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BORON TRIFLUORIDE ETHERATE-CATALYZED REARRANGEMENT OF 2,4,6,7-TETRAPHENYL-1,3-OXAZEPINE TO GIVE NOVEL PYRIDONE RING SYSTEM

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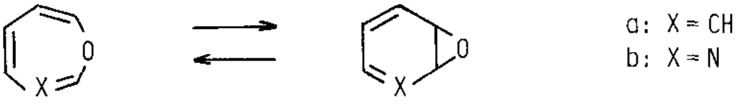
Abstract——The boron trifluoride etherate causes an efficient rearrangement of 2,4,6,7-tetraphenyl-1,3-oxazepine to lead to 2,2,4,6-tetraphenyl-3-pyridone and 3,3,4,6-tetraphenyl-2-pyridone. The BF_3-coordinated pyridine-2,3-oxide is proposed as a reasonable intermediate.

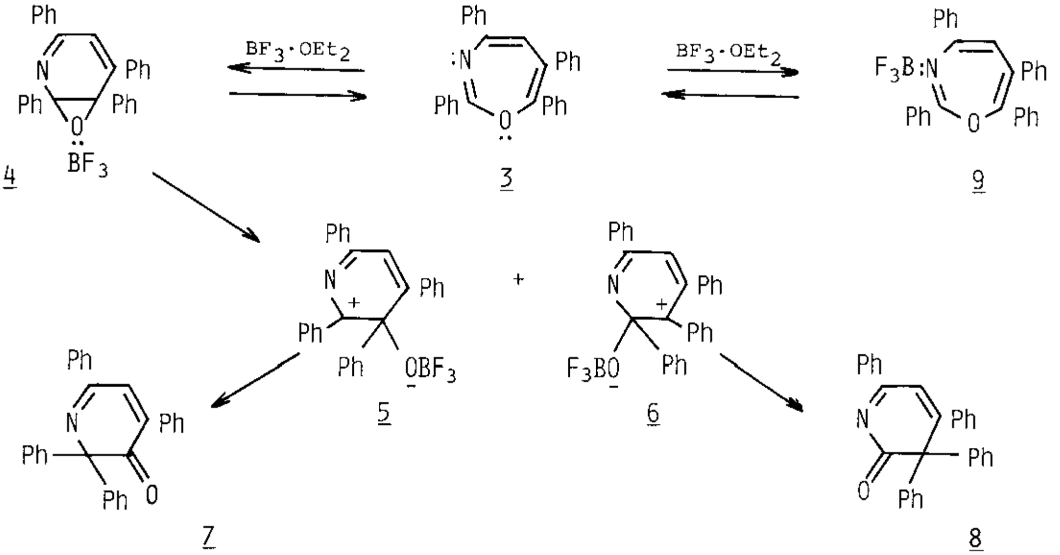
The equilibrium for the valence isomerization of heteropines (1)-arene oxide (2) generally lies on the side of 1. It was theoretically shown that protonation or coordination on the lone pair electron of the oxygen atom of 1a-2a strengthen the C-C bond of the oxirane ring in 2a so as to shift the equilibrium to the side of 2a.[1] The thermodynamic[2] and kinetic studies[3] of 1a-2a are suggestive for this prediction. Regarding the valence isomerization of 1,3-oxazepine (1b)-pyridine-2,3-oxide (2b), 2b is postulated in the photochemical reaction of pyridine N-oxide,[4,5] or in the thermal reaction of 2-phenyl-1,3-oxazepine leading to 2-phenyl-3-hydroxypyridine at high temperature.[6] In acid-catalyzed reaction of 2,4,5,6-tetraphenyl-1,3-oxazepine, protonation occurs on the nitrogen atom to result in a hydrolysis of the C=N bond.[7] However, the 1,3-oxazepine undergoes a facile rearrangement to give 3-hydroxypyridine derivative on silica gel.[4,8] Therefore, the coordination-effect on the equilibrium of 1b-2b is also suggested.



1 2

Scheme 1

We now report on the $BF_3 \cdot OEt_2$-catalyzed rearrangement of 1,3-oxazepine to lead to novel 2,2,4,6-tetraphenyl-3-pyridone and 3,3,4,6-tetraphenyl-2-pyridone ring system, suggesting the coordination of BF_3 shifts the equilibrium of 1b-2b to the side of 2b. 2,4,6,7-Tetraphenyl-1,3-oxazepine (3)[9] and a 0.1 molar equivalent quantity of $BF_3\cdot OEt_2$ in anhydrous benzene were heated under reflux for 6 h to result in the formation of 2,2,4,6-tetraphenyl-3-pyridone (7) (72%, mp 203-204 °C) and 3,3,4,6-tetraphenyl-2-pyridone (8) (10%, mp 162-163 °C). The elemental analyses are satisfactory for 7 and 8, and the structures were characterized on the basis of the following spectral data. For 7: ν_{max} ($CHCl_3$) 1672 cm^{-1}; λ_{max} (MeCN) 238 and 298 nm (log ε 4.02 and 3.72); δ_H ($CDCl_3$) 7.17 (1H, s), 7.20-7.65 (16H, m), 7.90-8.15 (4H, m); m/z (rel intensity), 399 (M^+, 100), 371 (99), 268 (6), 267 (9), 165 (95%). For 8: ν_{max} ($CHCl_3$) 1695 cm^{-1}; λ_{max} (MeCN) 248, 298sh, and 363 nm (log ε 4.26, 3.88, and 3.45); δ_H ($CDCl_3$) 6.75 (1H, s), 7.20-7.55 (16H, m), 7.90-8.15 (4H, m); m/z (rel intensity), 399 (M^+, 10), 371 (100), 268 (29), 267 (24), 165 (9).

