

Hydroxylation of Polycyclic Alkanes with Molecular Oxygen Catalyzed by *N*-Hydroxyphthalimide (NHPI) Combined with Transition Metal Salts

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Abstract: Adamantanes were successfully converted into the corresponding mono- and dihydroxy adamantanes with molecular oxygen in the presence of *N*-hydroxyphthalimide (NHPI) combined with cobalt salts under mild conditions. For example, exposure of adamantane under oxygen atmosphere in the presence of NHPI (10 mol%) and Co(acac)₂ (0.5 mol%) in acetic acid at 75 °C for 6 h afforded adamantane-1-ol (43 %) and adamantane-1,3-diol (40 %) along with adamantane-2-one (8 %) in 93 % conversion. Similarly, 1,3-dimethyladamantane produced 3,5-dimethyladamantane-1-ol (47 %) and 5,7-dimethyladamantane-1,3-diol (37 %). Copyright © 1996 Elsevier Science Ltd

The selective oxygenation of saturated hydrocarbons under mild conditions is one of the most challenging and promising targets in oxidation chemistry.¹ In particular, homogeneous catalytic oxidation of hydrocarbons with molecular oxygen is very important in the chemical industry.² Recently, we have developed a novel catalytic system consisting of *N*-hydroxyphthalimide (NHPI) and Co(acac)_n (n=2 or 3) that oxidizes alkanes, alkylbenzenes and alcohols with molecular oxygen without any reducing agents.^{3,4} There have been a few reports on the catalytic hydroxylation of adamantane (**1a**) using O₂ as the ultimate oxidant.⁵ In general, the direct hydroxylation of **1a** with O₂ in the absence of any reducing agents such as aldehyde is very difficult to carry out in higher conversion and selectivity.⁶ We have achieved the first successfully catalytic hydroxylation of adamantanes, **1a** and **1b**, with O₂ in higher conversions and selectivities. To our knowledge, this is the best result obtained by the direct hydroxylation of adamantanes using O₂ through the catalytic process. In this paper, we describe the oxidation of polycyclic alkanes such as adamantanes with molecular oxygen catalyzed by NHPI combined with several metal salts.

The results for oxidation of **1a** under various reaction conditions are shown in Table 1. The oxidation of **1a** in the presence of a catalytic amount of NHPI (10 mol%) and Co(acac)₂ (0.5 mol%) in acetic acid under oxygen

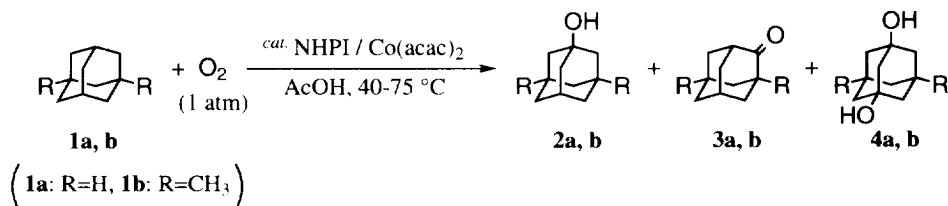


Table 1 Aerobic Oxidation of Adamantane (1a) Catalyzed by NHPI in the Presence of Transition Metal Salts^{a)}

Run	Metal Salt	Time / h	Conv. / %	Yield / % ^{b)}		
				2a	3a	4a
1	Co(acac) ₂	6	93	43	8	40
2	—	6	17	52	—	—
3 ^{c)}	Co(acac) ₂	6	no reaction			
4	Co(acac) ₃	6	91	47	8	37
5	Co(OAc) ₂	6	>99	21	6	54
6	Mn(acac) ₃	6	68	56	6	31
7	VO(acac) ₂	6	95	32	7	54
8	MoO ₂ (acac) ₂	6	85	54	6	31
9	Fe(acac) ₃	6	19	63	—	—
10	Cu(OAc) ₂	6	36	64	6	8
11 ^{d)}	Co(acac) ₂	10	73	56	14	25
12	Co(acac) ₂	2	50	80	6	12
13	Co(acac) ₂	15	>99	10	5	53

a) **1a** (3 mmol) was allowed to react with dioxygen (1 atm) in the presence of NHPI (10 mol%) and transition metal salts (0.5 mol%) in acetic acid (8 mL) at 75 °C. b) Based on **1a** reacted.

