JOC The Journal of Organic Chemistry

Article

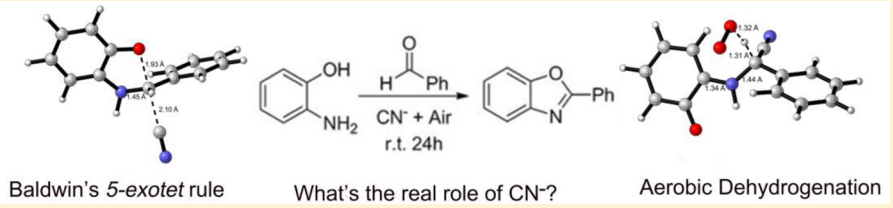
pubs.acs.org/joc

Mechanisms of Metal-Free Aerobic Oxidation To Prepare Benzoxazole Catalyzed by Cyanide: A Direct Cyclization or Stepwise Oxidative Dehydrogenation and Cyclization?

Weiqiang Chen,[†] Weili An,[†] Yongjian Wang,*[,‡] and Ao Yu*[,†]

[†]Institute of Applied Chemistry and Engineering, College of Chemistry, Tianjin Key laboratory of Biosensing and Molecular Recognition and [‡]College of Life Sciences, Nankai University, Tianjin 300071, China

Supporting Information



ABSTRACT: The detailed mechanism of the cyanide-catalyzed synthesis of benzoxazole from 2-aminophenol and benzaldehyde was investigated in depth using density functional theory (DFT). The metal-free aerobic oxidative process as well as the dehydrogenation detail were examined and described. Cyanide anion was proved to assist the oxygen atoms to undergo an aerobic dehydrogenation rather than direct cyclization which was predicted according to Baldwin's 5-*exotet* rule. The dehydrogenation pathway was thermodynamically favored over cyclization with an activation energy difference of 24.2 kcal/mol. Another point noteworthy was the observation that a trace amount of water could reduce the activation energy effectively during the condensation step ($\Delta\Delta G^{\ddagger}$ = 22.3 kcal/mol).

1. INTRODUCTION

Molecular oxygen is an ideal oxidant for its natural abundance, cheapness, and clean oxidative products, therefore it has gained a lot of attention in many chemical reactions.[1] However, the previously reported aerobic oxidative reactions often require a metal catalyst because the direct oxidation of organic substrates using O_2 under mild conditions is relatively difficult.[2] Nowadays, metal-free aerobic oxidative reactions have become a principal research area, and a number of methods have been established.[3] For example, though requiring a co-oxidant and high temperature, methods used for the selective oxidation of allylic/benzylic compounds to alcohols,[4] phenols,[5] and benzoic acids[6] have been reported and proved very appealing. To the best of our knowledge, very few metal-free oxidation mechanisms have been proposed for these aerobic processes in the absence of a co-oxidant, although a variety of explorative experiments have been carried out.

Recently, Cho et al. reported a series of works on an intriguing metal-free aerobic oxidative reaction in which benzofused azoles and their derivatives were synthesized efficiently via cyanide-catalyzed reactions (Scheme 1, eq 1).[7] Air was employed as the sole oxidant, and CN^- was designed to be an effective nucleophile used to catalyze the reactions under mild conditions without the need of a metal catalyst, acid, or co-oxidant, which was greatly different from most of the previously reported work (Scheme 1, eqs 2 and 3).[8−13] Cho et al. believed CN^- mainly facilitated the cyclization step through the nucleophilic attack of CN^- to afford a 5-*exotet* structure based on Baldwin's rule.[14] However, the controlled experiments showed a paradoxical outcome in which cyclization may still not occur in the absence of air (Scheme 2).

Considering that facile dehydrogenation and cyclization are still obscure and controversial, we were interested in the detailed oxidation mechanism of the reaction which will be of significance for designing metal-free reactions. In addition, Seo and Zang also reported the important applications of this type of reaction in aerobic oxidation using cyanide.[15] Thus, we report a complete DFT study using the M06-2X[16] method and propose new mechanisms for the reaction here.

