Ruthenium(II)-Catalyzed Oppenauer-Type Oxidation of Secondary Alcohols

Maria L. S. Almeida, Marion Beller, Guo-Z. Wang, and Jan-E. Bäckvall*

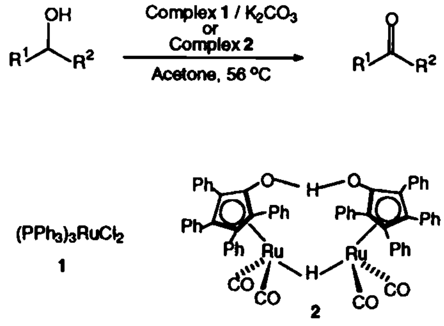
Abstract: Highly efficient ruthenium-catalyzed Oppenauer-type oxidations of secondary alcohols to ketones have been developed. The catalytic system consists of $[(PPh_3)_3RuCl_2]$ (**1**) and K_2CO_3 or $[(C_4Ph_4COHOCC_4Ph_4)(\mu\text{-H})(CO)_4Ru_2]$ (**2**) in refluxing acetone. The catalytic reaction is of high efficiency and permits a catalyst:substrate ratio of 1:1000 at 56 °C. In some cases the initial turnover rate exceeds $1500\,h^{-1}$. The reaction was found to be general and compatible with double bonds and oxidation-sensitive aromatics. With some allylic alcohols, isomerization to saturated ketones took place. The reaction proceeds by ruthenium-catalyzed dehydrogenation of the alcohol and subsequent hydrogen transfer to acetone. No primary kinetic isotope effect was observed for the catalytic reaction when α-deuterated 1-phenylethanol was employed as substrate ($k_H/k_D = 1.1$); this shows that β-hydride elimination from a ruthenium alkoxide intermediate is not the rate-limiting step.

Keywords
catalysis · dehydrogenations · oxidations · ruthenium complexes · secondary alcohols

Introduction

The oxidation of alcohols to carbonyl compounds is a fundamental reaction in organic synthesis. Several methods and reagents are available for carrying out this transformation;[1-10] the most common laboratory procedures employ chromium reagents and activated DMSO.[1,2] More recently, transition-metal-catalyzed oxidations of alcohols have been developed, and in particular ruthenium-catalyzed oxidations have attracted considerable interest.[5-10] The use of catalytic reactions in oxidations[5] is of importance in large-scale industrial processes from both an economic and an environmental point of view.

We have recently developed several efficient ruthenium-catalyzed procedures for the oxidation of alcohols to ketones or aldehydes.[8,10] These oxidations involve a ruthenium(II)-catalyzed dehydrogenation of the alcohol followed by transfer of the hydrogen to an oxidant or a ketone. In this paper we give a full account of the ruthenium-catalyzed Oppenauer-type[11] oxidation of secondary alcohols.[12] In this homogeneous hydrogen-transfer reaction, acetone is employed as solvent and hydrogen acceptor. Acetone, which is inexpensive and unreactive towards most organic functional groups, will therefore function as the formal oxidant of the process (Scheme 1). With catalyst **1** a catalytic amount of base, such as K_2CO_3, has a remarkable accelerating effect. An interesting observation that we recently made in this context is that small amounts of water (0.5–1%) are crucial for a fast and reproducible reaction.



Scheme 1.

Results and Discussion

Ruthenium-catalyzed Oppenauer oxidation: A variety of different ruthenium(II) complexes were investigated as catalyst precursors. Preliminary results showed that complexes **1** and **2** exhibited good catalytic activity and therefore the scope and limitations of the title reaction employing these catalysts were studied. A range of different substrates was employed; the results are summarized in Table 1. The oxidations were carried out in refluxing acetone with either complex **1** or **2** as catalyst. With the former catalyst it was necessary to add a catalytic amount of base (K_2CO_3) for an efficient reaction and also to use acetone containing small amounts of water (≈0.6%). With these simple catalytic systems secondary alcohols were readily oxidized to ketones by acetone in an efficient and selective manner.

