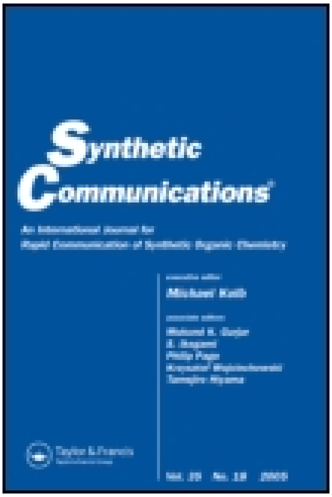

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Ruthenium Catalyzed Oxidation of 1,2-Diols to 1,2-Diketones Using Bromamine-T as an Oxidizing Agent

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Ruthenium Catalyzed Oxidation of 1,2-Diols to 1,2-Diketones Using Bromamine-T as an Oxidizing Agent

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Abstract: A variety of 1,2-diols were selectively oxidized to their corresponding 1,2-diketones with bromamine-T using $RuCl_3 \cdot xH_2O$ as catalyst in alkaline acetonitrile/water (1 : 1) medium. The reaction was pH dependent (pH 8.4), and at higher pH the rate of the reaction decreased significantly.

Keywords: Bromamine-T, 1,2-diketones, 1,2-diols, oxidation, ruthenium chloride

The oxidation of 1,2-diols to the corresponding 1,2-diketones has been reported by $RuCl_2(PPh_3)_3$ catalyzed hydrogen transfer,[1] 4-MeO-TEMPO,[2] 4-$PhCO_2$-TEMPO-electrolysis,[3] (4-AcNH-TEMPO)-OTs-TsOH,[4] H_2O_2-[C_5H_5N-$(CH_2)_5$ $CH_3[PO_4(W(O)(O_2)_2]_4]$,[5] and O_2-$Co(acac)_3$-*N*-hydroxyphthalimide.[6] Recently Khurana et al.,[7] reported the use of *N*-bromosuccinimide as an efficient reagent for this transformation, but bromination as the side reaction particularly in substituted hydrobenzoins was noticed. In continuation to our studies on oxidation,[8–12] herein we report a simple and convenient method for the oxidation of 1,2-diols (**1**) to 1,2-diketones (**2**) in near quantitative yields with bromamine-T as oxidant and ruthenium trichloride as the catalyst (Scheme 1).

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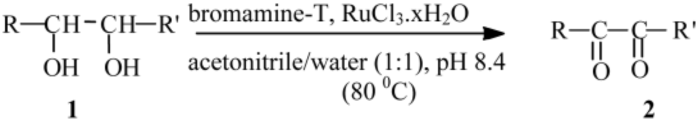

Scheme 1.

Oxidation of 1,2-diols **(1)** with catalytic amount of ruthenium trichloride in acetonitrile/water (1 : 1) at 80°C using bromamine-T with substrate/bromamine-T under alkaline pH (8.4) provided α-diketones (**2**) in almost quantitative yields. These results are summarized in Table 1. Hydrobenzoins in general were found to be more reactive than aliphatic diols and required lesser reaction time for their oxidation. Hydrobenzoins containing electron-donating groups were by far the most reactive substrates (Table 1).

The reaction was found to be highly dependant upon the pH of the reaction medium. At neutral pH, the oxidation of hydrobenzoin was found to be very slow and the reaction completed in 6 h while at pH 8.4 the same could be completed within 45 min. At higher pH (9–11), the rate of the reaction slowed down,[13] and after 12 h the reaction was incomplete. After several experimental investigations with respect to choice of solvents, 1 : 1 H_3CN-H_2O was found to be most efficient.