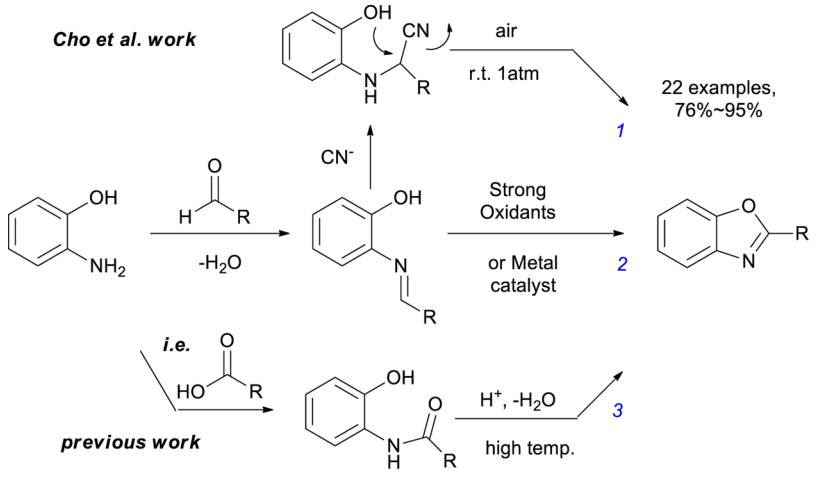
2. COMPUTATIONAL DETAILS

All the computations reported in this work were carried out using Gaussian 09 package.[17] All structures for the substrates, intermediates, transition states, and products were optimized using the M06-2X method in conjunction with 6-31+G(d)[18] basis set. The UM06-2X method was used for the doublet and triplet spin states structures and the corresponding $\langle S^2 \rangle$ values listed in the Supporting Information (SI). Frequency calculations were implemented at the same level of theory to confirm the optimized structures as the minima in energy (no imaginary frequency) and transition state (just one imaginary frequency). Single point energy calculations were performed at (U)M06-2X/6-311++G(3df,2pd)[18,19] level of theory in DMF, where the CPCM solvation model[20] and UAKS radii were used to account for the effect of implicit

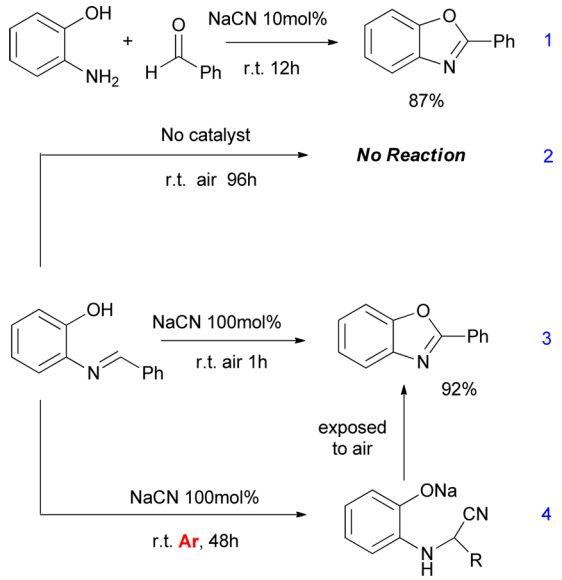
Received: August 8, 2016
Published: October 18, 2016

DOI: 10.1021/acs.joc.6b01939
J. Org. Chem. 2016, 81, 10857−10862

Scheme 1. Selected Methods Used for the Synthesis of Benzoxazoles



Scheme 2. Control Experiments Carried out by Cho *et al.*



solvation. All the energy data in this work are reported in kcal/mol, and the bond length data are reported in angstroms (Å).

3. RESULTS AND DISCUSSION

Amine-Aldehyde Condensation. According to Cho's work,[7a] this reaction can be generally considered to involve three steps: (1) An amine-aldehyde condensation reaction to afford a key phenolic Schiff base intermediate, (2) cyclization catalyzed by CN^- to afford a cyclic intermediate according to Baldwin's 5-*exotet* rule, and (3) a final oxidative dehydrogenation step to obtain benzoxazole (Scheme 1, eq 1). We first examined the condensation step and found that a trace amount of water plays a surprisingly significant role in reducing the activation energy. In the absence of water, condensation and dehydration are very difficult at room temperature because two relatively high activation free energy barriers must be overcome, which were 24.4 (**TS1**) and 42.7 kcal/mol (**TS2**), respectively (Figure 1). However, with the aid of water, the six-membered ring proton-transferred transition state **TS1W** and the subsequent **TS2W** are formed. Thus, the activation energies reduced to 6.6 and 20.4 kcal/mol, respectively.

It is noteworthy that in **TS2W**, the water molecule preferentially assists the proton to transform from the phenolic hydroxyl group instead of the imine N atom in *ortho*-position (**TS2N**). When compared to the commonly believed transition state **TS2N**, **TS2W** was 2.9 kcal/mol lower than **TS2N**. This unusual choice can be attributed to the higher acidity of phenolic hydroxyl group and the higher stability of **TS2W** which was more structurally stretched (see SI for the detailed structures). All in all, the relative energy difference between **TS2W** and **TS2** was up to 22.3 kcal/mol, which shows that the existence of a trace amount of water will accelerate the condensation step significantly.

