

The oxidation of alcohols in the present work was performed at room temperature by vigorous stirring a mixture of an alcohol in dichloromethane and an aqueous solution of potassium ruthenate in the presence of potassium peroxodisulfate ($K_2S_2O_8$) and Adogen 464 as a phase-transfer catalyst. Catalytic amounts of the expensive ruthenate were sufficient for the reaction since potassium peroxodisulfate quickly regenerates ruthenate ion during the reaction. The selectivity of this procedure is quite remarkable. Thus, the oxidation of benzyl alcohol (**1a**) is complete within 3 h to afford benzaldehyde (**2a**) in 92% yield. Benzhydrol (**1f**) and cinnamyl alcohol (**3a**) are also readily oxidized to benzophenone (**2f**; 90%) and cinnamaldehyde (**4a**; 91%), respectively. Similarly, other allylic and benzylic alcohols were converted into the corresponding aldehydes or ketones in high yields. When a mixture of a benzylic alcohol and a saturated alcohol or a mixture of an allylic alcohol and a saturated alcohol was treated with potassium ruthenate under the same conditions, only the benzylic or the allylic alcohol was oxidized.

Selective Oxidation of Allylic and Benzylic Alcohols Using Potassium Ruthenate (K_2RuO_4) Under Phase-Transfer Catalysis Conditions

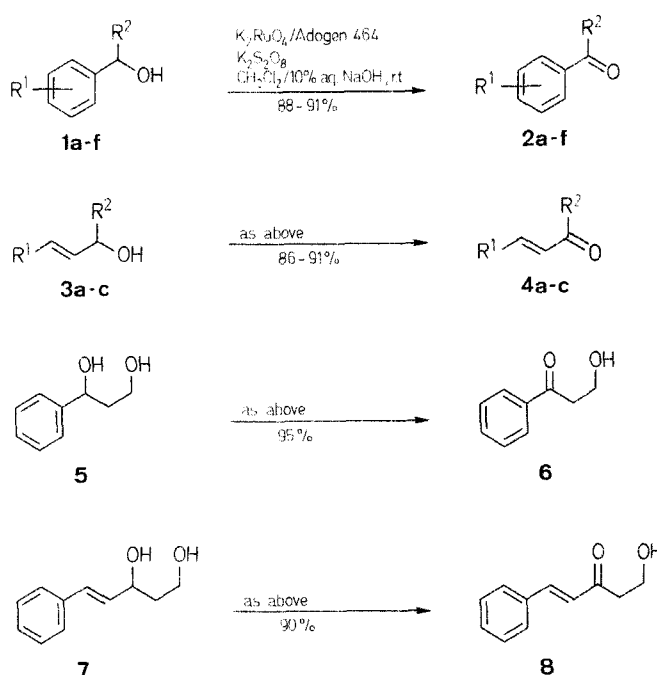
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Catalytic amounts of potassium ruthenate in the presence of potassium peroxodisulfate, which quickly regenerates ruthenate during reaction, selectively oxidize allylic and benzylic alcohols in the presence of Adogen 464 as phase-transfer catalyst at room temperature but do not affect saturated alcohols.

Selective oxidation of allylic and benzylic hydroxy groups in the presence of purely aliphatic hydroxy groups is a useful method in organic synthesis. Although there are several reagents available for this purpose, these oxidizing agents do not show sufficient selectivity, or are not generally applicable, or are not readily available. For example, the widely used manganese dioxide oxidizes aliphatic alcohols in certain cases.¹ Even chromium(VI) reagents such as bis(tetrabutylammonium) dichromate² and 4-dimethylaminopyridinium chlorochromate,³ which are superior to other selective oxidizing agents, still oxidize saturated primary and secondary alcohols to a significant extent.^{2,3} We have earlier reported that potassium ferrate under phase-transfer catalysis conditions selectively oxidizes allylic and benzylic alcohols.⁴

