HEXACARBONYLMOLYBDENUM- OR NONACARBONYLDIIRON-INDUCED REACTION OF 1,3-OXAZEPINE RING SYSTEM. EVIDENCE FOR THE VALENCE ISOMERIZATION BETWEEN 1,3-OXAZEPINE AND PYRIDINE-2,3-OXIDE

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Upon treatment with $[Mo(CO)_6]$ or $[Fe_2(CO)_9]$, phenyl-substituted 1,3-oxazepines undergo the C-2-O and C-7-O bond cleavage to give pyridine and pyrrole derivatives via a coordinated pyridine-2,3-oxide.

The equilibrium for the symmetry-allowed valence isomerization of oxepine (\underline{la}) -benzene oxide $(\underline{2a})$ generally lies on the side of \underline{la} .¹⁾ It is clear that temperature, solvent system, and substituent on the ring carbon atom contribute to the observed position of the equilibrium.¹⁾ It was also theoretically shown that the C-C bond of the epoxide ring in 2a is strengthened by protonation or coordination of the lone pair electron on the oxygen atom so as to shift the equilibrium of la-2a to the side of 2a.²⁾ The thermodynamic¹⁾ and kinetic studies³⁾ are suggestive of this prediction. Regarding the valence isomerization of 1,3-oxazepine (lb)pyridine-2,3-oxide (2b), the existence of 2b was postulated in the photochemical reaction of pyridine N-oxide derivatives $4,\overline{5}$ or in the thermal reaction of 1,3oxazepine derivative to give 3-hydroxypyridine derivative.⁶⁾ In acid-induced reaction of 2,4,5,6-tetraphenyl-1,3-oxazepine, protonation occurs on the nitrogen atom to results in a hydrolysis of the C=N bond.⁷⁾ However, 1,3-oxazepine rearranges to 3-hydroxypyridine derivative on silica gel. 4,8) Thus, the coordination effect on the equilibrium of <u>lb-2b</u> would be suggested.

We report hereon the $[Mo(CO)_6]$ - or $[Fe_2(CO)_9]$ -induced reaction of phenyl-substituted 1,3-oxazepines (3) to undergo the C-2-O and C-7-O bond cleavage leading to pyridine and pyrrole derivatives (4 and 6) in good combined yields via a coordinated pyridine-2,3-oxide (10) (Scheme 1).



The general procedure for the reactions was as follows. A solution of 1,3oxazepine 3 (1 mmol) and $[Mo(CO)_6]$ (2 mmol) or $[Fe_2(CO)_9]$ (3 mmol) in dry benzene (10 cm³) was refluxed under a nitrogen atmosphere for a period indicated in Table 1. The yields of the products summarized in Table 1 were determined through purification by TLC.

The reaction of $\underline{3a}^{9}$ with the metal carbonyls afforded phenyl-substituted pyridine $\underline{4a}$ and pyrrole $\underline{6a}$, while those of $\underline{3b}^{10}$ afforded $\underline{4b}$, $\underline{6b}$, and $\underline{7b}$. On the other hand, the reaction of $\underline{3c}^{10}$ afforded pyridine $\underline{5c}$, which resulted from the rearrangement of C-2-C-7 framework, in addition to $\underline{4c}$, $\underline{6c}$, and $\underline{7c}$. The products $\underline{4a}, \underline{b}, \underline{^{11}}, \underline{4c}, \underline{^{12}}, \underline{5c}, \underline{^{13}}, \underline{6a}, \underline{^{8}}, \underline{7b}, \underline{^{14}}$ and $\underline{7c}^{15}$ were identified by comparison with authentic samples, and the structures of $\underline{6b}, \underline{c}$ were characterized on the basis of physical data. The thermal reaction of 1,3-oxazepines at high temperatures was described to give pyrroles, which resulted from the cross-linked intermediate $\underline{8}$ followed by the bond cleavage. The thermal of $\underline{3a-c}$ without $[Mo(CO)_{6}]$ or $[Fe_{2}(CO)_{9}]$ under the present conditions afforded no product and the starting materials were recovered quantitatively. Thus, the present reaction is clearly differentiated from the purely thermal reaction.