Direct Catalyzed Cyclization. Without the aid of water, **INT2** can also turn into **INT3** via a proton-transferred equilibrium through **TS3** ($\Delta G^{\ddagger}$ = 16.2 kcal/mol). Then, the exposed O atom will attack the sp^2-hybridized C at the imine site. This direct cyclization reaction only needs 8.4 kcal/mol (**TS4**) and should be facile at room temperature. However, in the assumed subsequent aerobic oxidative process, a ca. 30−36 kcal/mol activation barrier must be overcome. This is difficult to achieve at room temperature (see SI for details) and rules out the possibility that the dehydrogenation step will occur from the already formed cyclized **INT4**, as described in many previous studies.[7,21] In this step, we also examined the effect of water, but no beneficial effect could be observed.

The spontaneous aerobic oxidation reaction is difficult. Cho et al. suggested that CN^- may exert a positive effect in two basic aspects. On one hand, CN^- will change the hybridization of α-C atom from sp^2 to sp^3 so that the cyclization was changed from 5-*endo-trig* to 5-*exotet*. On the other hand, it would force the σ^* orbital of the C−CN bond to be more appropriately oriented to the lone pair electrons of the O atom so that it facilitated the cyclization reaction. To check this idea, we located the classical S_N2 nucleophilic substitution transition state **TS6a** (Figure 2), in which the CN^- leaves and the C−O bond is formed simultaneously to afford a cyclic intermediate. It was found that the activation energy of **TS6a** was very high ($\Delta G^{\ddagger}$ = 47.9 kcal/mol) (Figure 3). When compared to the direct cyclization transition state **TS4** (Figure 1), the activation energy difference was up to 39.5 kcal/mol, distinctly negating the possibility that CN^- mainly functioned as a cyclization catalyst. Moreover, molecular orbital analysis also shows the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of **TS6a** have less overlap than those found for

DOI: 10.1021/acs.joc.6b01939
J. Org. Chem. 2016, 81, 10857−10862

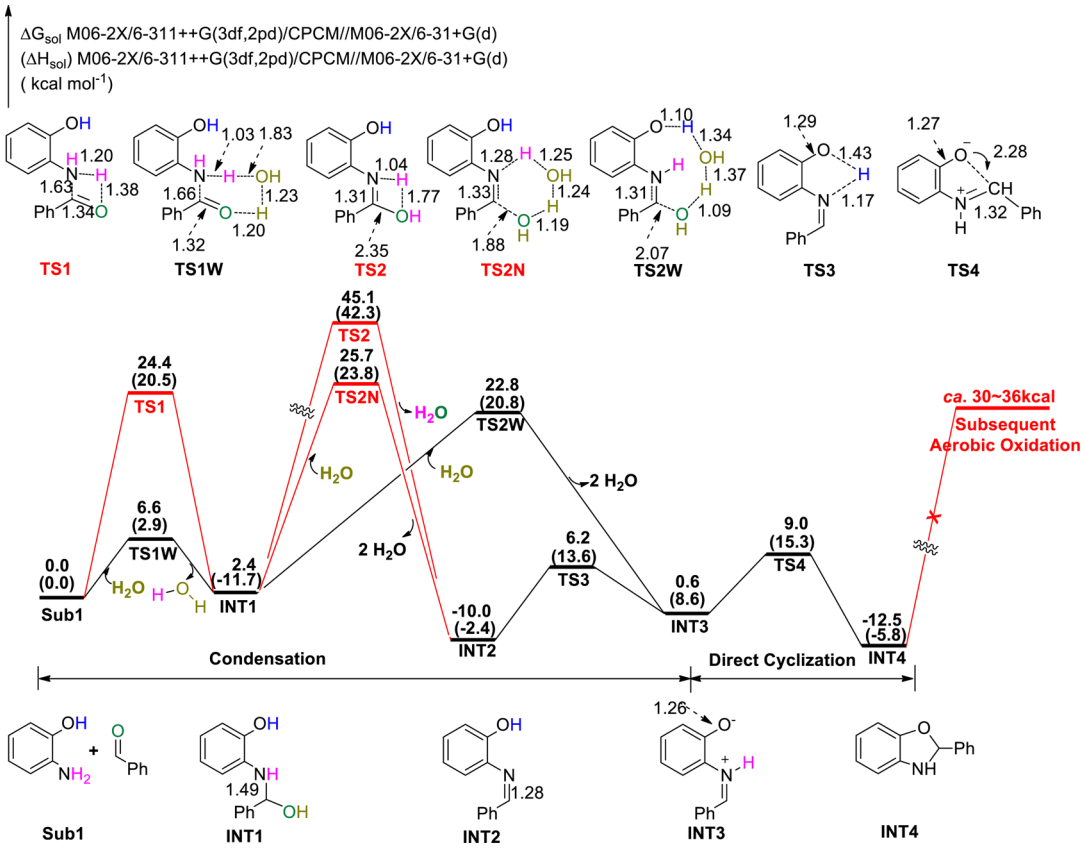


Figure 1. Potential energy surface for the condensation and direct catalyzed cyclization of 2-aminophenol and benzaldehyde.