Herein we report another new method for the selective oxidation of allylic and benzylic alcohols in the presence of saturated alcohols using catalytic amount of potassium ruthenate (K_2RuO_4) under phase-transfer catalysis conditions. Although K_2RuO_4 has a great potential for the oxidation of organic compounds, its utility as oxidizing agents is severely limited by its insolubility in organic solvents. Indeed, the oxidations of alcohols with ruthenate reported so far were conducted in aqueous medium and did not show selectivities for allylic and benzylic alcohols.^{5,6}



We further examined the selectivity of the present method by applying it to the oxidation of polyhydroxy compounds. Diol **5** containing both a benzylic and a saturated hydroxy group is oxidized to the β -hydroxyketone **6** in 95% yield. The ruthenate also selectively oxidizes the allylic hydroxy group of diol **7** without affecting the primary aliphatic hydroxy group to afford hydroxyketone **8** in 90% yield. The efficiency, the selectivity, and the easy handling of potassium ruthenate under phase-transfer catalysis conditions might render this method a useful alternative to other methods for the selective oxidation of allylic and benzylic alcohols.

Postassium ruthenate was prepared from ruthenium dioxide using the reported method.⁵ Adogen 464 was purchased from Aldrich Chemical Company and used without purification. All starting alcohols, except **3c**, **5**, and **7**, were obtained commercially and were used after distillation or recrystallization. Alcohol **3c**⁷ is a known compound and was prepared by reduction of ketone **4c**. All oxidation products, except **6** and **8**, are known compounds; carbonyl compounds **2a-f** and **3a-c** were identified by comparison of their spectral and physical data with those of authentic samples which were obtained commercially. The spectral data (IR and NMR) of all products, except for **6** and **8**, are also known.⁸

Yields were determined by the isolation of products or by GLC analyses of the crude products. GLC analyses were accomplished on a Hewlett-

Table. Oxidation of Allylic and Benzylic Alcohols with Potassium Ruthenate in the Presence of a Phase-Transfer Catalyst

Alcohols	R ¹	R ²	Reaction Conditions	Product	Yield ^a (%)	m. p. (°C) or b. p. (°C)/Torr	
						found	reported
1a	H	H	r.t., 3 h	2a	92 (95)	61–62/10	62/10 ¹⁰
1b	2-Cl	H	r.t., 1.5 h	2b	88 (95)	84/10	213–214/760 ¹⁰
1c	4-OCH ₃	H	r.t., 3.5 h	2c	(90)		
1d	4-NO ₂	H	r.t., 1.5 h	2d	(95)		
1e	H	CH ₃	r.t., 2 h	2e	92 (97)	79/10	54/2.5 ¹⁰
1f	H	C ₆ H ₅	r.t., 1 h	2f	90 (98)	48–49	48.5–49.0 ¹⁰
3a	C ₆ H ₅	H	r.t., 4 h	4a	91	119–120/10	120.0/10 ¹¹
3b	CH ₃	H	r.t., 0.5 h	4b	(99)		
3c	C ₆ H ₅	C ₆ H ₅	r.t., 1 h	4c	86 (90)	55–56	55–57 ¹²

^a Yields of isolated products. The values in parentheses refer to the yields determined by GLC.

Packard Model 5750 B flame ionization instrument or on a Hitachi Model 164-6051 thermal conductivity instrument by using a column of 10% PEG 20 M on Chromosorb W. IR spectra were run on a Shimadzu Model IR-435 spectrophotometer. ¹H-NMR spectra were obtained on a Varian EM-360 L spectrometer.

1-Phenyl-1,3-propanediol (5):

A solution of ethyl 3-hydroxy-3-phenylpropanoate⁹ (3.88 g, 20 mmol) in Et₂O (20 mL) is cooled in an ice bath and powdered LiAlH₄ (1.5 g) is added portionwise with stirring under nitrogen. After completion of the reaction, EtOAc (~3 mL) and then H₂O (~2 mL) are added in order to destroy unreacted LiAlH₄. The mixture is filtered and the residue is washed with Et₂O (2 × 10 mL). The combined filtrate and washings are dried (MgSO₄) and concentrated. The resultant crude product is purified on a column of silica gel (EtOAc/hexane 6:4 as eluent) to give pure **5**; yield: 1.8 g (60%); b.p. 128–132 °C/57 Torr.