Concerning the reaction mechanism, the thermal reaction of 3 with the metal carbonyls is considered to result in the formation of the complex 9 (Scheme 1). The coordination of $[MO(CO)_5]$ or $[Fe(CO)_4]$ species would shift the equilibrium of <u>9-10</u> to the side of <u>10</u> in some extent.³⁾ The existence of such complexed epoxides as in 10 has aslo been pointed out in the deoxygenation or rearrangement of phenylsubstituted epoxide with $[Mo(CO)_6]^{17}$ or $[Fe(CO)_5]^{18}$ Then, the C-2-O and C-7-O bond cleavage occurs in <u>10</u> to give the intermediates <u>11</u> and <u>12</u>.¹⁹⁾ The deoxygenation of 11 would give pyridines 4a-c.^{17,18}) The intermediate 12 may also possibly give <u>4a-c</u> in some extent. However, the reaction of <u>12</u> leading to <u>4a-c</u> may be slow as compared to that leading to $\underline{15}^{20}$ (vide infra). The C-C bond fission in <u>15</u> would afford pyrroles 6a-c. The reaction of 3b or 3c resulted in the formation of another pyrrole $\frac{7b}{2}$ or $\frac{7c}{2}$, respectively. The reaction of $\frac{6b}{6}$ with [Mo(CO)₆] or [Fe₂(CO)₀] did not afford <u>7b</u>. Therefore, <u>7b,c</u> could result from the C-N bond cleavage in 15 leading to 16 followed by debenzoylation. The pyrroles 7b,c may result from the C-C bond cleavage in 13 followed by debenzoylation. However, the reaction of 3b,c did not afford 14b,c, which is also expected from 13. Thus, the ring closure of 11 leading to 13 seems to be unfavorable. The formation of the unusual pyridine 5c from 3c is explained by the rearrangmenet of 15 leading to 17^{21} followed by deoxygenation.

Concerning the product ratio of 4/6+7, pyridine 4a predominates over pyrrole <u>6a</u> in the case of <u>3a</u>. On the contrary, pyrroles <u>6b,c</u> and <u>7b,c</u> predominate over pyridines 4b,c in the reaction of 3b,c. Concerning 3c, the electron-attracting nitrogen atom seems to favor the formation of 12c rather than 11c. The phenyl group (R^3) also stabilizes <u>12b</u> rather than <u>11b</u> in the case of <u>3b</u>. However, the phenyl groups (R^{\perp} and R^{4}) are fully conjugated with the pentadienyl moiety in <u>lla</u>. Therefore, lla is considered to be more stable than 12a. Thus, the product ratio of 4/6+7 are rationalized on the basis of the electronic effect of the phenyl group The deoxygenation of 12 leading to 4a-c seems to be a minor and the nitrogen atom. Furthermore, all of the $[Mo(CO)_6]$ -induced reaction of <u>3a-c</u> resulted in a process. high ratio of 4/6+7, as compared to the corresponding [Fe₂(CO)₉]-induced reaction. In the [Mo(CO),]-induced reaction, phenyl-substituted epoxide is deoxygenated to greater extent, ¹⁷⁾ unlike in the [Fe(CO)₅]-induced reaction. ¹⁸⁾ Thus, the direct deoxygenation process of <u>10</u> leading to 4a-c is suggested to occur in the [Mo(CO)₆]-

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1,3-Oxazepine Metal Reaction Product (yield/%) Ratio of R^4 R^5 Rl Carbonyl time/h 4 5 6 4/6+7 7 Fe₂ (CO) 9 <u>3a</u> Ph Ph н Ph Ph 11 69 0 23 0 3.0 Mo (CO) 6 7 day 52 0 15 0 3.4 Fe₂ (CO)₉ 3b Ph 3 18 72 5 0.23 \mathbf{Ph} н Ph Н 0 Mo (CO) 6 50 0.57 27 0 21 28 Fe₂ (CO)₉ 3 Ph 4 4 55 0.13 <u>3c</u> Ph н H н 4 Mo (CO) 6 48 22 2 41 0 0.53



induced reactions.¹⁷⁾

Attempted reaction of benz-1,3-oxazepine 18^{22} or 20^{23} with [Mo(CO)₆] or with $[Fe_2(CO)_q]$ in refluxing benzene for 24-48 h afforded no product, and <u>18</u> or <u>20</u> was recovered in 80-85% yield. This fact clearly indicates that the quinoid struc-



tures, 19 and 21, are not favored energetically even by the coordination of the $[MO(CO)_5]$ or $[Fe(CO)_4]$ species under the present conditions.

It is clearly suggested that the coordination of the $[Mo(CO)_5]$ or $[Fe(CO)_4]$ species on <u>3a-c</u> causes the C-O bond cleavage via an O-complexed pyridine-2,3-oxide, leading to the formation of pyridine and pyrrole derivatives.

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(Received March 9, 1985)