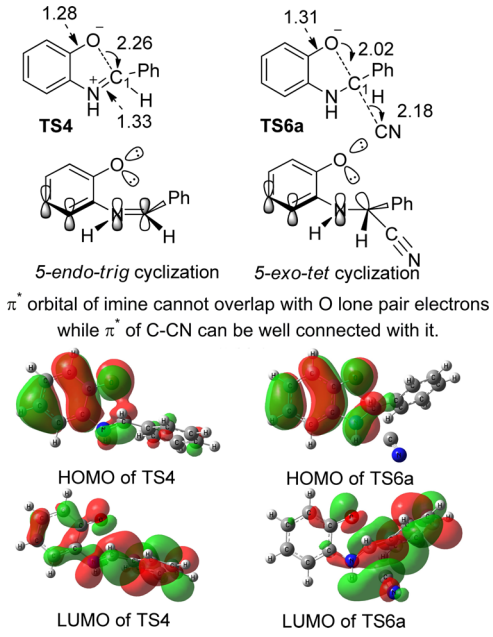


Figure 2. Proposed cyclization transition states reported by Cho et al. and our DFT calculated results.

TS4 (Figure 2). Therefore, we believe that CN^- was NOT directly facilitating the cyclization reaction according to Baldwin's 5-*exotet* rule and that **TS6a** was not a reasonable transition state for the cyclization step.

Oxidative Dehydrogenation and Cyclization. Under these circumstances, we suggest CN^- initially effects the oxidative dehydrogenation by O_2 and then leads to ring formation. Actually, a similar assumption was previously reported but was not exactly proved by experiment.[22] From this point of view, we located **TS6** ($\Delta G^{\ddagger}$ = 23.7 kcal/mol) in which triplet-state molecular O_2 directly abstracts the H atom from α-C_1 site to give **INT6** and a hydroperoxyl free radical (Figure 3). In addition, it was also taken into consideration whether H−N or H−C_1 was oxidatively dehydrogenized first. We found that, although the activation energy of **TS6b** ($\Delta G^{\ddagger}$ = 9.9 kcal/mol) was lower than that of **TS6**, the intermediate **INT6b**, formed by O_2 initially abstracting the H atom from β-N site, was 4.0 kcal/mol higher than the transition state **TS6b**. The higher energy of **INT6b** was mainly induced by the change in structural stability when the H atom of N was abstracted by O_2 to give the hydroperoxyl radical. The N−H bond shows more resistance than C_1−H to lose a hydrogen atom. And more importantly, when N−H loses a hydrogen atom, the remaining single electron of N would be inclined to interact with the π electron system of the adjacent benzene ring. This can be reflected from the changes in bond length observed for several bonds. As shown in Figure 4, when compared with the precursor **INT5**, the σ N_1−C_3 bond of **INT6b** was largely reduced in length from 1.42 to 1.33 Å, while the π bonds C_3−C_4, C_4−C_5, and C_3−C_6 increased in length from 1.45, 1.43, and 1.39 Å to 1.49, 1.44, and 1.43 Å, respectively. This bond length variation (0.01−0.09 Å) was responsible for the instability. On the contrary, when C_1−H loses a H atom, the remaining single electron tends to interact with the π bond of the cyanide group, which leads to a reductions in the σ C_1−C_2, N_1−C_1, and C_1−C_7 bond lengths from 1.48, 1.46, and 1.52 Å (**INT5**) to 1.41, 1.36, and 1.45 Å (**INT6**), respectively. However, the benzene ring was less influenced because the C−C bond lengths in **INT6** were not dramatically