C₉H₁₂O₂ calc. C 71.03 H 7.95
(152.2) found 71.07 8.02

IR (neat): $\nu = 3400(\text{OH}); 1050 \text{ cm}^{-1}$.

¹H-NMR (CDCl₃): $\delta = 1.80$ (q, 2H); 3.70 (t, 2H); 4.85 (t, 1H); 7.35 (m, 5H_{arom}).

1,3-Dihydroxy-5-phenyl-4-pentene (7):

Compound **7** is prepared from ethyl 3-hydroxy-5-phenyl-4-propenoate⁹ (2.34 g, 10 mmol) as described for the preparation of **5**. The crude product is recrystallized from benzene to afford pure **7**; yield: 1.19 g (62%); m.p. 65 °C.

C₁₁H₁₄O₂ calc. C 74.13 H 7.92
(178.2) found 75.04 8.03

IR (KBr): $\nu = 3480(\text{OH}); 1080 \text{ cm}^{-1}$.

¹H-NMR (CDCl₃): $\delta = 1.75$ (q, 2H); 3.70 (t, 2H); 4.40 (q, 1H); 5.75–6.50 (m, 2H); 6.85–7.30 (m, 5H_{arom}).

Oxidation of Alcohols 1, 3 to Carbonyl Compounds 2, 4; General Procedure:

A mixture of alcohol **1** or **3** (2 mmol) and Adogen 464 (53 mg) in CH₂Cl₂ (15 mL) and potassium ruthenate (0.04 mmol) and potassium peroxydisulfate (8 mmol) in 10% aqueous KOH (5 mL) is vigorously stirred at room temperature. The progress of the reaction is monitored by GLC and TLC. The layers are separated and the aqueous layer is extracted with CH₂Cl₂ (10 mL). The combined organic solution is washed with H₂O (10 mL), dried (MgSO₄), and concentrated, and a portion is analyzed by GLC. The crude product is purified by bulb-to-bulb distillation or recrystallization.

Oxidation of 1-Phenyl-1,3-propanediol (5) to 3-Hydroxy-1-phenyl-1-propanone (6):

Diol **5** (0.30 g, 2 mmol) is oxidized as described above to afford, after purification by column chromatography (EtOAc/hexane, 1:1) the pure hydroxyketone **6** as a colorless oil; yield: 0.28 g (95%).

C₉H₁₀O₂ calc. C 71.98 H 6.71
(150.2) found 71.90 6.62

IR (neat): $\nu = 3450(\text{OH}); 1690(\text{CO}); 1050 \text{ cm}^{-1}$.

¹H-NMR (CDCl₃): $\delta = 2.90$ (s, 1H); 3.25 (t, 2H); 4.10 (t, 1H); 7.30–8.30 (m, 5H_{arom}).

Oxidation of 1,3-Dihydroxy-5-phenyl-4-pentene (7) to 5-Hydroxy-1-phenyl-1-penten-3-one (8):

Diol **7** (0.27 g, 1.5 mmol) is oxidized as described above to afford, after purification by column chromatography (EtOAc/hexane, 1:1) the pure hydroxyketone **8** as a colorless oil; yield: 0.24 g (90%).

C₁₁H₁₂O₂ calc. C 74.98 H 6.86
(176.2) found 74.88 6.73

IR (neat): $\nu = 3450(\text{OH}); 1680(\text{CO}); 1050 \text{ cm}^{-1}$.

¹H-NMR (CDCl₃): $\delta = 2.98$ (t, 2H); 3.70–4.15 (m, 3H); 6.70 (d, 1H); $J = 16 \text{ Hz}$; 7.10–7.65 (m, 6H).

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