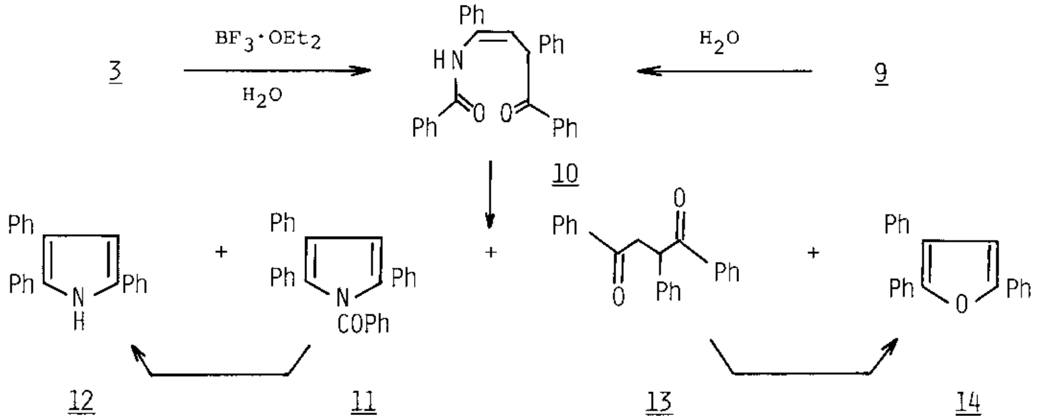


Scheme 2

The formation of 7 and 8 is best explained by the mechanism in Scheme 2. The key step is the coordination of BF_3 on the oxygen atom of 3 followed by the isomerization to give 4. The cleavage of either of the C-O bonds of 4 gives the intermediates 5 and 6. The phenyl migration in 5 and 6, and the subsequent decomplexation give 7 and 8. The predominant formation of 7 over 8 is ascribed to the more stable intermediate 5, the resonance hybrid of which can be stabilized by the phenyl groups. Treatment of 3 with $BF_3\cdot OEt_2$ at ambient temperature for 20 h afforded no pyridone, and 3 was recovered in 95% yield. This fact clearly suggests that the equilibrium of 3-4 is shifted to the side of 4 to some extent under reflux. The

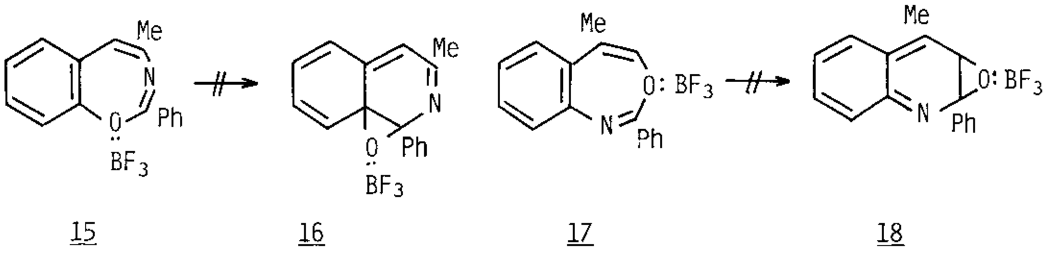
N-coordinated complex 9, which may exist in the equilibrium, could be inert under anhydrous conditions.

On the other hand, the reaction of 3 with $BF_3\cdot OEt_2$ in moist benzene proceeded even at ambient temperature to give 11[7] (1%), 12[10] (7%), and 13[7] (42%), in addition to 3 (39%). Under reflux, this reaciton is completed whithin 3 h to give 11 (7%), 12 (2%), 13 (59%), and 14[11] (24%), which results from the dehydration of 13 (Scheme 3). The similar type of reaction was observed when 2,4,5,6-tetraphenyl-1,3-oxazepine[7] and benz-1,3-oxazepines, 15[12] and 17,[13] were treated with proton acid, and the mechanism was nearly established. Hydrolysis of the C=N bond by proton generated from $BF_3\cdot OEt_2-H_2O$ gives 10. The complex 9, which could be inert under anhydrous conditions, may also react with water to give 10.



Scheme 3

The reaction of 15 or 17 with $BF_3\cdot OEt_2$ in anhydrous benzene under reflux for 6 h afforded no product, and 15 or 17 was recovered in 71 or 92% yield, respectively. Since the possible valence isomers, 16 and 18, contain a quinoid structure, therefore they would be unfavorable energetically[5] even in the presence of $BF_3\cdot OEt_2$, unlike the case demonstrated in 3-4 (Scheme 4).



Sheme 4

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