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Chemoselective C−H Oxidation of Alcohols to Carbonyl Compounds with Iodosobenzene Catalyzed by (Salen)chromium Complex

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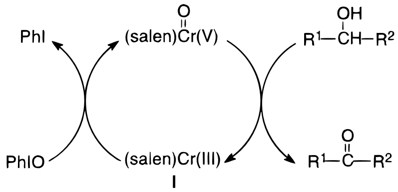
Primary and secondary alcohols with benzylically and allylically activated C−H bonds are chemoselectively oxidized to the corresponding carbonyl compounds by the (salen)Cr(III) complex **I** as the catalyst and iodosobenzene as the oxygen source; the oxidizing species is the Cr(V) oxo complex. Allylic alcohols with fully substituted double bonds give appreciable amounts of epoxides besides the C−H oxidation products enones, while saturated alcohols are less readily oxidized.

Introduction

The chemo-, regio-, and stereoselective oxidation of alcohols to carbonyl compounds is one of the fundamental organic transformations not only from the synthetic point of view, but it also enjoys significant biological and mechanistic interest. Thus, there has been much research on this oxidation, especially the search for versatile and selective reagents. Among the most widely used are chromium compounds; in fact, chromic acid is one of the most powerful and universal oxidants.[1] The Jones reagent (chromiumtrioxide/H_2SO_4), the Collins reagent (chromiumtrioxide/pyridine complex), pyridinium chlorochromate (PCC), poly(vinylpyridinium) chlorochromate (PVPCC), and pyridinium dichromate (PDC) are some of the more popular commercially available chromium-based oxidants used for such transformations.

The main drawback of these reagents is that in addition to their lack of generality, they have to be applied in stoichiometric amounts or even in large excess to effect complete conversion of the substrate. However, in view of the carcinogenicity of chromium compounds, health and environmental concerns limit their use for large-scale and industrial applications. Although much effort has been made in the development of methods for chromium-based *catalytic* oxidations in recent years,[2] there is still need for catalytic oxidations of *alcohols* with a wide scope of applicability. Indeed, ongoing research has been directed toward the development of such methods, especially for selective oxidations.[3] For example, oxochromium(V) heteropolytungstate complexes were reported to effect the catalytic allylic oxidation of cyclohexenol.[3c] Very recently, the chromium(VI)-catalyzed oxidation of allylic alcohols by *tert*-butyl hydroperoxide to carbonyl products has been developed.[4]

Scheme 1. Catalytic Cycle for the Oxidation of Alcohols to Carbonyl Compounds by (Salen)Cr(III)/PhIO



Presently, we report on the selective (salen)chromium(III)-catalyzed oxidation of a series of alcohols to the corresponding carbonyl compounds with iodosobenzene (PhIO) as the oxygen source (Scheme 1). The in-situ-generated (salen)oxochromium(V) complex is proposed as the actual oxidant, which shows a great preference for allylic oxidation versus epoxidation in allylic alcohols as substrates. Such (salen)oxochromium(V) complexes have been previously isolated and subsequently used in the epoxidation of olefins by Kochi's group;[5] the asymmetric version was recently established.[6]

Results and Discussion

To assess the general scope of the catalytic oxidation mediated by the (salen)oxochromium(III) complex **I**,[7] the saturated and benzylic primary and secondary alcohols **1** were chosen as substrates and PhIO as oxygen source. 4-Phenylpyridine *N*-oxide (PPNO) was used as additive, because it has been reported[5a] that this donor ligand enhances the reaction rates in the Cr(salen)-catalyzed oxidations. Unusually mild conditions (ca. 20 °C, in CH_2Cl_2, and a 0.15:0.30:1.00:1.50 ratio of catalyst **I**/PPNO/substrate/PhIO) afforded the corresponding carbonyl products **2** (eq 1).

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[1] (a) Hudlicky, M. *Oxidations in Organic Chemistry*; ACS Monograph 186; American Chemical Society: Washington DC, 1990. (b) Cainelli, G.; Cardillo, G. *Chromium Oxidations in Organic Chemistry*; Springer-Verlag: Berlin, Heidelberg, 1984; Chapter 4.

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[5] (a) Samsel, E. G.; Srinivasan, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1985**, *107*, 7606−7617. (b) Srinivasan, K.; Kochi, J. K. *Inorg. Chem.* **1985**, *24*, 4671−4679.

