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Oxidation of Ferrocenyl-Substituted Primary and Secondary Alcohols with Cr^{VI} and Mn^{VII} Compounds

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In our previous papers^(1, 2) we have reported the reaction conditions for the oxidation of some substituents on ferrocene without the occurrence of the competitive reaction of the oxidation of the ferrocene nucleus to the ferricenium ions. Such a selective oxidation is possible only when the reaction system does not contain any compounds with "acid" hydrogen. Especially good results were obtained in the oxidation of ferrocenyl-substituted primary and secondary alcohols in homogeneous solutions of aprotic solvents by bis(triphenylsilyl)chromate(VI)⁽¹⁾.

We report here the results of the oxidation of some ferrocenyl-substituted primary and secondary alcohols by more accessible oxidation reagents with fair solubility in organic aprotic solvents, e.g. tetra-*n*-butylammonium chromate, [(*n*-C₄H₉)₄N]₂[Cr₂O₇], pyridinium chlorochromate, [C₆H₅NH][CrOCl₃], and tetra-*n*-butylammonium permanganate, [(*n*-C₄H₉)₄N][MnO₄].

The oxidation was studied with the group of monosubstituted ferrocene derivatives (η⁵-C₅H₅)Fe(η⁵-C₅H₄CH(OH)R), where R is H(1), CH₃(2), C₆H₅(3), 4-C₆H₄Cl(4), 3,4-C₆H₃Cl₂(5), CH₃O(6), or C(CH₃)₃ (7). The oxidation takes place under mild conditions giving relatively high yields of the corresponding carbonyl compounds according to the reaction below.



The oxidation were carried out in three solvents recommended in the literature^(3–5) – dichloromethane, chloroform and pyridine at 25, 61 and 115 °C, respectively. The molar ratio of the oxidation reagent and the substrate was always 1 : 1 with regard to the limited oxidation capacity of the reagents.

The results of the oxidation reactions are shown in Table 1. The oxidations were carried out in the following way: the solu-

Table 1. Yields from the oxidation of alcohols (1–7) by Cr^{VI} and Mn^{VII} compounds.

Alcohol	Yields of carbonyl compounds (content of nonoxidized alcohol) (%)		
	[(C ₄ H ₉) ₄ N] ₂ [Cr ₂ O ₇]	[C ₆ H ₅ NH][CrO ₃ Cl]	[(C ₄ H ₉) ₄ N][MnO ₄]
1	67(14)	55(38)	72(24)
2	62(28)	63(25)	79(8)
3	61(28)	62(25)	71(10)
4	70(20)	55(40)	76(16)
5	67(25)	76(14)	63(32)
6	66(31)	73(25)	52(42)
7	68(25)	79(14)	48(42)

tion of the substrate and the oxidation reagent (10 mmol) in dichloromethane (250 cm³) was heated in dark under reflux for 3 hours. After cooling, the reaction mixture was shaken 3 times with 20 cm³ of 5% solution of NaHSO₃ to remove the rest of the oxidation reagent, filtered, and then the organic layer was separated, dried with Na₂SO₄, and evaporated to dryness. The resulting product was dissolved in the mixture of benzene-diethylether (1 : 1, v/v) and separated on a chromatographic column filled with active Al₂O₃ (Beckmann II). The elution was carried out with the mixture of benzene-diethylether (1 : 1, v/v). The content of the products was determined by weighing. The identification of the resulting compounds was made on the basis of melting points, chemical analysis, thin-layer chromatography, infrared spectra and H¹ n.m.r. spectra.

As seen from Table 1, with the reaction conditions given above the oxidation of the ferrocenyl-substituted primary and secondary alcohols to the corresponding carbonyl compounds proceeds with yields of 50–70%. Some of the starting alcohol remains in the reaction mixture. The reaction losses based on the starting alcohol content do not exceed 20%. These are due to the destruction of the sandwich structure of the ferrocene nucleus and to the formation of ethers derived from the starting alcohols. These ethers are stable to oxidation, and prolonged boiling in the presence of oxidation reagents, total destruction of the ferrocene skeleton takes place.

