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2-Arylbenzoxazoles from Phenolic Schiff's Bases by Thianthrene Cation Radical

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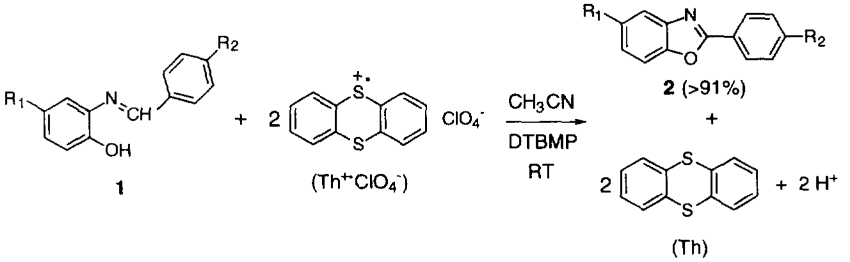
Abstract: 2-Arylbenzoxazoles **2** have been made in 91-97% yields from phenolic Schiff's bases **1** by thianthrene cation radical perchlorate ($Th^{+\cdot}ClO_4^-$) in the presence of 2,6-di-*tert*-butyl-4-methylpyridine.

In spite of the various preparative methods of 2-arylbenzoxazoles **2**,[1] oxidative intramolecular cyclization of phenolic Schiff's base **1** by chemical oxidation seems to be a general method. Thus, moderate to good yields (24-89%) have been reported in the reaction of **1** with oxidants such as barium manganate,[2] lead tetraacetate,[3] nickel peroxide,[4] and copper(I) chloride in the presence of dioxygen[5] as shown in Table 1.

We report herein that thianthrene cation radical perchlorate ($Th^{+\cdot}ClO_4^-$) can convert **1** to **2** in excellent yields as shown in eq 1.



(1)

The yields% and mp's of the products **2** obtained in eq 1 are compared with those of reported values in Table 1 which shows clearly the drastic improvement in yields (>91%) under much milder reaction conditions.[6] Particularly noteworthy in our reactions is an intramolecular participation of the phenolic OH in the cyclization, a first example in $Th^{+\cdot}$ chemistry, instead of the expected intermolecular cyclization and nucleophilic substitution.[7] *i.e.* generally 1,3-oxazole and 5-(hydroxyaryl)thianthreniumyl perchlorate are reported to be formed in the reaction of $Th^{+\cdot}$ with either 2,6-di-*tert*-butyl-4-R- or 2,6-disubstituted phenols in nitrile solvents respectively.

Table 1. Comparisons of Yield%[a]and mp of **2** Obtained from the Reaction of **1** and $Th^{+\cdot}ClO_4^-$ with Those of Reported Values

1		**2** (Yield%)		mp	
R_1	R_2	observed	reported	observed	reported
H	H	97.0	89-70[b]	100-101	102[b], 102-103[c]
H	OMe	95.0	85-24[d]	99-100	100-101[c], 102-104[e]
H	NO_2	91.3	80-41[f]	266-268	267-268[f], 266[g]
t-Butyl	H	93.0	-	81-82	81.5-82[h]
t-Butyl	NO_2	95.2	-	190-192[i]	-

[a] The yield was quantitatively determined. [b] ref. 3 and 5. [c] ref. 4. [d] ref. 1(a) and 8. [e] ref. 7. [f] ref. 8. [g] ref. 2. [h] ref. 9.
[i] This benzoxazole is a new compound.

In conclusion, oxidative intramolecular cyclization of **1** to **2** was achieved in a quantitative yield by $Th^{+\cdot}$ in mild conditions. Further investigations are now in progress to clarify the mechanistic insights.

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REFERENCES AND NOTES

1. (a) Perry, R. J.; Wilson, B. D.; Miller, R. J. *J. Org. Chem.* **1992**, *57*, 2883-2887. (b) Kondo, T.; Yang, S.; Huh, K. -T.; Kobayashi, M.; Kotachi, S.; Watanabe, Y. *Chem. Lett.* **1991**, 1275-1278. (c) E.-Sheikh, M. I.; Marks, A.; Biehl, E. R. *J. Org. Chem.* **1981**, *46*, 3256-3259.
2. Srivastava, R. G.; Venkataramani, P. S. *Syn. Commun.* **1988**, *18*, 1537-1544.
3. Stephens, F. F.; Bower, J. D. *J. Chem. Soc.* **1949**, 2971-2972.
4. Nakagawa, K.; Onoue, H.; Sugita, J. *Chem. Pharm. Bull.* **1964**, *12*, 1135-1138.
5. Speier, G. *J. Mol. Catal.* **1987**, *41*, 253-260.
6. Our reactions were completed within 5 min at room temperature. However, each of other oxidants is reported to require higher temperature (usually >100°C) and much longer reaction times (> 1 hr).
7. Shin, S. -R.; Shine, H. J. *J. Org. Chem.* **1992**, *57*, 2706-1710.
8. Lacán, M.; Rogić, V.; Tabaković, I.; Galijaš, D.; Solomun, T. *Electrochim. Acta* **1983**, *28*, 199-207.
9. Duennenberger, M.; Maeder, E.; Siegrist, A. E.; Liechti, P. *Ger.* 1,201,953 (*CA* **1966**, *64*, 5099).

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