonstrated that pyridinium *N*-imines (**1a-c**) and quinolinium *N*-imine (**2**) are electron donors and oxidized with nitrosonium tetrafluoroborate.

Pyridinium *N*-imines having no electron withdrawing group at the imino position are usually unstable.[1] However, tricyclic pyridinium *N*-imines (**1**) were isolated as stable solids and the stability is attributed to the steric protection of the imino position by bulky substituents.[2] We have now carried out X-ray analysis of **1a** to reveal characteristics of the structure. We have also investigated redox reactions of **1** and related compounds since ylides (**1**) have both electron donating and accepting parts and are expected to provide an efficient redox system.

Pyridinium *N*-imines (**1a-c**) were prepared by 1,3-dipolar cycloaddition of pyridinium *N*-imines with 2,5-dimethyl-3,4-diphenylcyclopentadienone followed by dehydrogenation.[2] For comparison, quinolinium *N*-imine (**2**)[2] and pyrido-[1,2-*b*]indazole (**3**) containing a resonance contribution of pyridinium *N*-imine[3] were also prepared. Although the structures of **1** were deduced on the

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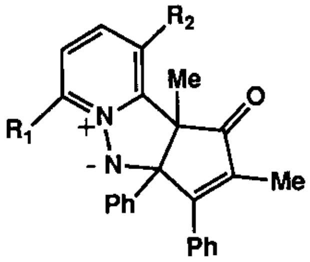
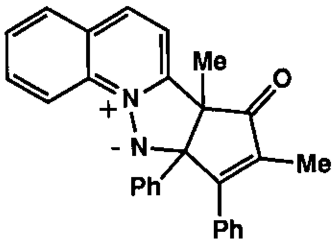
[†] Dedicated to Prof. Masatomo Hamana on the occasion of his 75th birthday.



1a; R_1=R_2=H
1b; R_1=H, R_2=Me
1c; R_1=R_2=Me



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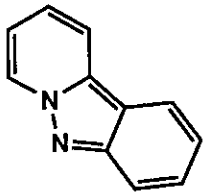

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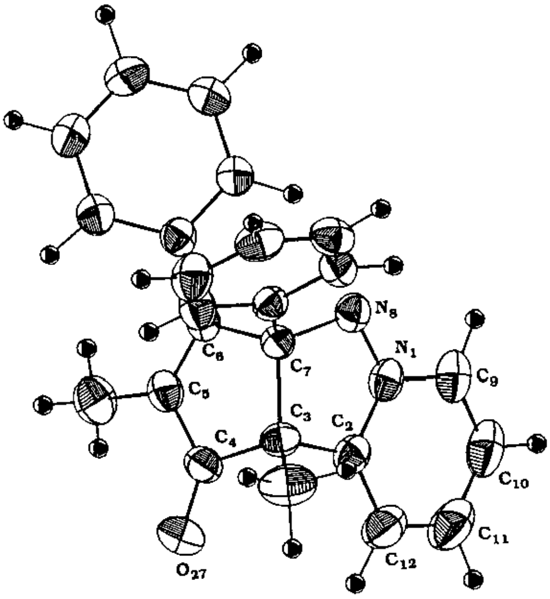
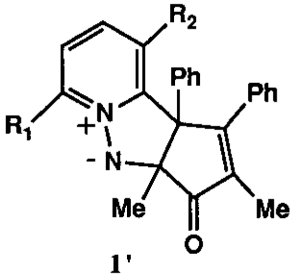


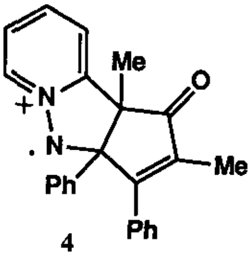
Figure 1. Structure of **1a**: Selected bond lengths (Å): N_1-C_2 1.372(3); N_1-C_9 1.372(3); C_9-C_{10} 1.373(5); C_{10}-C_{11} 1.390 (5); C_{11}-C_{12} 1.375(3); C_{12}-C_2 1.378(4); C_2-C_3 1.498(3); C_3-C_7 1.577(4); C_7-N_8 1.481(2); N_1-N_8 1.337(3)



1'

basis of the spectral data,[2] it was difficult to clearly distinguish between **1** and the isomers (**1'**). The X-ray analysis of **1a** could confirm the structure. The molecular structure with selected bond lengths is shown in Figure 1.[4] The pyrazolopyridine skeleton is almost planar. The N_1-N_8 bond distance (1.34 Å) lies between those of an N-N single bond and an N-N double bond, indicating a conjugation of the imino group with the pyridine ring. On the other hand, the C_7-N_8 bond length (1.48 Å) is normal as a C-N single bond. The distance between the N_8 and C_2 atom (2.32 Å) is shorter than that between the N_8 and C_9 atom (2.37 Å). This fact is consistent with the result that *preferential* N_8-C_2 *bond formation leading to a* 1,2-diazepine derivative takes place upon irradiation.[5]

The cyclic voltammetry (CV) of **1a-c**, **2**, and **3** in acetonitrile showed reversible oxidation waves at 0.72, 0.76, 0.75, 0.66, and 1.07 V vs. SCE.[6] On the other hand, the reduction potentials were below -2.0 V vs. SCE in acetonitrile. This observation indicates that the ylides (**1a-c**) and (**2**) are electron donors and the electron accepting ability of the pyridinium ring is diminished by the electron donating imino group. The reversible nature in the CV suggests that the cation radicals formed by one electron oxidation of **1** are stable during the CV measurement. In order to obtain cation radical (**4**), reactions of **1a** with oxidizing agents were examined. Reaction of **1a** with nitrosonium tetrafluoroborate[7] afforded a BF_4 salt (**5**) in 80% yield,



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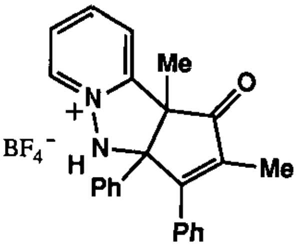

5

6

while the presence of cation radical (**4**) was not detected. The similar reaction of quinolinium *N*-imine (**2**) gave a high yield of the corresponding BF_4 salt. Tropylium tetrafluoroborate (**6**) also oxidized **1a** to give the salt (**5**) with formation of cycloheptatriene. These results indicate that the cation radical (**4**) is relatively unstable and easily undergoes hydrogen abstraction. On the other hand, reaction of **3** with nitrosonium tetrafluoroborate gave no oxidation product probably due to the lower oxidation potential of **3** compared with those of **1** and **2**.

REFERENCES AND NOTES

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4. Crystal data for **1a**: $C_{24}H_{20}N_{2}O$, M=352.43, monoclinic, space group *C2/c*, a=18.532(5), b=8.518(2), c=26.918(6) Å, β=118.34(1) °, V=3740.0(2) $Å^3$, Z=8, D_{calcd}=1.25 g cm^{-3}, MoK_α radiation. The final R value is 5.43% for 2952 reflections with $|F_o|>3\sigma|F_o|$.
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6. Measured at a Pt electrode in acetonitrile with 0.1 M Et_4NClO_4 as a supporting electrolyte; scan rate 100 mV s^{-1}.
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