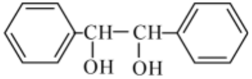
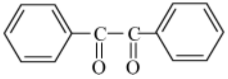
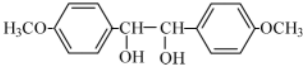
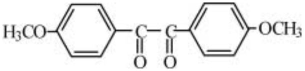
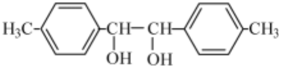
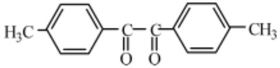
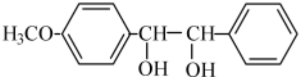
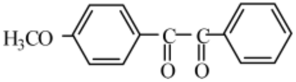
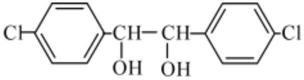
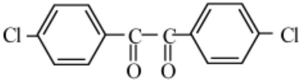
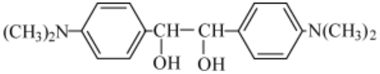
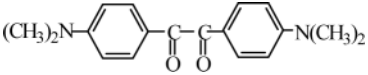
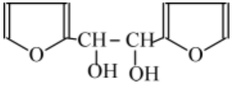
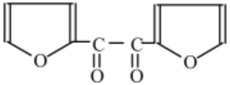
In the absence of the Ru-catalyst the oxidation of hydrobenzoin to benzil did not take place after 12 h, however, with addition of 0.5 mol % ruthenium trichloride to the reaction mixture the transformation occurred in 45 min.

We have developed a very simple and efficient method for the oxidation of 1,2-diols to 1,2-diketones with bromamine-T/ruthenium system under mild reaction conditions.

Typical Experimental Procedure

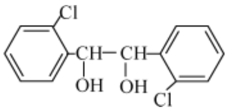
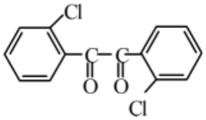
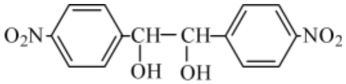
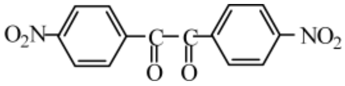
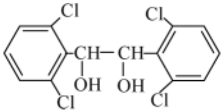
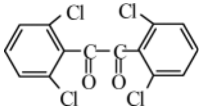
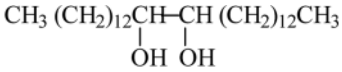
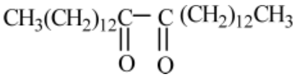
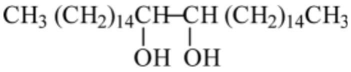
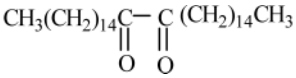
To a stirred solution of hydrobenzoin (1 mmol, 214 mg) in alkaline (pH 8.4) acetonitrile/water (1 : 1) mixture (5 mL), $RuCl_3 \cdot xH_2O$ (1 mg, 0.5 mol%) was added and heated at 80°C for 45 min. The progress of the reaction was monitored by TLC (SiO_2) using benzene/ethyl acetate (9 : 1) as eluent. After completion of the reaction, solvent was evaporated under reduced pressure and the residue dissolved in dichloromethane. The dichloromethane layer was washed twice with water and dried over anhydrous sodium sulphate followed by evaporation. The residue was purified on silica gel using ethyl acetate/hexane (1 : 4) as eluent to yield benzil (199 mg, 95%) which was identified by comparing the physical and spectral data with those of authentic sample.

Table 1. Oxidation of 1,2-diols with bromamine-T using $RuCl_3 \cdot xH_2O$ as catalyst[a]

Entry	Substrate	Product	Reaction time (min)	Yield[b]
1			45	95
2			8	97
3			10	95
4			15	96
5			20	92
6			12	96
7			5	97

(*continued*)

Table 1. Continued.

Entry	Substrate	Product	Reaction time (min)	Yield[b]
8			25	90
9			30	92
10			25	85
11	 $\mathrm{CH_3(CH_2)_{12}\underset{OH}{CH}-\underset{OH}{CH}(CH_2)_{12}CH_3}$	 $\mathrm{CH_3(CH_2)_{12}\underset{O}{\underset{\|}{C}}-\underset{O}{\underset{\|}{C}}(CH_2)_{12}CH_3}$	55	80
12	 $\mathrm{CH_3(CH_2)_{14}\underset{OH}{CH}-\underset{OH}{CH}(CH_2)_{14}CH_3}$	 $\mathrm{CH_3(CH_2)_{14}\underset{O}{\underset{\|}{C}}-\underset{O}{\underset{\|}{C}}(CH_2)_{14}CH_3}$	60	80

[a] Reaction conditions: Substrate/Bromamine-T (1 : 2), $RuCl_3 \cdot xH_2O$ (0.5 mol%), Acetonitrile/water(1 : 1), pH 8.4. at 80°C.

[b] Isolated yields.

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