Benzylic alcohols gave the highest yields and turnover rates and the oxidation worked well with as little as 0.1 mol% of catalyst **1** (Table 1, entries 1, 4, and 5). A control experiment showed that for these reactive substrates, the reaction can be

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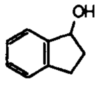
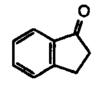
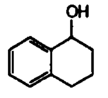
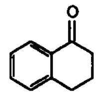
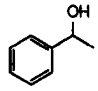
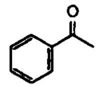
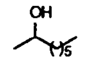
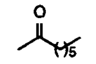
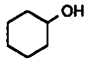
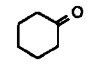
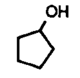
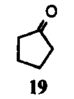
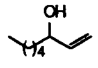
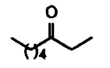
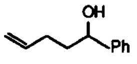
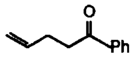
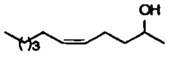
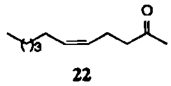
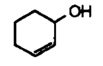
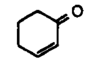
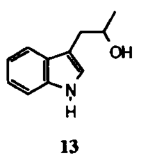
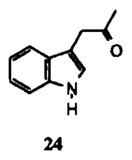
[*] Prof. J.-E. Bäckvall, Dr. M. L. S. Almeida, Dr. M. Beller, Dr. G.-Z. Wang
Department of Organic Chemistry, University of Uppsala
Box 531, S-75121 Uppsala (Sweden)
Fax: Int. code +(18)50-8542

0947-6539/96/0212-1533 $ 15.00+.25/0

Table 1. Ruthenium-catalyzed oxidation of secondary alcohols to ketones by acetone [a].

Entry	Substrate	Catalyst (mol %)	Time (h)	Product	% Yield [b]
1	 3	1 (0.1)[c]	1.5	 14	90
2		1 (0.2)	1		99[d]
3		2 (0.1)	17		87
4	 4	1(0.1)	7	 15	90
5	 5	1 (0.1)[e]	3	 16	87
6		2 (0.1)	22		92
7	 6	1 (0.2)	24	 17	71
8		2 (0.1)	20		82
9	 7	1 (1)	24	 18	20
10		2 (0.1)	24		60[d]
11	 8	1 (0.25)	2	 19	90[d]
12		2 (0.1)	22		88[d]
13	 9	1 (0.2)	24	 20	42[d]
14		2 (0.1)	24		96[d]
15	 10	2 (0.5)	24	 21	73
16	 11	2 (0.5)	24	 22	74
17	 12	2 (0.25)	4	 23	76
18	 13	2 (0.25)	20	 24	91

[a] Unless otherwise stated, the reactions were carried out on a 1–5 mmol scale in refluxing acetone (1–5 mL) under N_2. With catalyst 1, 0.1 equiv of K_2CO_3 is used. [b] Isolated yields after column chromatography unless otherwise noted. [c] Performed on a 50 mmol scale in 50 mL of acetone. [d] Determined by GC. [e] Performed on a 120 mmol scale in 100 mL of acetone.

performed in an open-air system. It was demonstrated that the initial turnover rate for substrate **3** was more than 1500 h^{-1}. For these substrates, the catalytic system **1**/K_2CO_3 was superior to catalyst **2**. In two cases (entries 1 and 5) the oxidations were run on a slightly larger scale (50–120 mmol) to demonstrate the practical use of the reaction. In both cases good isolated yields were obtained.