DOI: 10.1021/acs.joc.6b01939
J. Org. Chem. 2016, 81, 10857−10862

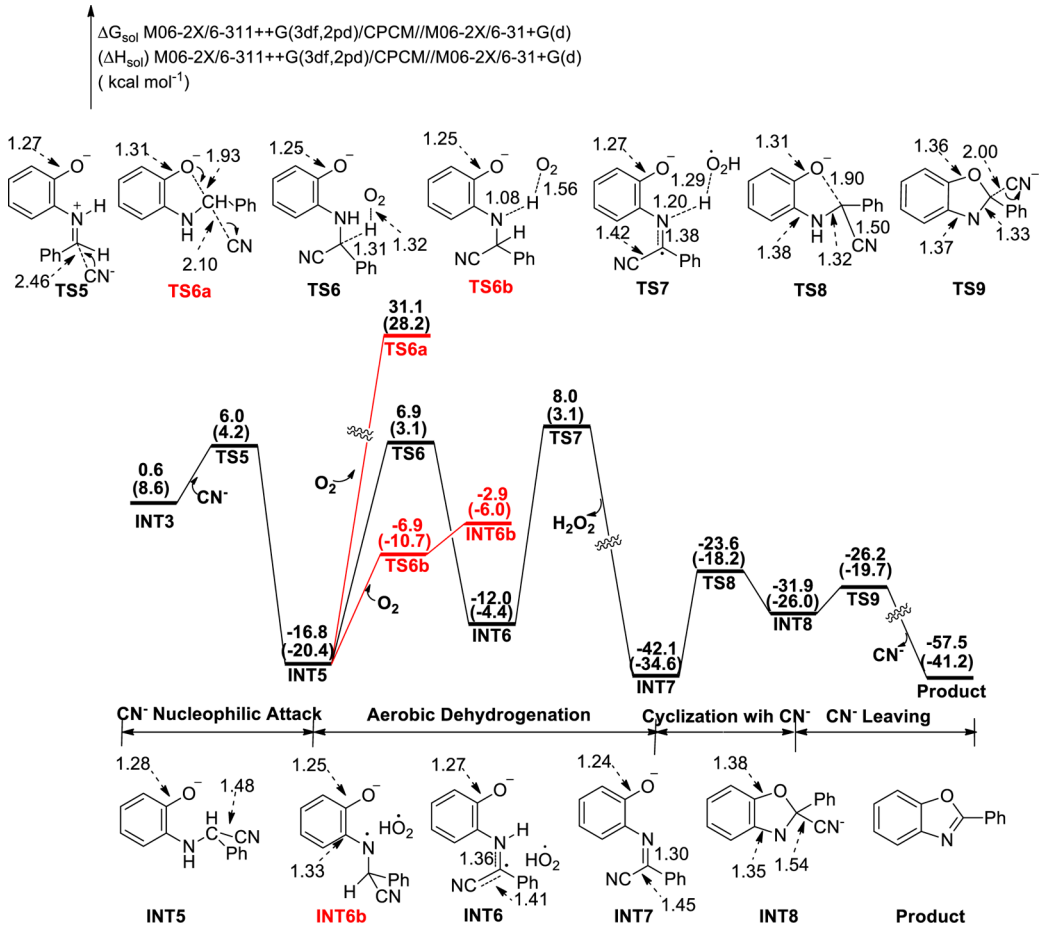


Figure 3. Potential energy surface for the oxidative dehydrogenation and cyclization of 2-aminophenol with benzaldehyde.

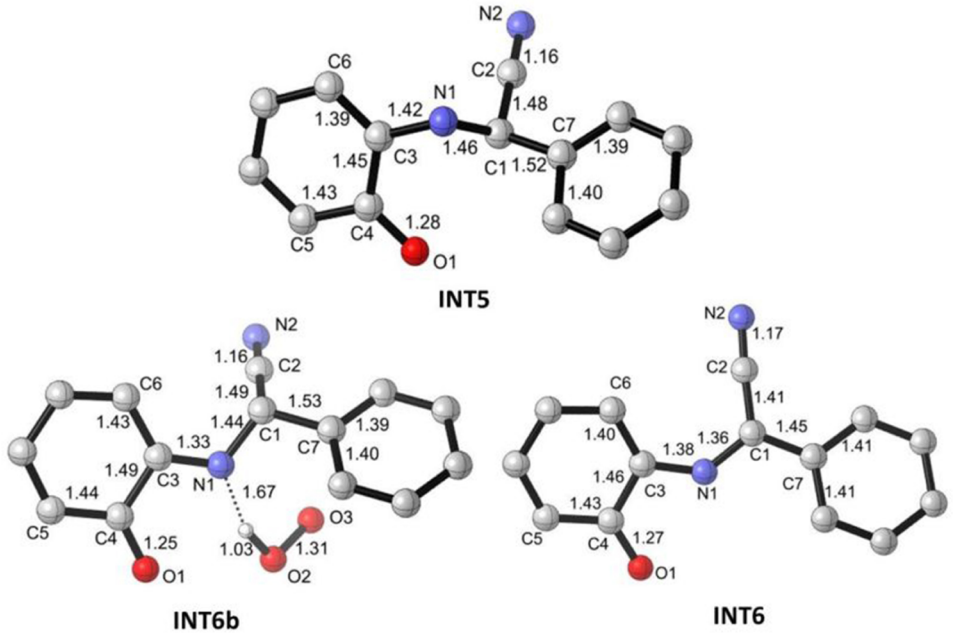


Figure 4. Structural analysis of **INT5**, **INT6**, and **INT6b**.

changed (<0.02 Å). The improved stability of **INT6** can be attributed to the capto-dative effect.[23] This effect has been employed in previous work to account for the findings observed for a similar carbene-catalyzed Benzoin condensation reaction.[24]