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Table 2.

Oxidation reagent	Yields (%)		Reaction conditions			
	Carbonyl compound	Starting alcohol	Ether	Solvent	Temperature (°C)	Time (h)
[(C ₄ H ₉) ₄ N] ₂ [Cr ₂ O ₇]	38	10	38	CHCl ₃	61	1
	20	4	44	CHCl ₃	61	30
	53	22	9	pyridine	115	3
[C ₆ H ₅ NH][CrO ₃ Cl]	64	19	12	CHCl ₃	61	3
	12	45	15	pyridine	115	3
[(C ₄ H ₉) ₄ N][MnO ₄]	24	65	4	CH ₂ Cl ₂	25	4
	60	25	11	CHCl ₃	61	3
	62	24	8	pyridine	25	72
	45	8	39	pyridine	115	3

The results obtained with all the three solvents show that the nature of the solvent does not substantially affect the oxidation results. In chloroform and pyridine the oxidation can be carried out at higher temperatures. In these cases the yields of the carbonyl compounds do not change substantially and in some

cases are even lower due to the competitive reactions. This is also evident from Table 2, where the results of the oxidation of (1-hydroxyethyl)ferrocene (compound No. 2) at various reaction conditions are summarized.

Thus, all the oxidation reagents studied can be used successfully with carefully chosen reaction conditions for sensitive oxidations of primary and secondary alcohols bound to the ferrocene nucleus. The selective oxidation affords carbonyl compounds.

All the ferrocene derivatives and oxidation reagents used were prepared and purified according to the literature data^(1, 3, 4, 6).

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Optically Active Rhenium Carbonyl-Quinone Radical Complexes: Stereoselectivity in Ligand Substitution of Organometallic Complexes

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The isolation of optically active radicals has eluded chemists for many years. It is particularly difficult to resolve optical activity in organic radicals during a chemical reaction due to their chemical reactivity and probable loss of chirality in the derived carbon radicals caused by the change in symmetry. Recently, we have been able to take advantage of the facile thermal substitution of CO in the rhenium carbonyl-quinone radical complexes by a variety of ligands to produce stable, isolable radical complexes⁽¹⁾. If the substituting ligand is optically active, then it follows that the resulting daughter radical complex will also be chiral. Thus, the optically active carbonyl (3,5-di-*tert*-butyl-*o*-quinone)rhenium-DIOP radical complexes were prepared, isolated and characterized⁽²⁾. This class of optically active metal-quinone radical complexes is clearly different from the numerous cases of organometallic complexes where chirality is induced on a metal containing unpaired d-electron⁽³⁾.

The binding of a ligand to a metal, and hence its reactivity while coordinated, often depends upon the other ligands already coordinated. If the ligand already bound in the radical is optically active, then it is reasonable to expect that the

interaction of the chiral radical with a racemic mixture of another optically active ligand will have some degree of stereoselectivity. For example, the resolution of racemic mixtures of aminoacids has been accomplished by passing them through a column containing Cu²⁺ ions bound to an optically active anionic resin⁽⁴⁾. This aspect of the transition metal chemistry is important, as most biological metal-enzyme reactions are stereospecific, although the details of the chiral intermediates are often incomplete.

We wish to report here the two different types of stereoselective reactions involving the optically active rhenium-quinone radical complexes. The first type occurs when a racemic mixture of camphorquinone reacts with Re(CO)₃(+)-DIOP or Re(CO)₃(-)-DIOP radical fragments. The second type of reactions involves the rhenium-quinone-L* radical complex (having an optically active L* ligand already bound) undergoing substitution by a racemic mixture of a different ligand.

When an excess of racemic d,l-camphorquinone was photolysed in benzene solution in the presence of Re₂(CO)₁₀ and (+)-DIOP, it was found that the unreacted camphorquinone (CQ) exhibited optical activity and gave a negative rotation. Likewise, when (-)-DIOP was used instead, the excess of CQ

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