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Brief Communications

The $Mn(acac)_3$—RCN—CCl_4 system as a new efficient reagent for the oxidation of secondary alcohols into ketones

R. I. Khusnutdinov, ★ ***N. A. Schadneva, A. R. Baiguzina, and U. M. Dzhemilev***

Institute of Petrochemistry and Catalysis, Academy of Sciences of the Bashkortostan Republic
and Ufa Research Center, Russian Academy of Sciences,
141 prosp. Oktyabrya, 450075 Ufa, Russian Federation.
Fax: +7 (347 2) 31 2750. E-mail: ink@anrb.ru

The $Mn(acac)_3$—RCN—CCl_4 system was found to be efficient for the oxidation of secondary alcohols into the corresponding ketones in 80—93% yields. The oxidation proceeds through the formation of alkyl hypochlorites, which are generated from CCl_4 and the alcohols in the presence of the $Mn(acac)_3$—RCN catalytic system (R = Me, Et, and Ph).

Key words: secondary alcohols, catalysis, manganese complexes, nitriles, oxidation, ketones.

Various oxidants such as *m*-chloroperbenzoic acid, CrO_3, sodium hypochlorite, *N*-chlorosuccinimide, and transition metal salts are used in synthetic practice to oxidize secondary alcohols into ketones.[1—7]

The goal of the present work was to study the mechanism of their oxidation in the presence of manganese compounds.

Results and Discussion

We established for the first time that manganese compounds activated by nitriles catalyze the oxidation of secondary alcohols into corresponding ketones in the presence of CCl_4. Alkyl hypochlorites were found to be intermediate products generated from CCl_4 and an alcohol under the action of manganese compounds as catalysts. The catalyst participates both in the formation of alkyl hypochlorite and in its subsequent dehydrochlorination. The generation of hypochlorite was detected by iodometric titration throughout the reaction time (the concentration of active chlorine was 3.0—3.5 mg mL^{-1}).

After the reaction was completed, the reaction mixture contained HCl and $CHCl_3$ in equimolar amounts with respect to the ketone obtained (GLC, mass spectrometry, and titration with 0.1 *N* NaOH). This suggests that the oxidation of, *e.g.*, isopropyl alcohol follows the pathway as below (Scheme 1).

Scheme 1

$$\mathrm{MeCH(OH)Me + CCl_4} \xrightarrow{[\mathrm{Mn}]}$$

$$\longrightarrow \mathrm{Me_2CHOCl + CHCl_3} \xrightarrow{-\mathrm{HCl}} \mathrm{Me_2C{=}O}$$

Because of the low stability of isopropyl hypochlorite, a model reaction with its authentic sample was not carried out. Stable *tert*-butyl hypochlorite[8] quantita-

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tively oxidizes Pr^{i}OH into acetone in the presence of a Mn-containing catalyst under mild conditions (–5 °C, 20 min); when heated with manganese compounds without any alcohol, this reagent decomposes and becomes ineffective.

The most effective catalyst based on the tested manganese compounds ($MnCl_2$, $MnSO_4$, $Mn(OAc)_2$, $Mn(C_{17}H_{35}CO_2)_2$, $Mn(acac)_3$, and MnO_2) was obtained from $Mn(acac)_3$ and organic nitriles such as MeCN, EtCN, and PhCN (2—4 mol) as activating ligands. Insofar as the presence of any of the above nitriles increased both the conversion of the starting alcohol and the reaction rate, and the course of the reaction only slightly depends on their structure, subsequent experiments were carried out with the most accessible acetonitrile. Carbon tetrachloride was taken in considerable excess (ROH : CCl_4 was 1 : (2—5)) since it served as both a reagent and a solvent. The oxidation was completed over 3 h; on prolonged heating, chlorine-containing ketones were formed. The selected data obtained are presented in Scheme 2.

Optimum molar ratios between the components of the catalytic system and the reagents, as well as the preferable reaction conditions, were determined: [Mn] : [RCN] : [ROH] : [CCl_4] = 1 : (2—4) : (100—200) : (200—500), 200 °C, 1—3 h (sealed tube). Under these conditions, the yields of the corresponding ketones **2a—d**, **4a—d**, **6**, and **8** are virtually independent of the structure of the starting alcohol (**1a—d**, **3a—d**, **5**, and **7**), reaching 83—93%. In the case of cholesterol **9**, the yield of ketone **10** did not exceed 80% for possible side reactions caused by the double bond in compound **9**.