c) In the absence of NHPI. d) Under air atmosphere.

atmosphere (1 atm) at 75 °C for 6 h (standard conditions) produced adamantane-1-ol (**2a**) (43 %), adamantane-1,3-diol (**4a**) (40 %) along with a small amount of adamantane-2-one (**3a**) (8%) (Run 1). It is worth noting that the present oxidation produces diol **4a** in relatively high yield, since **4a** is rarely produced by conventional aerobic oxidations.^{5,6} In the oxidation of **1a** with 2,6-dichloropyridine *N*-oxide catalyzed by a Ru complex, **4a** is reported to be formed in 25 % yield.⁷ Leaving out Co(acac)₂ from the catalytic system led to a significant decrease in the conversion of **1a** (Run 2). Needless to say, the oxidation did not take place in the absence of NHPI (Run 3). Oxidations of **1a** using NHPI combined with Co(acac)₃ or Co(OAc)₂ gave almost the same results as those with Co(acac)₂. Replacing Co(acac)₂ with Mn(acac)₃ resulted in a slight decrease in the conversion of **1a**. It is interesting to note that VO(acac)₂ and MoO₂(acac)₂, which are rarely employed in aerobic oxidation, promote the hydroxylation of **1a** to give **2a** and **4a** in good yields. Fe(acac)₃ and Cu(acac)₂ were inefficient in this oxidation. The oxidation of **1a** in air under these conditions afforded **2a** (56 %), **3a** (14 %) and **4a** (25 %) in 73 % conversion. When the reaction was prolonged for 15 h, diol **4a** was obtained in 53 % yield.

Since adamantane-1,3-diol (**4a**) is an interesting material as a component of diols in polymer chemistry, stepwise hydroxylation of **2a** was examined. The hydroxylation of **2a** under the standard conditions afforded **4a** in 76 % yield along with a small amount of adamantane-1,3,5-triol (**5**) (18 %). **4a** was prepared from **2a** with ozone on silica gel in 43 %.⁸

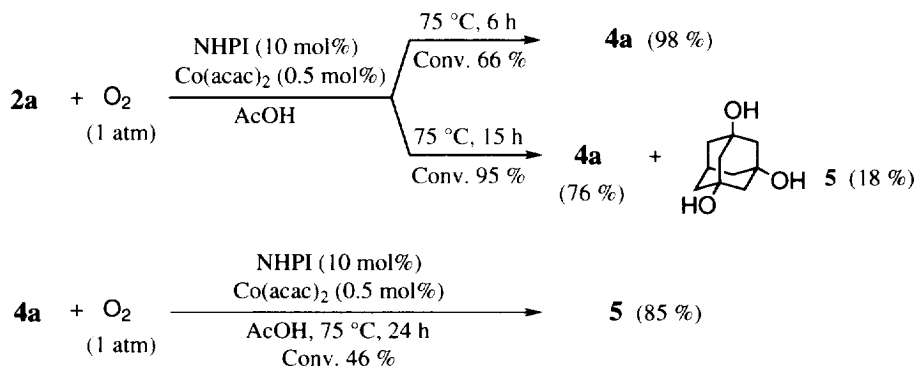


Table 2 shows the results for the oxidation of various polycyclic alkanes by the NHPI / Co(acac)₂ system. 1,3-Dimethyladamantane (**1b**) was also oxidized with dioxygen by the NHPI / Co(acac)₂ system. As expected, **1b** was more easily oxidized than **1a** to form 3,5-dimethyladamantan-1-ol (**2b**) (47 %) and 5,7-dimethyladamantan-1,3-diol (**4b**) (37 %). Methyl substituents of **1b** did not oxidize under these reaction conditions. It is surprising that the hydroxylation of **1b** is promoted even at 40 °C to form **2b** in high selectivity (87 %), although the conversion was moderate (46 %).