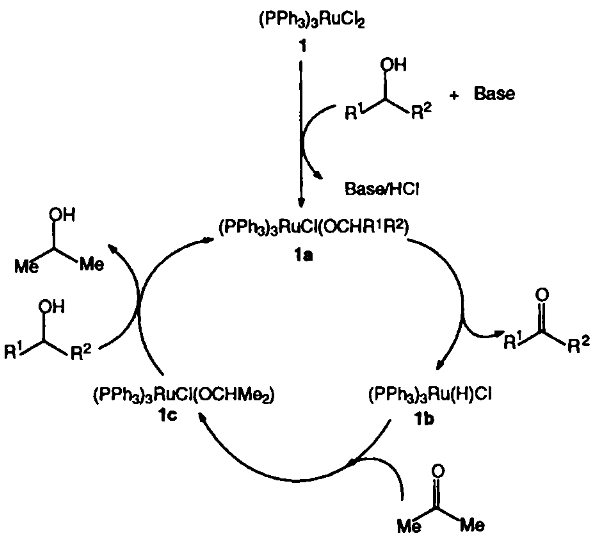
The reaction works well with aliphatic alcohols, although at a slightly higher catalyst/substrate ratio and longer reaction times (Table 1, entries 7, 8, 13, 14, and 16). The reactivity of cyclic alcohols toward oxidation is dependent on the ring size. The oxidation of cyclohexanol was sluggish when catalyzed by complex **1**; a better conversion was obtained with complex **2** (Table 1, entries 9 and 10). Cyclopentanol reacted faster than cyclohexanol and showed a reactivity similar to that of the benzylic alcohols (Table 1, entries 11 and 12).

Complex **1** turned out to be a poor catalyst for oxidation of allylic and acyclic unsaturated alcohols. While substrate **9** gave a moderate yield of the isomerized product **20**[13] with this catalyst (Table 1, entry 13), alcohol **10** afforded only traces of a mixture of the saturated and unsaturated ketone, and **11** gave a mixture of the β- and γ-unsaturated ketones. However, with complex **2** as catalyst, alcohols **9**, **10**, and **11** reacted cleanly and selectively to furnish ketones **20**, **21**, and **22**, respectively, in good yields. The allylic alcohol **9** was quantitatively isomerized[13] to the saturated ketone, whereas substrates **10** and **11** were converted to the corresponding unsaturated ketones (Table 1, entries 14, 15 and 16). 2-Cyclohexenol (**12**), which even after 24 h gave poor conversion to the unsaturated ketone with catalyst **1**, was fully converted after only 4 h with catalyst **2**, and the unsaturated ketone **23** was isolated in 76% yield (Table 1, entry 17). With the tryptophol derivative **13**, which contains a sensitive aromatic (indole) moiety, complex **1** had poor catalytic activity too. However, complex **2** catalyzed the oxidation of **13** in a clean and selective reaction to give indolylacetone **24** in high yield (Table 1, entry 18).

It is interesting to note that the present oxidation system is compatible with double bonds as well as with oxidation-sensitive aromatics (indole). We have compared our catalytic system with the recently published catalytic system $RuCl_3$–$Co(OAc)_2$, which is cocatalyzed by acetaldehyde and employs molecular oxygen as the oxidant.[9b] Attempts to use the latter system for oxidation of alcohols **10**, **11**, and **12** resulted in formation of complex mixtures of products of competing epoxidation and allylic oxidation reactions. The latter oxidation system involves cobalt-mediated radical chain reactions of the aldehyde with O_2 to give peracid.

Mechanism: It is generally proposed that the oxidation of alcohols catalyzed by low-valent ruthenium complexes involves the formation of a ruthenium alkoxide[10, 14] followed by β-hydride elimination[15] to produce a carbonyl compound and a hydride complex.[6, 7b, 8, 10, 16–18] The hydride complex can in turn react with a hydrogen acceptor[6, 8, 10, 16, 17] or an oxidant[7b, 10a, c, d] or produce molecular hydrogen.[15a, 18] With complex **1** as the catalyst it is likely that the catalytic cycle involves hydride complex **1b** as the active species (Scheme 2). Complex **1b** is formed after dehydrogenation of the alcohol by **1** in the presence of base. The function of K_2CO_3 can be understood in terms of generating a more nucleophilic alkoxide,[15a] and as a base, it will move the equilibrium towards the formation of the alkoxide **1a**. Reaction of **1b** with acetone produces complex **1c** by insertion of acetone in the ruthenium–hydride bond. Exchange reaction of **1c** with a molecule of the substrate alcohol gives isopropanol and regenerates complex **1a**.