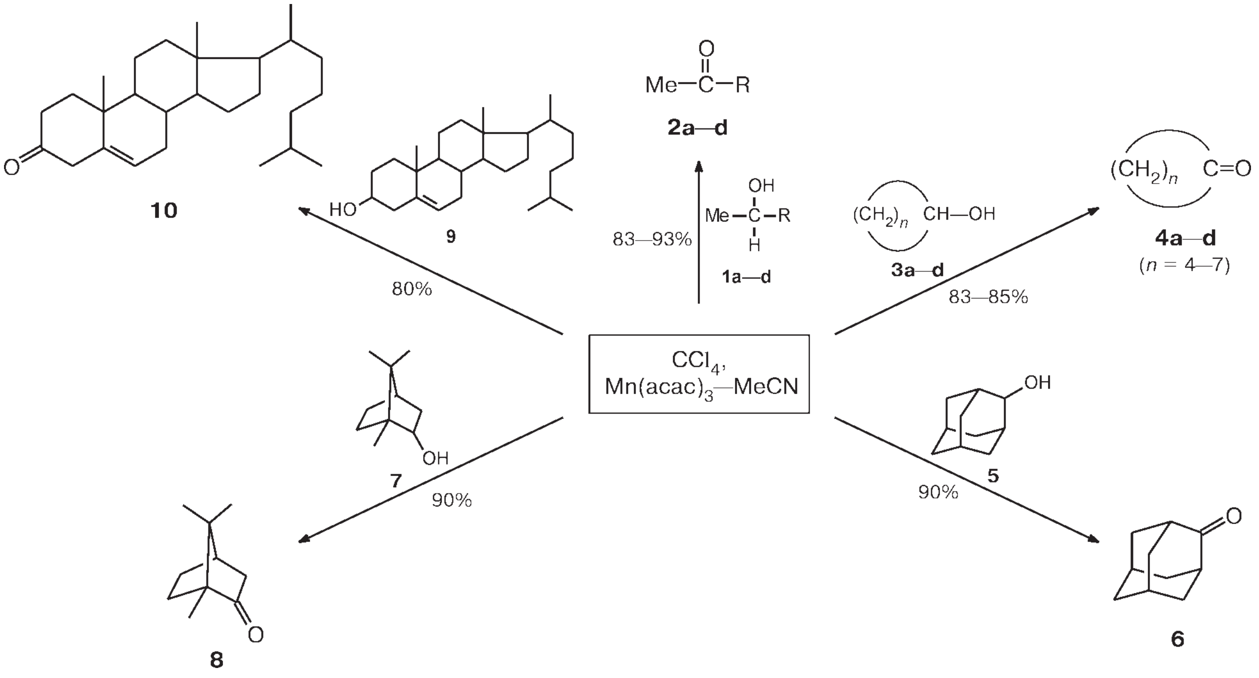
Experimental

^{13}C NMR spectra were recorded on a JEOL FX-Q spectrometer (22.5 MHz) in $CDCl_3$; the chemical shifts (δ) are referenced to Me_4Si. IR spectra were recorded on a UR-20 spectrometer (pellets with KBr or thin film). Mass spectra were recorded on a Finnigan MAT-112S GL-MS spectrometer (EI, 70 eV, direct inlet). Chromatographic analysis was performed on a Chrom-5 instrument (flame ionization detector, column 1200 × 33 mm, SE-30 silicon (5%) on Chromaton *N*-AW-HMDS as the stationary phase, temperature was elevated from 50 to 250 °C at a rate of 8 °C min^{-1}, helium as a carrier gas (47 mL min^{-1}) or column 3000 × 3 mm, PEG-6000 on the same support as the stationary phase, working temperature 50—170 °C, helium as a carrier gas).

The concentration of the hypochlorite was determined using iodometric titration.[9] The yield of acetone was determined by GLC with ethyl methyl ketone as the internal standard. The yields of ketones **2**, **4**, **6**, **8**, and **10** are given with respect to the isolated product.