[6] (a) Bousquet, C.; Gilheany, D. G. *Tetrahedron Lett.* **1995**, *36*, 7739−7742. (b) Ryan, K. M.; Bousquet, C.; Gilheany, D. G. *Tetrahedron Lett.* **1999**, *40*, 3613−3616. (c) Daly, A. M.; Dalton, C. T.; Renehan, M. F.; Gilheany, D. G. *Tetrahedron Lett.* **1999**, *40*, 3617−3620.

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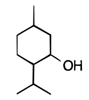
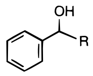
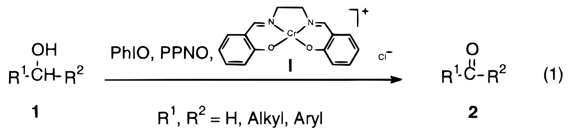
Table 1. Oxidation of Saturated and Benzylic Alcohols with Iodosobenzene Catalyzed by the Chromium(III) Salen Complex I[a]

entry	alcohol		time (h)	convn (%)[b]	yield (%)[b, c]
1	$CH_3(CH_2)_8CH_2OH$	**1a**	72	18	> 95
2		**1b**	72	21	> 95
3		**1c** (H)	14	93	62
4		**1d** (Me)	14	68	> 95
5		**1e** (c-C_3H_5)[d]	14	50	> 95
6		**1f** (c-C_3H_4-Ph)[e]	14	89	78
7		**1g** (t-Bu)	14	26	77

[a] Reaction conditions: 0.3 equiv of 4-phenylpyridine *N*-oxide (PPNO), 0.15 equiv of catalyst **I**, 1.5 equiv of PhIO, CH_2Cl_2, 20 °C. [b] Determined by ^1H NMR analysis of the crude reaction products with an internal standard (1,3,5-trioxane); error ± 5% of the stated values; the mass balances were ≥80% in every case except for entry 3 (64%). [c] Yields of the respective carbonyl products **2** based on 100% conversion of the alcohol; all products are known and have been identified by ^1H and ^{13}C NMR spectroscopy. [d] Cyclopropyl. [e] Used as mixture of diastereomers.



The results in Table 1 demonstrate that the oxidation is relatively sluggish for the saturated, unactivated substrates (entries 1 and 2) *n*-decanol (**1a**) and menthol (**1b**), since only ca. 20% conversion to the corresponding carbonyl compounds **2a** and **2b** was achieved, even on prolonged (72 h) reaction time. In contrast, the primary benzyl alcohol (**1c**) was oxidized to **2c** (entry 3) in 93% conversion in only 14 h. As to the oxidation of the secondary benzylic alcohols **1d**−**g** (entries 4−7), the significantly lower conversion (26%, entry 7) of the sterically hindered *tert*-butyl-substituted substrate **1g** compared to that of the other secondary alcohols **1d**−**f** (50−89%, entries 4−6) implies that the CH insertion is sensitive to steric effects. The cyclopropyl-substituted derivatives **1e** and **1f** (entries 5 and 6) were oxidized smoothly to the corresponding ketones without any ring-opening products, as established by careful ^1H NMR analysis (eq 2). For this purpose, substrate **1f** was obtained as a 67:33 mixture of diastereomers by $NaBH_4$ reduction of the ketone **2f** in ethanol[8] and subsequently used as such in the Cr-catalyzed oxidation. In view of Hill's radical mechanism,[3c] the cyclopropylcarbinyl radical is expected to intervene. However, since the reported[9] rate constant for the ring opening of the (2-phenylcyclopropyl)phenylmethyl radical is only 3.6 × 10 ^{8} s^{-1} at 40 °C (no rate data are available for the hydroxy-substituted radical derived from the carbinol **1f**), the cyclopropylcarbinyl radical, if formed, persists and does not rearrange.

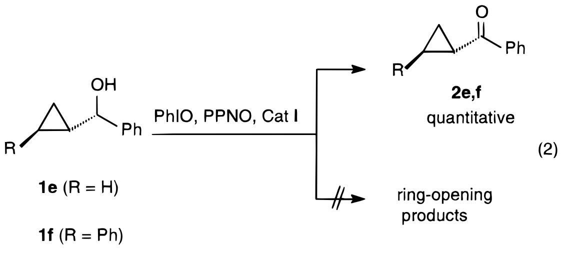
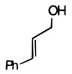
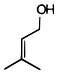
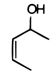
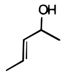
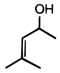
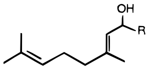
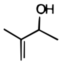
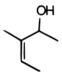
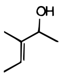
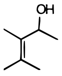
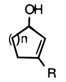
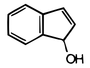