It was found that the rate of the oxidation depended dramatically on the presence of small amounts of water. Figure 1 shows the rate of the oxidation of 1-indanol,[19] determined from kinetic measurements, as a function of the amount of water



Scheme 2. Catalytic cycle for the dehydrogenation of alcohols by acetone in the presence of complex **1**.

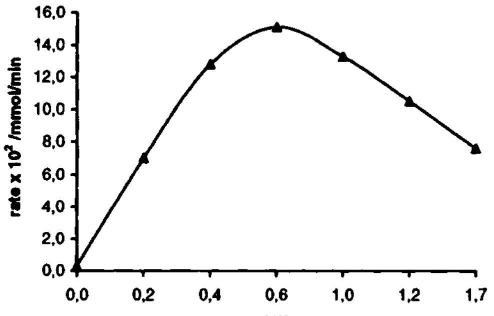
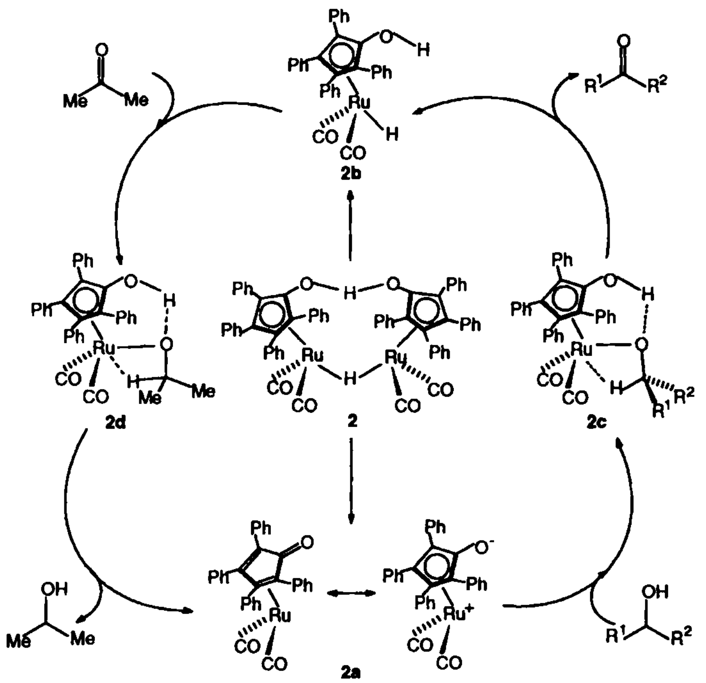


Fig. 1. Influence of water on the initial rate of oxidation of 1-indanol. Conditions: [1-indanol] = 1.0 M, [$(PPh_3)_3RuCl_2$] = 2×10^{-3} M, in refluxing acetone with 0.1 mmol K_2CO_3 per mL of solvent.

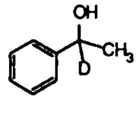
(0–1.7%) in the acetone. Under dry conditions a very slow reaction took place. Addition of small amounts of water up to 0.6% dramatically increased the rate of the oxidation. For a higher concentration of water the rate was decreased, probably owing to a competing nucleophilic attack by water on the metal center. The most likely explanation of this remarkable effect is that the surface of the K_2CO_3 is activated by water. In this way the K_2CO_3 may more efficiently abstract the proton from the alcohol.