The starting alcohols were commercial propan-2-ol (**1a**), 2-phenylethanol (**1b**), 1-cyclopropylethanol (**1c**), 1-adamantylethan-2-ol (**1d**), cyclopentanol (**3a**), cyclohexanol (**3b**), cycloheptanol (**3c**), cyclooctanol (**3d**), adamantan-2-ol (**5**), borneol (**7**), and cholesterol (**9**). They were distilled or crystallized before use. Carbon tetrachloride and acetonitrile were purified according to the known procedures.[10]

Scheme 2



R = Me (**a**), Ph (**b**), $H_2C\text{–}CH$ (**c**), Ad (**d**)
CH_2

Table 1. Reaction conditions and the yields and physicochemical data of the compounds obtained

Compound	Reaction conditions		Yield (%)	B.p./°C (p/Torr) or [m.p./°C][a]	IR, ν/cm^{-1}	^{13}C NMR, δ
	T/°C	t/h				
Acetone (**2a**)	200	1	93	56 {56.2}[12]	1712 (C=O)	30.7 (Me); 206.7 (C=O)
Acetophenone (**2b**)	200	3	83	99 (35) {202.3}[12]	1720 (C=O)	137.4 (C(1), Ph); 128.6 (C(2), C(6), Ph); 128.4 (C(3), C(5), Ph); 132.9 (C(4), Ph); 196.9 (C=O); 25.7 (Me)
Acetylcyclopropane (**2c**)	200	1	82	114—115 {114}[12]	1715 (C=O)	10.3 (C(1), C(2), *cyclo*-C_3H_5); 21.2 (C(3), *cyclo*-C_3H_5); 208.0 (C=O); 29.9 (Me)
1-Acetyladamantane (**2d**)	200	3	90	[53—53.5] {53—55}[12]	1704 (C=O)	45.7 (C(1)); 37.4 (C(2), C(8), C(9)); 27.2 (C(3), C(5), C(7)); 36.1 (C(4), C(6), C(10)); 210.2 (C=O); 24.1 (Me)
Cyclopentanone (**3a**)	200	3	84	130—131 {130}[12]	—	219.6 (C=O)
Cyclohexanone (**3b**)	200	3	85	46.5 (15) {155.6}[12]	—	219.8 (C=O)
Cycloheptanone (**3c**)	200	3	83	75 (20) {179}[12]	—	213.9 (C=O)
Cyclooctanone (**3d**)	200	3	83	78 (20) {195—197}[12]	—	216.7 (C=O)
Adamantan-2-one (**6**)[b]	200	3	90	[256—257] (subl.) {256—258}[14]	—	216.7 (C(2), C=O)
Camphor (**8**)[c]	200	3	90	[177—178] {178.5}[12]	1730 (C=O)	217.5 (C(2), C=O)
Cholest-5-en-3-one (**10**)[d]	200	3	80	[118.5—119] {119}[15]	1730 (C=O)	205.0 (C=O)

[a] The literature data are given in braces.

[b] Found (%): C, 79.61; H, 9.52. $C_{10}H_{14}O$. Calculated (%): C, 79.95; H, 9.39.

[c] Found (%): C, 78.91; H, 10.48. $C_{10}H_{16}O$. Calculated (%): C, 78.90; H, 10.59.

[d] Found (%): C, 83.96; H, 11.89. $C_{27}H_{44}O$. Calculated (%): C, 84.31; H, 11.53.

Manganese compounds ($MnCl_2$, $MnSO_4$, $Mn(OAc)_2$, and $Mn(C_{17}H_{35}CO_2)_2$) were preliminarily recrystallized and dried in a vacuum desiccator; $Mn(acac)_3$ was prepared as described in Ref. 11 and dried *in vacuo* (20 h, 80 °C).

Oxidation of secondary alcohols (general procedure). Manganese tris(acetylacetonate) (0.1 mmol), MeCN (0.2—0.4 mmol), a corresponding secondary alcohol (10—20 mmol), and CCl_4 (20—50 mmol) were placed in a glass tube or a steel microautoclave (V = 17 mL) (in an atmosphere of argon). The tube was sealed (or the microautoclave was hermetically closed). The reactions mixtures were stirred at 200 °C for 1—3 h. Then the tube (autoclave) was cooled to ~20 °C, and the reaction mixture was filtered through a silica gel layer with hexane—ether (1 : 1) as an eluent. The solvent was removed, and the residue was distilled or crystallized from EtOH.

The structures of the ketones obtained were proved by comparing them with the authentic samples and the reference data.[12—15] The reaction conditions and the yields and physicochemical properties of the compounds obtained are given in Table 1.

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