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Ytterbium Catalyzed Oxidation of Alcohols to Aldehydes and Ketones by Means of Iodosylbenzene

Toshiaki YOKOO, Kozo MATSUMOTO, Koichiro OSHIMA,* and Kiitiro UTIMOTO*
Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01

Treatment of a 1,2-dichloroethane solution of various alcohols with iodosylbenzene in the presence of a catalytic amount of ytterbium(III) nitrate provided the corresponding carbonyl compounds in good to excellent yields.

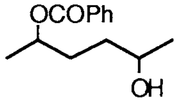
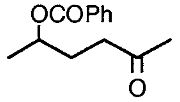
For about a decade there has been an increasing interest of organic chemists in the lanthanoids and several reports on the synthetic utility of lanthanoid compounds have appeared in the literature.1) The exploitation of these compounds for oxidation reaction, however, has been limited. Only cerium(IV) ammonium nitrate has been widely used for the oxidation of various functional groups.2) Here we wish to report a new method for the oxidation of alcohols to carbonyl compounds with iodosylbenzene in the presence of ytterbium catalysts.3)

We have examined several combinations of oxidants and ytterbium catalysts in order to find a suitable system for the oxidation of primary alcohols into aldehydes. Among them, iodosylbenzene-ytterbium catalyst system proved to be effective for the oxidation of primary alcohols. In the oxidation of 1-dodecanol (1.0 mmol) with iodosylbenzene (1.5 mmol) in the presence of ytterbium catalysts (0.1 mmol) at 80 °C for 4 h, the yields of dodecanal were as follows: $Yb(NO_3)_3$, 77%; $Yb(OAc)_3$, 62%; $YbCl_3$, 30%; $Yb_2(SO_4)_3$, 28%; $Yb(O\textit{i}Pr)_3$, 40%. Other lanthanoid nitrates such as $Tb(NO_3)_3$, $Ho(NO_3)_3$, and $Lu(NO_3)_3$ were as effective as ytterbium nitrate. The yields of dodecanal were 70% ($Tb(NO_3)_3$), 64% ($Ho(NO_3)_3$), and 84% ($Lu(NO_3)_3$), respectively under the same reaction conditions. The representative results with $PhI{=}O\text{-}Yb(NO_3)_3$ are shown in Table 1.

Olefinic alcohols such as 11-dodecen-2-ol and carveol were not good substrates for the oxidation with $NaBrO_3\text{-}(NH_4)_2Ce(NO_3)_6$2) since oxidation of olefinic linkage into bromohydrin competed with the oxidation of hydroxyl moiety. This difficulty was overcome by the use of $PhI{=}O\text{-}Yb(NO_3)_3$. Treatment of 11-dodecen-2-ol or 10-undecen-1-ol with iodosylbenzene in the presence of ytterbium nitrate gave 11-dodecen-2-one or 10-undecenal in good yield. Oxidation proceeded smoothly for the substrates having various functional groups such as ester and ether. The $PhI{=}O\text{-}Yb(NO_3)_3$ system was effective not only for the oxidation of primary alcohols but also for the oxidation of secondary alcohols. Whereas most oxidants react more rapidly with secondary alcohols,4) $PhI{=}O\text{-}Yb(NO_3)_3$ reagent shows a preference for primary alcohols. For example, the competitive reaction of 1-dodecanol and 2-dodecanol revealed that 1-dodecanol was oxidized twice as fast as 2-dodecanol. In the same way, benzylic and allylic alcohols were more reactive than their saturated counterparts. Thus, geraniol was oxidized twice as fast as β-citronellol, but geranial was obtained in only 35% yield along with unidentified complex by-products. Ytterbium acetate gave better results compared to ytterbium nitrate in terms of yields in the case of allylic alcohol such as geraniol or carveol, although the longer reaction period was required (Runs 8 and 15 in Table 1).

Table 1. Oxidation of Alcohol with $PhI=O\text{-}Yb(NO_3)_3$ [a)]

$$\begin{matrix}\mathrm{R^1R^2CHOH\ or} \\ \mathrm{R^3CH_2OH}\end{matrix} \xrightarrow[\mathrm{ClCH_2CH_2Cl}]{\mathrm{PhI{=}O\ /\ Yb(NO_3)_3}} \begin{matrix}\mathrm{R^1R^2C{=}O\ or} \\ \mathrm{R^3CHO}\end{matrix}$$

Run	Alcohol	Time / h	Product	Yield / %
1	2-Decanol	4	2-Decanone	100
2	Cyclododecanol	5	Cyclododecanone	93
3	4-*t*-Butylcyclohexanol	4	4-*t*-Butylcyclohexanone	90
4	*l*-Menthol	5	*l*-Menthone	71
5	11-Dodecen-2-ol	5	11-Dodecen-2-one	77
6	PhCH(OH)Me	3	PhCOMe	63
7	5α-Cholestan-3β-ol	6	5α-Cholestan-3-one	83
8	Carveol	12	Carvone	70 [b)]
9		4		86
10	1-Decanol	3.5	Decanal	77
11	10-Undecen-1-ol	4	10-Undecenal	71
12	$PhCOO(CH_2)_3CH_2OH$	7	$PhCOO(CH_2)_3CHO$	71
13	$PhCH_2O(CH_2)_3CH_2OH$	5	$PhCH_2O(CH_2)_3CHO$	63
14	$MeOOC(CH_2)_4CH_2OH$	4	$MeOOC(CH_2)_4CHO$	76
15	Geraniol	12	Geranial	60 [b,c)]

a) Alcohol (1.0 mmol), iodosylbenzene (1.5 mmol), and $Yb(NO_3)_3$ (0.1 mmol) were employed.
b) Ytterbium acetate was used instead of ytterbium nitrate. c) Pure *E* isomer.

Ytterbium nitrate tetrahydrate (43 mg, 0.1 mmol) was added to a suspension of iodosylbenzene (0.33 g, 1.5 mmol) and 1-decanol (0.16 g, 1.0 mmol) in 1,2-dichloroethane (10 ml). The mixture was heated at 80 °C for 3.5 h. The resulting mixture was poured into water and extracted with ethyl acetate (10 ml x 3). Purification by silica gel column chromatography gave decanal (0.12 g) in 77% yield.

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