Complex **2** has previously been used as catalyst precursor in the oxidation of secondary alcohols[10c,d] and in the disproportionation of aldehydes to esters.[17] Under our mild conditions, **2** was the most stable catalyst and showed a general good catalytic activity for the dehydrogenation of secondary alcohols. The proposed catalytic cycle, based on the mechanistic considerations of Shvo et al.,[20] is presented in Scheme 3. An interesting property of catalyst **2** is that it can be split into the monomeric species **2a** and **2b**. When this catalyst is used, no additional base is required, since the negatively charged oxygen of the bisionic species **2a** behaves like a base and will be able to abstract a proton from the alcohol to give **2c**. Subsequent β-hydride elimination from **2c** affords the ketone and the hydride intermediate **2b**. The catalytic cycle is completed by insertion of acetone into the ruthenium–hydride bond of **2b** followed by release of isopropanol.



Scheme 3. Mechanism for the dehydrogenation of alcohols by acetone in the presence of complex **2**.

In order to gain further insight into the mechanism we determined the isotope effect for the cleavage of the α-hydrogen bond of the alcohol; for the $RuCl_2(PPh_3)_3$-catalyzed oxidation of α-deuterated 1-phenylethanol ([D$_1$]**5**) in acetone the isotope effect was $k_H/k_D = 1.1$. This result shows that the rate-limiting step in this case is not the β-hydride elimination from the intermediate alkoxide ruthenium complex **1a**.



[D1]5

Conclusion

The procedure described herein offers significant advantages over other oxidation methods. It is mild and can be used in the presence of oxidation-sensitive functional groups. The mildness is due to the fact that acetone is the formal oxidant and the catalyst is present only in very small amounts (typically 1/1000 or 1/500 molar ratio to substrate). To the best of our knowledge, this is the first general procedure described for efficient transition-metal catalyzed Oppenauer oxidation. The ruthenium complex **1** is the catalyst of choice for the oxidation of secondary benzylic alcohols and cyclopentanol. On the other hand, complex **2** has a broader scope with high conversions and selectivity, although it is slower than **1** with some substrates.

Experimental Section

General methods: NMR spectra were recorded in $CDCl_3$ by means of a Varian 300 spectrometer, ^{1}H NMR at 300 MHz and ^{13}C NMR at 75.4 MHz with [D$_1$]chloroform (^{1}H, $\delta = 7.26$; ^{13}C, $\delta = 77.0$) as internal standard. GC analyses were performed on a Varian 3400 gas chromatograph with a 30 m DB-5 J & M fused silica column. All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware. Solvents and solutions were transferred by syringe–septum and cannula techniques. Acetone (Baker, reagent grade) was used without further purification and was degassed by bubbling a stream of nitrogen through it for 15 min prior to cannula transfer. The alcohols **3**–**9** were purchased from Aldrich and the ruthenium complex **1** from Strem Chem.

Preparation of substrates: The following substrates were prepared according to literature procedures: ruthenium complex **2** [17]; 2-cyclohexenol (**12**) [21], and 1-(3-indolyl)-2-propanol (**13**) [22]. Alcohol [D$_1$]**5** was prepared by reduction of acetophenone with $LiAlD_4$ by a standard procedure.

