Russian Journal of Organic Chemistry, Vol. 37, No. 11, 2001, pp. 1600–1602. From Zhurnal Organicheskoi Khimii, Vol. 37, No. 11, 2001, pp. 1673–1675.

Oxidation of Benzyl Alcohols under Mild Heterogeneous Conditions[*]

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Received March 13, 2001

Abstract—A combination of iodic acid with ammonium dichromate in the presence of wet SiO_2 was used as an efficient oxidizing agent for the transformation of benzyl alcohols to the corresponding aldehydes and ketones in *n*-hexane or without a solvent at room temperature with excellent yields.

Multivalent metal oxides and their mineral salts are often used for oxidation of organic functional groups. Classical reagents of this type are manganese dioxide (MnO_2), potassium permanganate ($KMnO_4$), chromium trioxide (CrO_3), potassium chromate (K_2CrO_4), and potassium dichromate ($K_2Cr_2O_7$) [1]. These oxidants are widely used both in laboratory and in industry, but they are not free from disadvantages. A rigorous control of the experimental conditions is required to obtain satisfactory and reproducible results. The other disadvantages which, in spite of their power, restrict their application in multistep organic synthesis are the lack of selectivity, the necessity of using strongly acidic and aqueous media, low yields of the products, and tedious isolation procedures [2]. For example, overoxidation of aldehydes to carboxylic acids is frequently an unavoidable side process. Furthermore, some oxidation procedures require elevated temperature which promotes undesirable secondary reactions. Likewise, the presence of strong acids or bases which are necessary adjuncts in some reactions often leads to detrimental side processes. For instance, the oxidation of primary alcohols to aldehydes with a chromium(VI) salt in sulfuric acid is often accompanied by formation of a semiacetal from the aldehyde and initial alcohol and subsequent ready oxidation of that intermediate to the corresponding ester [3].

Along this line, we examined the applicability of potentially useful oxidants for selective oxidation and oxidative deprotection of various functional groups [4–10]. Unfortunately, these oxidants cannot be applied to compounds which are susceptible to nitration [11–14]. To overcome the above limitations we tried to find a new reagent or a system of reagents. In addition, both clean and easy procedure for treatment of the reaction mixtures was important. Very recently, along with the other authors, we have demonstrated that heterogeneous oxidizing systems have many advantages, including simple experimental procedures, mild reaction conditions, and minimization of chemical wastes, as compared to analogous homogeneous systems [15–17]. These results encouraged us to seek for a completely heterogeneous system for the oxidation of benzyl alcohols. For this purpose, we have studied a system based on *in situ* generation of H_2CrO_4 at low concentration on the SiO_2 surface by the action of very mild inorganic acid, HIO_3 (pK_a ~1), on ammonium dichromate. The present communication reports on a simple and convenient procedure for effective transformation of benzyl alcohols **I** into the corresponding aldehydes or ketones **II** under mild heterogeneous conditions. Various alcohols **I** were subjected to oxidation in the system

$$\underset{\textbf{Ia–Il}}{R^1R^2CHOH} \xrightarrow{(NH_4)_2Cr_2O_7,\ HIO_3,\ \text{wet } SiO_2} \underset{\textbf{IIa–IIl}}{R^1R^2C{=}O}$$

I, **II**, R^1 = Ph (**a**), 4-$CH_3C_6H_4$ (**b**), 4-ClC_6H_4 (**c**), 2-ClC_6H_4 (**d**), 4-BrC_6H_4 (**e**), 4-$CH_3C_6H_4$ (**f**), 2-$NO_2C_6H_4$ (**g**), $PhCH_2OC_6H_4$ (**j**); R^1 = Ph, R^2 = CH_3 (**h**); R^1 = R^2 = Ph (**i**); R^1R^2 = $(CH_2)_5$ (**k**); R^1 = $PhCH_2$, R^2 = CH_3 (**l**).

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[*] The original article was submitted in English.

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Oxidation of alcohols **I** to aldehydes or ketones **II** with the system $(NH_4)_2Cr_2O_7$–HIO_3–wet SiO_2 in hexane and without a solvent at room temperature