When both the electron-donating amine and electron-withdrawing cyanide are simultaneously connected to the carbon free radical generated from **TS6**, the two groups will jointly stabilize the radical intermediate by delocalizing the radical ion

DOI: 10.1021/acs.joc.6b01939
J. Org. Chem. 2016, 81, 10857−10862

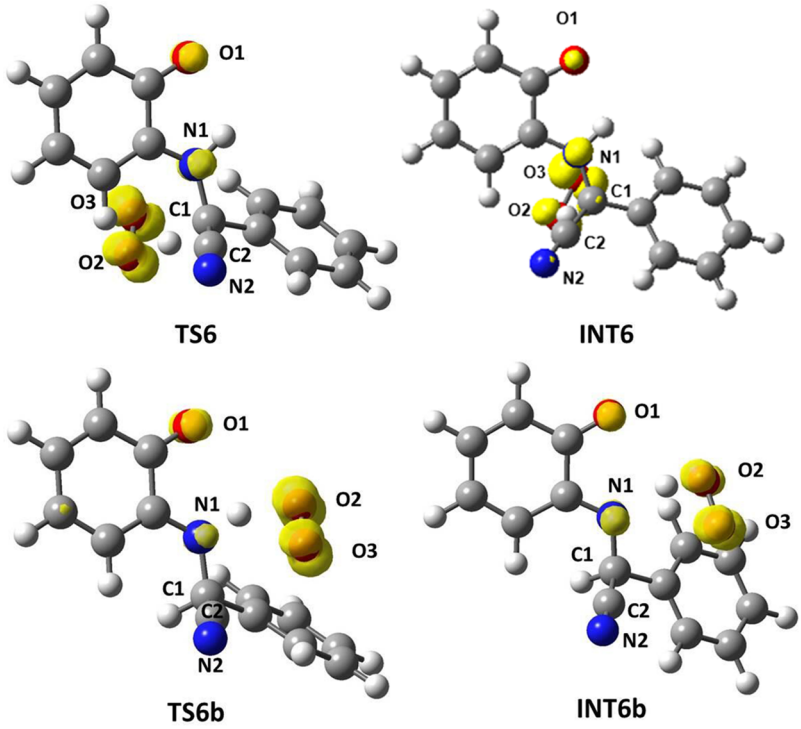


Figure 5. Spin population analyses and structures of **TS6**, **INT6**, **TS6**, and **INT6b** (isovalue = 0.02).

Table 1. Atomic spin densities of selective atoms in TS6, INT6, TS6b and INT6b

	values						
substance	C_1	C_2	N_1	N_2	O_1	O_2	O_3
TS6	−0.001	0.036	0.254	0.000	0.232	0.452	0.626
INT6	0.220	−0.076	0.269	0.102	0.121	0.296	0.718
TS6b	−0.024	0.018	0.242	0.000	0.287	0.415	0.606
INT6b	−0.031	0.030	0.300	0.000	0.253	0.332	0.685

via resonance. To test this idea, we implemented electron spin population analyses for all structures with a single electron, as shown in Figure 5 and Table 1, which clearly demonstrate the free radical sites and spin densities. In **INT6**, the single electron was delocalized very well in C_1, N_1, and N_2, and the N_2 atom of the cyanide group has more distribution than in **INT6b**. So, we can draw our conclusion that the capto-dative effect makes the radical intermediate stable.

It is noteworthy that the large energy difference between **TS6** and **TS6a** ($\Delta\Delta G^{\ddagger}$ = 24.2 kcal/mol) significantly demonstrates the real role of CN^-: CN^- assists the aerobic dehydrogenation by stabilizing the radical instead of directly catalyzing the cyclization in accordance with Baldwin's 5-*exotet* rule.

When triplet oxygen finishes abstracting the H atom from C_1, the hydroperoxyl free radical generated can spontaneously abstract another H atom from β-N to produce planar **INT7** and hydrogen peroxide via **TS7** ($\Delta G^{\ddagger}$ = 20.0 kcal/mol).

Naturally, **TS8** ($\Delta G^{\ddagger}$ = 18.5 kcal/mol) was the transition state in the eventual cyclization step, and it resembles **TS6a**, whereas CN^- would not leave immediately. After the formation of the C−O bond, CN^- will leave via **TS9** ($\Delta G^{\ddagger}$ = 5.7 kcal/mol) to afford the benzoxazole product. Hereby, a complete mechanism was proposed. The whole potential surface was relatively smooth, and the highest energy barrier was 23.7 kcal/mol (TS6) during the oxidative dehydrogenation step, which was in good accordance with the mild experimental conditions used.