1-Phenyl-4-penten-1-ol (10): Freshly distilled benzaldehyde (212 mg, 2 mmol) was added to a cooled (0 °C) solution of 4-butenylmagnesium bromide (9 mL, 3 mmol, 0.328 M in THF) through a syringe over 5 min. The mixture was kept at 0 °C for 30 min and then at room temperature for 1 h. The reaction was quenched with water (1 mL), acidified with 1 M aqueous sulfuric acid, and diluted with ether (20 mL). The organic layer was separated, washed with $NaHCO_3$ (2 × 5 mL) and brine (2 × 5 mL), and dried (Na_2SO_4). The solvent was evaporated and the residue chromatographed on silica (CH_2Cl_2) to give 310 mg (90%) of the product as a yellowish liquid. The spectral data were in accordance with the literature [23]: ^1H NMR: δ = 7.361–7.270 (m, 5H), 5.845 (ddt, J = 17.1, 10.5, 6.5 Hz, 1H), 5.043 (ddd, J = 17.1, 3.6, 1.5 Hz, 1H), 4.986 (ddd, J = 10.5, 3.1, 1.2 Hz, 1H), 4.732–4.678 (m, 1H), 2.194–2.088 (m, 2H), 1.790–1.971 (m, 3H); ^{13}C NMR: δ = 144.59, 138.16, 128.48, 127.59, 125.88, 114.98, 74.04, 38.04, 30.07.

***Z*-5-Undecen-2-ol (11)**: A solution of methyllithium (2.0 mL, 3.24 mmol, 1.6 M in diethyl ether) was diluted with THF (4 mL), cooled to −78 °C, and treated dropwise with 4-decenal (500 mg, 3.24 mmol). The resulting solution was stirred at −78 °C for about 30 min, warmed to room temperature, quenched with saturated NH_4Cl (10 mL), diluted with ether, and separated. The organic layer was washed with $NaHCO_3$ (25 mL) and brine (2 × 25 mL), dried ($MgSO_4$), evaporated, and chromatographed (CH_2Cl_2) to give 425 mg (77%) of the product. The spectral data were in accordance with the literature [24]: ^1H NMR: δ = 5.437–5.296 (m, 2H), 3.814 (m, J = 6.3 Hz, 1H), 2.150–2.000 (m, 4H), 1.544–1.229 (m, 9H), 1.19 (d, J = 6.3 Hz, 3H), 0.882 (t, J = 6.9 Hz, 3H); ^{13}C NMR: δ = 130.68, 129.00, 67.90, 39.10, 31.50, 29.37, 27.17, 23.68, 23.46, 22.55, 14.06.

General procedure for ruthenium-catalyzed oxidation of alcohols by acetone: The substrate, catalyst **1** and K_2CO_3 (10 mol%), or catalyst **2** without base, were weighed into a two-necked round-bottomed flask equipped with a condenser and a magnetic stirring bar. The reaction system was flushed with nitrogen for 15 min. Acetone (containing 0.6% of water when complex **1** was employed) was added through a syringe, and the resulting solution was refluxed under nitrogen while stirred. The reaction was monitored by GC or TLC. After the appropriate reaction time, the reaction mixture was filtered through Celite and the solvent evaporated. The resulting crude mixture was then chromatographed on silica with the solvent system indicated, allowing isolation of the products.

Kinetic experiments: Solutions in acetone of substrate (1 M), **1** (2×10^{-3} M), and K_2CO_3 (0.1 M) were oxidized under the standard reaction conditions. Samples were withdrawn and immediately quenched with ether every fifth minute during the first 30 min of the reaction and at intervals of 10 min thenceforth. The samples were filtered through silica, diluted with ether, and analyzed by GC by means of the internal standard method. The rates of oxidation were determined from the slopes of the straight lines.

1-Indanone (14): 1-Indanol (**3**, 6.71 g, 50.0 mmol), **1** (48 mg, 0.050 mmol), and K_2CO_3 (691 mg, 5.0 mmol) allowed to react in acetone (50 mL) for 1.5 h gave 5.93 g (90%) of the product after chromatography (CH_2Cl_2). The product was characterized by comparison with an authentic sample.

1-Keto-1,2,3,4-tetrahydronaphtalene (15): α-Tetralol (**4**, 1.46 g, 10 mmol), **1** (9.6 mg, 0.010 mmol), and K_2CO_3 (138 mg, 1.0 mmol) in acetone (10 mL) for 7 h afforded 1.29 g (90%) of the product after chromatography (CH_2Cl_2). The product was characterized by comparison with an authentic sample.