Table 2. Oxidation of Allylic Alcohols with Iodosobenzene Catalyzed by the Chromium(III) Salen Complex I[a]

entry	alcohol		time (h)	convn (%)[b]	**4** : **5**[b,c]	yield **4** (%)[b]
1		**3a**	6	> 95	> 95 : 05	95
2		**3b**	14	95	> 95 : 05	80
3		**3c**	6	58	> 95[d]: 05	41
4		**3d**	6	78	> 95 : 05	74
5		**3e**	6	67	78 : 22 (85 : 15)	75[e]
6		**3f** (H)	14	> 95	> 95 : 05	77
7		**3g** (Me)	6	30	> 95 : 05	95
8		**3h**	6	62	> 95 : 05	31
9		**3i**	6	48	70[f]: 30 (--)[g]	54[e]
10		**3j**	6	63	84 : 16 (60 : 40)	81[e]
11		**3k**	6	63	48 : 52 (92 : 08)	68[e]
12		**3l** (1, H)	14	66	> 95 : 05	74
13		**3m** (2, H)	12	90	> 95 : 05	84[h]
14		**3n** (3, Me)	14	> 95	> 95 : 05	86
15		**3o**	6	95	> 95 : 05	88

[a] Reaction conditions: As in Table 1, except entry 7, 0.5 equiv of PhIO. [b] Determined as in Table 1; mass balances were ≥80% in most cases except for the substrates **3c** (entry 3) and **3h** (entry 8) due to high volatility. [c] Ratio of α,*β*-enone **4** to epoxy alcohol **5**, the threo/erythro diastereomeric ratios of epoxy alcohols are given in parentheses; determined by ^1H NMR spectroscopy of the crude product; error ± 5% of the stated values. [d] Observed as cis,trans mixture of 61:39 for the enones **4c/4d**. [e] Yield of **4** + **5**. [f] Observed as cis,trans mixture of 70:30 for the enones **4i/4j**. [g] Epoxy alcohols observed as a mixture of all threo/erythro stereoisomers; the stereoisomeric ratios were not determined because of severe signal overlap in the ^1H NMR spectrum. [h] Determined by GLC analysis with *n*-decanol as the internal standard; error ± 2% of the stated values.

Since this catalytic oxidation is promoted by benzyl substitution, it was anticipated that allylic alcohols should react readily under these conditions; however, in these bifunctional substrates also epoxidation of the double bond is possible, besides allylic CH insertion (eq 3). As the results for a series of structurally varied cyclic and acyclic allylic alcohols **3** convey (Table 2), with few exceptions (entries 5 and 9−11), the allylic oxidation products **4** were formed nearly exclusively. Even for the

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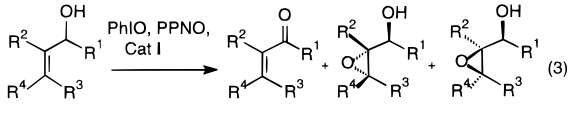
[8] Patro, B.; Ila, H.; Junjappa, H. *Tetrahedron Lett.* **1992**, *33*, 809−812.

[9] (a) Hollis, R.; Hughes, L.; Bowry, V. W.; Ingold, K. U. *J. Org. Chem.* **1992**, *57*, 4284−4287. (b) Newcomb, M. *Tetrahedron* **1993**, *49*, 1151−1176.



3 4 *threo*-5 *erythro*-5 (3)

exceptions, at best equal amounts of epoxidation and CH insertion had occurred, as displayed by the tetrasubstituted allylic alcohol **3k** (entry 11). Evidently, increased methyl substitution promotes epoxidation sufficiently to compete with the usually preferred CH insertion. Of note is the high threo diastereoselectivity in the epoxidation of the chiral allylic alcohols **3e** and **3k** (entries 5 and 11), but not for **3j** (entry 10). For the former two derivatives, 1,3-allylic strain operates, which conformationally aligns the allylic hydroxy group for favored threo attack through hydrogen bonding with the (salen)oxochromium(V) complex. Such hydroxy group directivity has been reported for the related epoxidation by the (salen)oxomanganese(V) complex[10] and for the diperoxo complex of methyltrioxorhenium,[11] which implies similar hydrogen-bonded transition structures also for the (salen)oxochromium(V) oxidant.