cis-Decalin (**6**) was hydroxylated at 60 °C to form bicyclo[4.4.0]decan-1-ol (**7**) in which the tertiary C-H bond was selectively oxidized. However, the oxidation of *trans*-decalin (**8**) under the same conditions was difficult and most of **8** was recovered unchanged. The reaction of **8** at higher temperature (75 °C) yielded **7** in low selectivity. Unlike **1a**, tetrahydrodicyclopentadiene (THDCP) (**9**) was oxidized to diketone (**10**)⁹ rather than hydroxyketone. Diketone **10** was formed in excellent selectivity when VO(acac)₂ was used in place of Co(acac)₂. The oxidation of tetracyclo[6.2.1.0^{2,7}.1^{3,6}]dodecane (TCDD) (**11**) led to a complex mixture of degradation products other than diketone **12**.¹⁰

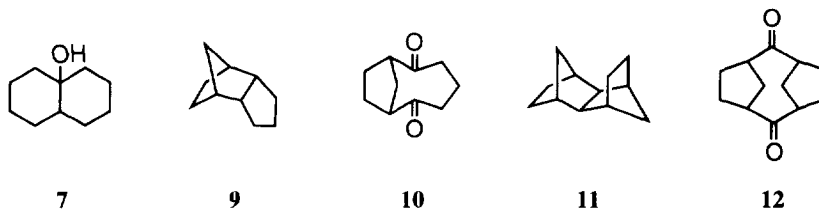
Table 2 Aerobic Oxidation of Various Polycyclic Alkanes by NHPI / Co(acac)₂ System^{a)}

Run	Substrate	Temp. / °C	Time / h	Conv. / %	Product (Yield / %) ^{b)}
1	1b	75	6	>99	2b (47), 4b (37)
2	1b	75	15	>99	2b (23), 4b (64)
3	1b	40	24	46	2b (87), 4b (6)
4 ^{c)}	<i>cis</i> -decalin (6)	60	15	97	bicyclo[4.4.0]decan-1-ol (7) (56) ^{d)}
5 ^{c)}	<i>trans</i> -decalin (8)	75	6	49	7 (32) ^{e)}
6 ^{c)}	<i>endo</i> -THDCP (9)	65	15	80	bicyclo[5.2.1]decane-2,6-dione (10) (54)
7 ^{c), f)}	9	65	6	39	10 (98)
8	TCDD (11)	85	15	69	tricyclo[6.2.1.1 ^{3,6}]dodecane-2,7-dione (12) (13)

a) Substrate was allowed to react with dioxygen (1 atm) in the presence of NHPI (10 mol%) and Co(acac)₂ (0.5 mol%) in acetic acid.

b) Based on substrates reacted. c) Benzonitrile was used as a solvent. d) The ratio of *cis*-**7** and *trans*-**7** was 1 : 3.6.

e) The ratio of *cis*-**7** and *trans*-**7** was 1 : 3.5. f) VO(acac)₂ was used in place of Co(acac)₂.



In conclusion, polycyclic alkanes were efficiently oxygenated with molecular oxygen using a combined catalytic system of NHPI and $\text{Co}(\text{acac})_2$ under mild conditions. This method provides a novel, direct aerobic hydroxylation route of polycyclic alkanes.

Acknowledgment

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- Bicyclo[5.2.1]decane-2,6-dione (**10**): IR 2948, 1698, 1141, 896 cm^{-1} ; ^{13}C NMR δ 23.6, 25.2, 30.8, 39.0, 51.5, 213.3; ^1H NMR δ 1.01-1.81 (m, 6H), 1.95-2.02 (m, 2H), 2.24-2.31 (m, 4H), 2.45-2.63 (m, 2H); MS *m/e* 166 (M^+ , 17), 138 (13), 125 (13), 97 (100).
- Tetracyclo[6.2.1.1.3⁶]dodecane-2,7-dione (**12**): IR 2938, 1671, 1280, 859 cm^{-1} ; ^{13}C NMR δ 29.8, 30.4, 52.9, 216.1; ^1H NMR δ 1.93-2.42 (m, 13H), 3.19-2.26 (m, 3H); MS *m/e* 192 (M^+ , 0.2), 164 (6), 151 (100), 123 (34), 95 (9).

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