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Triflic Acid an Efficient Catalyst for the Thiele-Winter Reaction

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Abstract: Triflic acid is a convenient and non hazardous acid for the Thiele-Winter reaction of quinones. The synthetic scope of the Thiele-Winter reaction was increased by the use of triflic acid.
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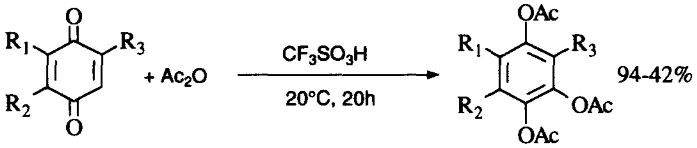
The Thiele-Winter reaction[1-2] is the reaction of quinones with acetic anhydride, and is generally catalysed by sulfuric acid. This reaction is of interest[3] for the synthesis of triacetoxyaromatic precursors of hydroxyquinones. Sulfuric acid leads to the formation of tars in some cases, due to its oxidative character. Zinc chloride was proposed as a milder catalyst[2] but generally chloroquinones[3] are formed as a secondary product. Boron trifluoride[4] and perchloric acid[5] have been proposed and in some cases a better yield than with sulfuric acid has been obtained. Unfortunately quinones with an electron-donating group[6] like 2-methylnaphthoquinone (**6**) (menadione) do not gave a triacetate with boron trifluoride or sulfuric acid as catalyst.

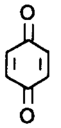
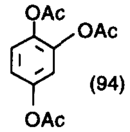
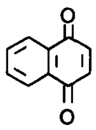
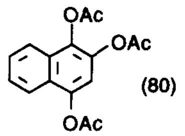
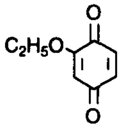
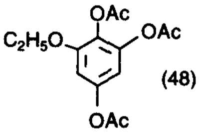
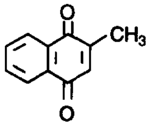
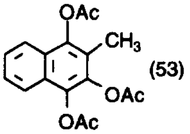
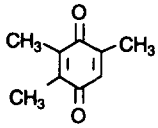
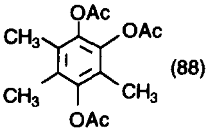
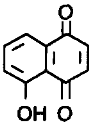
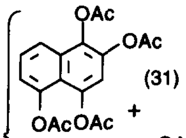
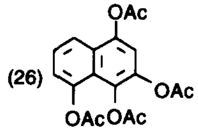
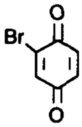
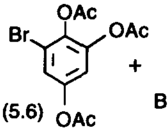
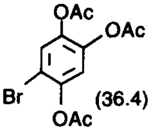
The yield depends on the nature of quinone and on the nature of catalyst. A study in our laboratory[7] of the catalysed reaction with different superacids has shown that the limiting step of the Thiele-Winter reaction is the protonation of the quinone. Sulfuric acid was not acidic enough to produce a large concentration of protonated menadione and due to oxidative nature tarry products are formed. During our study, we have found that commercially available triflic acid is an efficient and convenient catalyst[8] for the Thiele-Winter reaction (Scheme 1).



Scheme 1: Thiele-Winter reaction in presence of triflic acid at room temperature

Triflic acid is more acidic than sulfuric acid, non oxidative and is a much better replacement for perchloric acid or chlorosulfonic acid. Menadione (**6**) gave a triacetate, precursor of the antibiotic phthiocol[5] with a yield of 31% with chlorosulfonic acid, 43% with perchloric acid and 53% with triflic acid, respectively under similar conditions (20° C, 20 h). The results obtained with different quinones with triflic acid at room temperature are reported in Table 1. We obtained Thiele-Winter products with triflic acid as a catalyst in the

Table 1: Thiele-Winter reaction in the presence of triflic acid at 20°C, yield of isolated products

Nº	Reactant	Products (% yield)	Nº	Reactant	Product s (% yield)
1		 (94)	5		 (80)
2		 (48)	6		 (53)
3		 (88)	7		 (31) +  (26)
4		 (5.6) +  (36.4)			

reaction with quinones as compared to the same reaction carried out under classical conditions[3,6]. Sulfuric acid does not give Thiele-Winter reaction respectively with **2**, **3**, **4** or **6**. The synthetic scope of Thiele-Winter reaction was increased by the use of triflic acid.

References and Note

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8. For example, menadione (10 mmol) in acetic anhydride (0.2 mol) and triflic acid (5 mmol) was stirred at room temperature for 20 h. The mixture was poured on ice and filtered. The triacetate was crystallised from methanol. All triacetates showed correct, PMR, CMR, IR, mass spectra and elemental analyses (C,H).
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