4. CONCLUSIONS

In summary, a computational study of the detailed mechanisms on the preparation of benzoxazole gives a significant theoretical insight into the amine-aldehyde condensation, CN^--catalyzed dehydrogenation, and final cyclization reactions. CN^- was found to function mainly as a locating group to trigger the aerobic oxidative dehydrogenation at the α-carbon instead of catalyzing the direct cyclization expected by Baldwin's 5-*exotet* rule. This can facilitate triplet oxygen dehydrogenation because of the capto-dative effect to stabilize the intermediates, which reduces the activation energy to make the reaction progress smoothly. In addition, a trace amount of water will assist the proton to transfer from the hydroxyl group primarily but not from imine N atom, which is generally accepted during the condensation step. This study has provided a novel insight into the design of metal-free aerobic oxidative reactions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01939.

Structures of all transition states and intermediates, Cartesian coordinates and energies of all stationary points involved in this study, and the $\langle S^2 \rangle$ values of doublet or triplet spin state structures (PDF)

DOI: 10.1021/acs.joc.6b01939
J. Org. Chem. 2016, 81, 10857−10862

AUTHOR INFORMATION

Corresponding Authors

*E-mail: yongjian_wang@nankai.edu.cn.
*E-mail: esr@nankai.edu.cn.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support from the National Natural Science Foundation of China (51173083, 21577071) and Key Program of Natural Science Foundation of Tianjin (14JCZDJC40300) is acknowledged.

REFERENCES

(1) (a) Stahl, S. S. *Science* **2005**, *309*, 1824. (b) Piera, J.; Bäckvall, J. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 3506. (c) Roduner, E.; Kaim, W.; Sarkar, B.; Urlacher, V. B.; Pleiss, J.; Gläser, R.; Einicke, W.-D.; Sprenger, G. A.; Beifuß, U.; Klemm, E.; Liebner, C.; Hieronymus, H.; Hsu, S.-F.; Plietker, B.; Laschat, S. *ChemCatChem* **2013**, *5*, 82. (d) Guo, Z.; Liu, B.; Zhang, Q.-H.; Deng, W.-P.; Wang, Y.; Yang, Y.-H. *Chem. Soc. Rev.* **2014**, *43*, 3480.

(2) (a) Ueda, S.; Nagasawa, H. *Angew. Chem., Int. Ed.* **2008**, *47*, 6411. (b) Ueda, S.; Nagasawa, H. *J. Org. Chem.* **2009**, *74*, 4272. (c) Shi, Z.-Z.; Zhang, C.; Tang, C.-H.; Jiao, N. *Chem. Soc. Rev.* **2012**, *41*, 3381. (d) Zhao, H.-Q.; Wang, M.; Su, W.-Q.; Hong, M.-C. *Adv. Synth. Catal.* **2010**, *352*, 1301.

(3) (a) Jursic, B. S.; Douelle, F.; Bowdy, K.; Stevens, E. D. *Tetrahedron Lett.* **2002**, *43*, 5361. (b) Melone, L.; Punta, C. *Beilstein J. Org. Chem.* **2013**, *9*, 1296. (c) Chen, K.-X.; Zhang, P.-F.; Wang, Y.; Li, H.-R. *Green Chem.* **2014**, *16*, 2344.

(4) Punta, C.; Rector, C. L.; Porter, N. A. *Chem. Res. Toxicol.* **2005**, *18*, 349.

(5) (a) Fukuda, O.; Sakaguchi, S.; Ishii, Y. *Adv. Synth. Catal.* **2001**, *343*, 809. (b) Aoki, Y.; Sakaguchi, S.; Ishii, Y. *Adv. Synth. Catal.* **2004**, *346*, 199. (c) Aoki, Y.; Hirai, N.; Sakaguchi, S.; Ishii, Y. *Tetrahedron* **2005**, *61*, 10995.

(6) (a) Lu, T.; Mao, Y.; Yao, K.; Xu, J.; Lu, M. *Catal. Commun.* **2012**, *27*, 124. (b) Ding, H.-L.; Zeng, L.-P. *Adv. Mater. Res.* **2013**, *709*, 74. (c) Tomás, R. A. F.; Bordado, J. C. M.; Gomes, J. F. P. *Chem. Rev.* **2013**, *113*, 7421.

(7) (a) Cho, Y. H.; Lee, C. Y.; Cheon, C. H. *Tetrahedron* **2013**, *69*, 6565. (b) Cho, Y. H.; Lee, C. Y.; Ha, D. C.; Cheon, C. H. *Adv. Synth. Catal.* **2012**, *354*, 2992.

(8) (a) Wei, C.-X.; Wu, D.; Sun, Z.-G.; Chai, K.-Y.; Quan, Z. S. *Med. Chem. Res.* **2010**, *19*, 925. (b) Soares, A. M. S.; Costa, S. P. G.; Goncalves, M. S. T. *Tetrahedron* **2010**, *66*, 8189.