Acetophenone (16): 1-Phenylethanol (**5**, 14.7 g, 120 mmol), **1** (115 mg, 0.12 mmol), and K_2CO_3 (1.6 g, 12 mmol) in acetone (120 mL) for 3 h gave 12.5 g (87%) of the product after chromatography (CH_2Cl_2). The product was characterized by comparison with an authentic sample.

2-Octanone (17): 2-Octanol (**6**, 1.30 g, 10.0 mmol), **1** (19.2 mg, 0.020 mmol), and K_2CO_3 (138 mg, 1.0 mmol) in acetone (10 mL) for 24 h gave 920 mg (71%) of the product after chromatography (CH_2Cl_2). The product was characterized by comparison with an authentic sample.

1-Phenyl-4-penten-1-one (21): 1-Phenyl-4-penten-1-ol (**10**, 100 mg, 0.620 mmol) and **2** (3.4 mg, 0.0031 mmol) in acetone (2 mL) for 24 h gave 73 mg (73%) of the product after chromatography (CH_2Cl_2). The spectral data were in accordance with the literature [25]: ^1H NMR: δ = 7.982–7.432 (m, 5H), 5.908 (ddt, J = 16.8, 10.2, 6.6 Hz, 1H), 5.091 (ddd, J = 17.1, 3.6, 1.5 Hz, 1H), 5.017 (ddd, J = 10.1, 3.5, 1.2 Hz, 1H), 3.079 (t, J = 7 Hz, 2H), 2.536–2.461 (m, 2H); ^{13}C NMR: δ = 199.40, 137.25, 136.87, 132.98, 128.55, 127.99, 115.25, 37.69, 28.10.

***Z*-5-Undecen-2-one (22)**: *Z*-5-Undecen-2-ol (**11**, 100 mg, 0.59 mmol) and **2** (3.3 mg, 0.0030 mmol) in acetone (2 mL) for 24 h gave 74 mg (74%) of the product after chromatography (CH_2Cl_2/pentane, 1:1). Spectral data in accordance with the literature [24]: ^1H NMR: δ = 5.457–5.302 (m, 2H), 2.497–2.437 (m, 2H), 2.299–2.205 (m, 2H), 2.122 (s, 3H), 2.027–1.909 (m, 2H), 1.359–1.200 (m, 6H), 0.864 (t, J = 7.2 Hz, 3H); ^{13}C NMR: δ = 208.65, 131.62, 128.07, 43.58, 32.44, 31.33, 29.93, 29.11, 26.83, 22.49, 14.03.

2-Cyclohexenone (23): 2-Cyclohexenol (**12**, 100 mg, 1.0 mmol) and **2** (2.7 mg, 0.0025 mmol) in acetone (2 mL) for 6 h gave 75 mg (76%) of the product after chromatography (CH_2Cl_2). The product was characterized by comparison with an authentic sample.

1-(3-Indolyl)-2-propanone (24): 1-(3-Indolyl)-2-propanol (**13**, 100 mg, 0.57 mmol) and **2** (1.6 mg, 0.0014 mmol) in acetone (2 mL) for 20 h gave 90 mg (91%) of the product after chromatography (CH_2Cl_2/ether, 10:2). The spectral data were in agreement with the literature [26]: ^1H NMR: δ = 8.269 (br signal, NH; 1H), 7.624 (d, J = 7.8 Hz, 1H), 7.447 (d, J = 7.8 Hz, 1H), 7.335–7.193 (m, 3H), 3.905 (s, 2H), 2.253 (s, 3H); ^{13}C NMR: δ = 207.57, 136.11, 127.18, 123.13, 122.26, 119.75, 118.61, 111.24, 108.68, 40.76, 28.88.

Acknowledgments: Financial support from the Swedish Natural Science Research Council and the Swedish Research Council for Engineering Sciences is gratefully acknowledged.

Received: May 30, 1996 [F378]

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