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A concise synthesis of 2-arylbenzoxazoles, **5a-f**, is described that occurs *via* the oxidative cyclization of Schiff's bases, **1a-f**, using relatively benign reagent, manganese triacetate.

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Manganese triacetate, is rapidly evolving as a new and exceptionally versatile reagent in organic synthesis [1-3]. Recently, it has been employed in the lactonization of olefins [2], oxidative cycloadditions [3] and deoxygenation of carbonyl compounds [4]. Oxazole derivatives have attracted attention in view of their applications in industry, agriculture, and because of their biological and analytical significance [5]. In a recent example, the benzoxazole ring system is key part of the antitumor metabolite, UK-1, produced by *Streptomyces sp.* 517-02 [6]. A variety of methods have been developed for the synthesis of benzoxazoles using reagents such as barium manganate [7], lead tetraacetate [8], nickel peroxide [9], copper chloride [10], thianthrene cation radical [11], and hypervalent iodine reagent [12]. However, only a limited number of methods are available for the synthesis of benzoxazoles under milder reaction conditions. Herein, we report a direct conversion of readily available Schiff's bases, **1a-f**, to benzoxazoles, **5a-f**, using manganese triacetate, a relatively benign oxidizing reagent [1b,3]. The reaction occurs readily in refluxing toluene in contrast to conventional benzene or acetic acid that are normally used as solvents in oxidative reaction promoted by man-

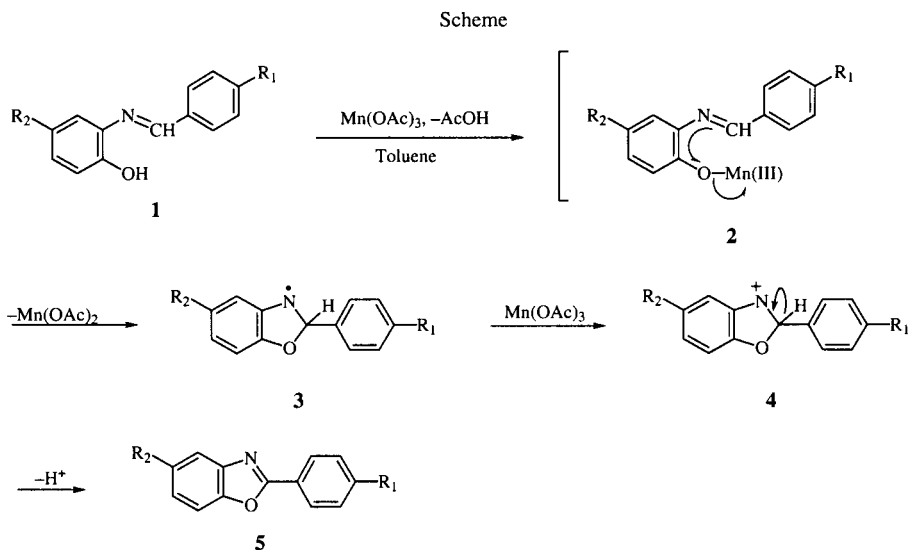
gane triacetate; toluene does not appear to participate in the radical oxidation process described herein.

Table
Synthesis of 2-Arylbenzoxazoles, **5a-f**, from Phenolic Schiff's Bases using Manganese Triacetate

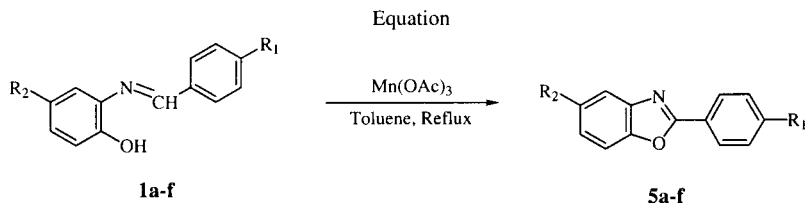
Entry	R ₁	R ₂	Yield (%) [a]	Mp (°C)	
				observed	reported
5a	H	H	94	101	100-101 [11]
5b	H	CH ₃	92	102	103 [12]
5c	CH ₃	H	91	112-113	113-114 [12]
5d	Cl	H	91	146-47	147 [12]
5e	OCH ₃	H	92	98-99	99-100 [11]
5f	NO ₂	H	94	267-68	266-268 [11]

[a] Unoptimized yields of pure products that exhibited physical and spectral properties in accordance with the assigned structures.

The treatment of *N*-benzylidene-*o*-hydroxyphenylamines with 2 equivalents of manganese triacetate in refluxing toluene afford 2-phenylbenzoxazoles exclusively. The plausible reaction pathway presumably involves the enolization of Schiff's base, **1**, to afford Mn(III) enolate, **2**, that loses Mn(II) to provide nitrogen



radical, **3**, which is subsequently oxidized by a second equivalent of manganese triacetate to give nitrogen cation, **4**. Finally, **4** loses a proton to deliver benzoxazole, **5**. This pathway involves the consumption of two equivalents of manganese triacetate as is borne out by the experimental fact that the reaction does not lead to completion with one equivalent of manganese triacetate even upon refluxing for an extended period of time.



In conclusion, this novel method provides a ready entry to the 2-arylbenzoxazoles, **5**, via manganese triacetate promoted oxidative intramolecular cyclization of readily accessible phenolic Schiff's bases, **1**.

EXPERIMENTAL

Melting points were determined on a Mel-Temp II hot stage apparatus using Fluke 51 K/J digital thermometer and are uncorrected. The ^1H and ^{13}C nmr spectra were recorded in deuteriochloroform on Jeol Eclipse 300 (300 MHz for ^1H nmr and 75 MHz for ^{13}C nmr) spectrometers using tetramethylsilane as an internal standard and tlc was performed on silica gel plates supplied by Analtech using hexane:ethyl acetate (9:1, v/v) as the solvent system. Manganese triacetate was obtained from Aldrich Chemical Co. and the various Schiff's bases were prepared according to the literature procedure [8]. The oxidative cyclization of *N*-(4-methylbenzylidene)-*o*-hydroxyphenylamine (**1a**) is representative of the general procedure employed.

To a stirred solution of the Schiff's base, **1c**, (0.211 g, 1 mmole) in toluene (10 ml) was added manganese triacetate (0.536 g, 2 mmoles) and the reaction mixture was refluxed for 1 hour (the reaction was monitored by thin layer chromatography for completion). The precipitated manganese diacetate was then separated by filtration and the solvent was removed under reduced

pressure. The crude product was crystallized from aqueous ethanol to afford 190 mg (91%) of 2-(4-methylphenyl)benzoxazole, mp 112-113°, lit mp 113-114° [12]; ^1H nmr (deuteriochloroform): δ 2.42 (s, 3H, CH₃), 7.32-7.36 (m, 4H, 3-, 6-, 3'- and 5'-H), 7.55-7.59 (m, 1H, 5-H), 7.75-7.77 (m, 1H, 4-H), 8.15 (dd, 2H, J = 2.19, 8.25 Hz, 2' and 6'-H); ^{13}C nmr (deuteriochloroform): δ 21.7 (CH₃), 110.6 (C-7), 119.9 (C-4), 124.6 (C-6), 125.0 (C-5), 127.7 (C-2' and C-6'), 129.7 (C-3', C-5' and C-1'), 142.1 (C-4'), 142.3 (C-3a), 150.8 (C-7a), 163.4 (C-2).

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