In the oxidation of the *Z*-configured allylic alcohols **3c** and **3i**, cis−trans isomerization of the resulting enones was observed, as displayed by *Z*/*E* ratios of 61:39 (**4c/4d**) and 70:30 (**4i/4j**) (entries 3 and 9). In contrast, no such isomerization was noted in the catalytic oxidation of the *E*-configured substrates **3d** and **3j** since the corresponding *E*-configured ketones **4d** and **4j** are thermodynamically favored and persist. Geraniol (**3f**) was oxidized under similar conditions to geranial (**4f**) in a good yield (entry 6); however, ^{1}H NMR analysis of the crude product showed that ca. 5% isomerization at the enone double bond had occurred and traces (<5%) of the epoxidation at the C-7 position of geranial (**4f**) were detected. The methyl derivative **3g** (entry 7) was oxidized with only 0.5 equiv of PhIO to its enone **4g** in 30% conversion without side products.

The hydroxy-protected derivatives of substrate **3e**, namely OMe (**6a**),[12] OSiMe$_2$*t*-Bu (**6b**), and OAc (**6c**), were not oxidized (no CH insertion nor epoxidation) under the same reaction conditions (data not shown). This emphasizes the importance of hydrogen bonding between the substrate and the (salen)oxochromium(V) complex for both the CH insertion and epoxidation.

To assess whether the salen ligand sphere is necessary for the Cr(III)-catalyzed selective oxidation of alcohols, $CrCl_3 \cdot 3THF$ instead of catalyst **I** was tested as catalyst for the oxidation of **3e.** Although the reaction was accelerated (complete substrate conversion within <30 min), a complex mixture was obtained, with the enone **4e** as the major oxidation product; no conversion was observed for this case without PPNO. These results demonstrate that the Cr(salen) complex is superior to $CrCl_3 \cdot 3THF$ in the catalytic oxidation of allylic alcohols.

Conclusion

We have developed a convenient catalytic oxidation (PhIO/cat **I,** CH_2Cl_2, ca. 20 °C) of primary and secondary alcohols with allylically and benzylically activated CH bonds. The corresponding carbonyl compounds have been obtained in good yield on the semipreparative scale. With the exception of the tetrasubstituted derivative **3k,** allylic alcohols are chemoselectively oxidized to enones by CH insertion rather than epoxidation of the double bond.

Experimental Section

General Aspects. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AC 200 (^{1}H, 200 MHz; ^{13}C, 50 MHz), a Bruker AC 250 (^{1}H, 250 MHz; ^{13}C, 63 MHz), or a Bruker DMX 600 (^{1}H, 600 MHz) spectrometer against $CDCl_3$ or tetramethylsilane (TMS) as reference standard on the δ scale (ppm). Perkin-Elmer 1600 series FTIR-spectrophotometer was used for IR spectra. TLC analysis was conducted on precoated silica gel foils 60 F_{254} (20 × 20 cm) from Merck, Darmstadt. Spots were visualized either by UV irradiation (254 nm), by a 5% polymolybdic acid in ethanol, or by a solution of 0.5 g of 2,4-dinitrophenylhydrazine in 2.5 mL of concentrated H_2SO_4, which was diluted with 100 mL of absolute ethanol. Silica gel (63−200 and 32−63 μm) from Woelm, Erlangen, was used for column and flash chromatography. Solvents were dried by standard methods and purified by distillation before use. GLC analysis was performed on a Carlo Erba instrument HRGC 5160 gas chromatograph, equipped with a 30 m × 0.25 mm HP-5 capillary column and an FID detector. Melting points (uncorrected) were determined on a Reichert Thermovar apparatus. All commercial reagents were used without further purification.

Starting Materials. Iodosobenzene (98% by iodometry[13]) was prepared by hydrolysis of the corresponding diacetate according to the literature method[14] and was stored at −20 °C.

The alcohols **1a**−**e**,**g** and the allylic alcohols **3b**,**f**,**n** were commercially (Fluka, Aldrich) available. The benzylic alcohol **1f** [15] and the allylic alcohols **3c**,[16] **3d**,[17] **3e**,[18] **3g**,[19] **3h**,[20] **3i**,[21] **3j**,[19] **3l**,[22] **3m**,[23] **3o**,[24] **6a**,[25] **6b**,[26] and **6c**[27] were synthesized analogously to known methods.