(9) (a) Boyle, K. E.; MacMillan, K. S.; Ellis, D. A.; Lajiness, J. P.; Robertson, W. M.; Boger, D. L. Bioorg. *Bioorg. Med. Chem. Lett.* **2010**, *20*, 1854. (b) Sheng, C.-Q.; Che, X.-Y.; Wang, W.-Y.; Wang, S.-Z.; Cao, Y.-B.; Yao, J.-Z.; Miao, Z.-Y.; Zhang, W.-N. *Eur. J. Med. Chem.* **2011**, *46*, 1706. (c) Bastug, G.; Eviolitte, C.; Marko, I. E. *Org. Lett.* **2012**, *14*, 3502.

(10) (a) Wilfred, C. D.; Taylor, R. J. K. *Synlett* **2004**, *9*, 1628. (b) Wu, M.; Hu, X.; Liu, J.; Liao, Y.; Deng, G.-J. *Org. Lett.* **2012**, *14*, 2722.

(11) (a) Fukuda, S.; Nakamura, A.; Shimizu, M.; Okada, T.; Oohida, S.; Asahara, T. Patent US2004/14977 A1, 2004. (b) Viirre, R. D.; Evindar, G.; Batey, R. A. *J. Org. Chem.* **2008**, *73*, 3452. (c) Shoar, R. H.; Heidary, M.; Farzaneh, M.; Malakouti, R. *Synth. Commun.* **2009**, *39*, 1742. (d) Chen, S.; Zheng, K.; Chen, F. *Tetrahedron Lett.* **2012**, *53*, 6297.

(12) (a) Chen, Y.-X.; Qian, L.-F.; Zhang, W.; Han, B. *Angew. Chem., Int. Ed.* **2008**, *47*, 9330. (b) Williams, T. J.; Fairlamb, I. J. S. *Tetrahedron Lett.* **2013**, *54*, 2906. (c) Gu, L.-J.; Jin, C.; Guo, J.-M.; Zhang, L.-Z.; Wang, W. *Chem. Commun.* **2013**, *49*, 10968.

(13) (a) Chen, W.-H.; Pang, Y. *Tetrahedron Lett.* **2009**, *50*, 6680. (b) Cao, K.; Tu, Y.; Zhang, F. *Sci. China: Chem.* **2010**, *53*, 130. (c) Chen, W.-H.; Wright, B. D.; Pang, Y. *Chem. Commun.* **2012**, *48*, 3824.

(14) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, *18*, 734.

(15) (a) Seo, H.-A.; Cho, Y.-H.; Lee, Y.-S.; Cheon, C.-H. *J. Org. Chem.* **2015**, *80*, 11993. (b) Zang, L.-B.; Wei, D.-Y.; Wang, S.-C.; Jiang, S.-M. *Tetrahedron* **2012**, *68*, 636.

(16) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215−241.

(17) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision B.01; Gaussian, Inc.: Wallingford, CT, 2009.

(18) Hehre, W. J.; Radom, L.; Schleyer, P. V. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(19) (a) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. V. R. *J. Comput. Chem.* **1983**, *4*, 294. (b) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265.

(20) (a) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995. (b) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. *J. Comput. Chem.* **2003**, *24*, 669. (c) Takano, Y.; Houk, K. N. *J. Chem. Theory Comput.* **2005**, *1*, 70. (d) Klamt, A.; Schüürmann, G. *J. Chem. Soc., Perkin Trans. 2* **1993**, *3*, 799.

(21) (a) Xiao, T.-B.; Xiong, S.-W.; Xie, Y.; Dong, X.-C.; Zhou, L. *RSC Adv.* **2013**, *3*, 15592. (b) Zhang, C.; Zhang, L.-R.; Jiao, N. *Green Chem.* **2012**, *14*, 3273. (c) Nguyen, T. B.; Ermolenko, L.; Al-Mourabit, A. *Green Chem.* **2013**, *15*, 2713. (d) Li, C.; Zhang, F.; Yang, Z.; Qi, C.-Z. *Tetrahedron Lett.* **2014**, *55*, 5430.

(22) Lin, S.-X.; Wei, Y.; Liang, F.-S. *Chem. Commun.* **2012**, *48*, 9879.

(23) Viehe, H. G.; Janousek, Z.; Merenyi, R.; Stella, L. *Acc. Chem. Res.* **1985**, *18*, 148.

(24) Rehbein, J.; Ruser, S.-M.; Phan, J. *Chem. Sci.* **2015**, *6*, 6013.

DOI: 10.1021/acs.joc.6b01939
J. Org. Chem. 2016, 81, 10857−10862