***N*,*N'*-Ethylenebis(salicylideneiminato)chromium(III) Chloride (I).** To a suspension of 2.59 g (9.96 mmol) of bis(salicyliden)ethylenediamine in 50 mL of absolute ethanol was added a suspension of 1.31 g (10.7 mmol) of anhydrous chromous chloride in ethanol (20 mL) within 15 min with vigorous stirring under an Ar-gas atmosphere at room temperature (ca. 20 °C) for 1 h. The dark-brown solution was allowed to reflux in the presence of air for 2 h. The solvent was removed (ca. 20 °C, ca. 20 Torr), and the residue was suspended in water (50 mL) and allowed to stir for 2 h in the

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[11] Adam, W.; Mitchell, C. M.; Saha-Möller, C. R. *J. Org. Chem.* **1999**, *64*, 3699−3707.

[12] A small amount (ca. 5%) of enone **4e** was detected by ^{1}H NMR spectroscopy.

[13] Lucas, J.; Kennedy, E. R.; Formo, M. W. *Org. Synth.* **1955**, *3*, 483−485.

[14] Saltzman, H.; Sharefkin, J. G. *Org. Synth.* **1973**, *5*, 658−659.

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presence of air at ca. 20 °C. The undissolved, yellowish-brown material was collected by filtration on a G4 sintered-glass funnel and was washed with water (3 × 10 mL). The material was extracted with water (2 × 500 mL) by heating in an open glass beaker, with vigorous stirring for 2 h. After filtration and concentration of the filtrate at normal pressure by evaporation, a reddish brown material precipitated; more material precipitated on cooling overnight, which was collected and dried under reduced pressure (120 °C, ca. 10^{-2} Torr, P_2O_5, 12 h) to afford 1.2 g (31%, yield not given in ref 6) dark-brown, hygroscopic product, mp (dec) 338−340 °C. IR (KBr): 3026, 1800, 1496, 1027, 893 cm^{-1}. EIMS m/z (relative intensity): 318 ($M^+ - Cl$, 100). Anal. Calcd for $C_{16}H_{14}ClCrN_2O_2$: C, 54.32; H, 3.99; N, 7.92. Found: C, 53.64; H, 4.12; N, 7.93.

Catalytic Oxidations. General Procedure for the Oxidation of the Saturated Alcohols 1a,b, Benzylic Alcohols 1c−g, and Allylic Alcohols 3a−o Catalyzed by the Chromium Complex I. To a solution of the substrate (0.50−1.00 mmol) in 5−10 mL of dichloromethane were added 0.3 equiv of 4-phenylpyridine *N*-oxide (PPNO) and 0.15 equiv of catalyst **I** with stirring, followed by 1.5 equiv of iodosobenzene under an Ar-gas atmosphere. A color change of brown to dark green and then back to brown was observed. TLC monitoring showed a positive hydrazone test (yellow spots characteristic of the carbonyl products). After the mixture was stirred for the times specified in the Tables 1 and 2, the solvent was evaporated carefully (25 °C, 400−600 Torr) and the brown residue was prepurified by passing through a short silica gel (5−8 g) column. Elution employed first petroleum ether (50−70 mL) to separate the iodobenzene and then ether (70−100 mL) to obtain the carbonyl products, epoxy alcohols, and unreacted alcohols as mixtures. This treatment was necessary to remove the paramagnetic chromium species, which causes severe line broadening in the NMR spectrum and prevents a quantitative product analysis. The solvent was removed as above, and the products were identified by TLC and ^1H and ^{13}C NMR spectroscopy. Conversions, mass balances, chemo- and stereoselectivities (threo/erythro), and yields were quantified by ^1H NMR analysis by calibration against an internal standard (see Tables 1 and 2).

Product Identification. The carbonyl compounds **2a**−**e**,**g** and **4a**,**b**,**e**,**f**,**h**,**j**,**l**−**n** are commercially available and were identified by comparison with authentic samples. The ketones **2f**,[28] **4c**,[29] **4d**,[30] **4g**,[31] **4i**,[32] **4k**,[33] and **4o**[34] and the epoxy alcohols *threo*/*erythro*-**5e**,**i**−**k**[35] were identified by comparison with the literature known NMR data.

Oxidation of (*E*)-4,8-Dimethyl-3,7-nonadien-2-ol (3g). The substrate (1.00 mmol) was processed as above, except that 0.5 mmol of iodosobenzene was used.

2-Cyclohexen-1-ol **(3m)** was oxidized according to the general procedure. Analysis was performed by GLC after filtration of the reaction mixture over silica gel and addition of the internal standard *n*-decanol. 2-Cyclohexen-1-one **(4m)** was identified as the sole oxidation product by comparison of its retention time (t_R) of the authentic material. Temperature program: 40 °C (5 min) → 20 °C/ min → 200 °C (5 min); t_R (min): 6.86 (**3m**), 7.76 (**4m**), 11.17 (**1a**).

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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