Run no.	Alcohol no.	Product no.	$(NH_4)_2Cr_2O_7$,[a] mmol	HIO_3,[a] mmol	Time, min	Yield,[b] %
1	**Ia**	**IIa**	0.75	5	30	87
2	**Ia**[c]	**IIa**	0.75	5	10	90
3	**Ib**	**IIb**	0.75	5	35	90
4	**Ib**[c]	**IIb**	0.75	5	10	85
5	**Ic**	**IIc**	0.75	5	45	85
6	**Ic**[c]	**IIc**	0.75	5	10	90
7	**Id**	**IId**	0.75	5	120	90
8	**Id**[c]	**IId**	0.75	5	15	92
9	**Ie**	**IIe**	0.75	5	60	92
10	**Ie**[c]	**IIe**	0.75	5	15	91
11	**If**	**IIf**	0.75	5	135[d]	90
12	**If**[c]	**IIf**	0.75	5	30	90
13	**Ig**	**IIg**	0.75	5	30[d]	[e]
14	**Ig**[c]	**IIg**	0.75	5	30	89
15	**Ih**	**IIh**	0.75	5	120	86
16	**Ih**[c]	**IIh**	0.75	5	10	83
17	**Ii**	**IIi**	0.75	5	75	82
18	**Ii**[c]	**IIi**	0.75	5	60	85
19	**Ij**	**IIj**	0.75	5	30	[e]
20	**Ij**[c]	**IIj**	0.75	5	45	89
21	**Ik**	**IIk**	0.75	5	60	[e]
22	**Il**	**IIl**	0.75	5	60	[e]
23	**Ia**[c]	**IIa**	0	5	240	0
24	**Ia**[c]	**IIa**	0.75	0	600	0

[a] Per mmole of alcohol **I**; the ratio wet SiO_2–substrate was 0.3 g per mmol.

[b] Isolated product.

[c] Solvent-free conditions.

[d] Under reflux.

[e] Mixture of products.

consisting of $(NH_4)_2Cr_2O_7$, HIO_3, and wet SiO_2 in hexane (odd run numbers in table). The reactions were carried out at room temperature, and the products were formed in high yields. The oxidation of benzyl alcohols **I** under solvent-free conditions also gives only the corresponding aldehyde or ketone **II** (even run numbers in table). The reaction is very fast. However, this procedure is not suitable for the oxidation of aliphatic alcohols (see table, run nos. 21 and 22). The reaction under study readily occurs on mixing $(NH_4)_2Cr_2O_7$, HIO_3, wet SiO_2, *n*-hexane (if required), and the substrate and stirring the resulting heterogeneous mixture at room temperature. Highly pure aldehyde or ketone **II** can be isolated by mere filtration and evaporation of the solvent. The results and conditions are summarized in table.

No oxidation occurred in the absence of ammonium dichromate or iodic acid (see table, runs nos. 23 and 24). These findings indicate that neither ammonium dichromate nor iodic acid alone can act as oxidant.

To conclude, it should be noted that the cheapness and availability of the reagents, easy and clean isolation procedure, and high yields of the products make the proposed method attractive for large-scale applications. The method is very simple, and contamination by overoxidation by-products is avoided. In addition, a new point is that the reaction is heterogeneous, which may be important in an industrial setting. We believe that our procedure provides an essential addition to the existing methods. Detailed study of the oxidation of various classes of organic compounds with the above oxidant system is now in progress.

EXPERIMENTAL

Commercial reagents from Fluka, Merck, Riedel-dehaen AG, and Aldrich chemical companies were used. The oxidation products were identified by comparing their spectral (IR and ^{1}H NMR), TLC, and physical parameters with those reported for authentic samples [9, 10].

Oxidation of 4-chlorobenzyl alcohol (Ic) to 4-chlorobenzaldehyde (IIc) (*general procedure*). *a*. 4-Chlorobenzyl alcohol (**Ic**), 0.253 g (2 mmol), was added to a suspension of 1.76 g (10 mmol) of HIO_3, 0.6 g of wet SiO_2 (50 wt %), and 0.378 g (1.5 mmol) of $(NH_4)_2Cr_2O_7$ in 6 ml of hexane, the mixture was stirred for 45 min at room temperature (the progress of the reaction was monitored by TLC) and filtered, and the precipitate was washed with methylene chloride (2 × 5 ml). The washings were combined with the filtrate, treated with 4 g of anhydrous $MgSO_4$ (20 min), and the drying agent was filtered off. Evaporation of the solvent, followed by column chromatography on silica gel, gave 0.212 g (85%) of 4-chlorobenzaldehyde (**IIc**).

b. Without a solvent. 4-Chlorobenzyl alcohol (**Ic**), 0.253 g (2 mmol), was added to a mixture of 1.76 g (10 mmol) of HIO_3, 0.6 g of wet SiO_2 (20 wt % of water), and 0.378 g (1.5 mmol) of $(NH_4)_2Cr_2O_7$, and the mixture was shaken for 10 min at room temperature (the progress of the reaction was monitored by TLC). The mixture was treated with 2 × 5 ml of CH_2Cl_2 and filtered. The filtrate was treated with 4 g of anhydrous $MgSO_4$ (20 min), and the drying agent was filtered off. The solvent was removed from the filtrate, and the residue was subjected to column chromatography on silica gel to obtain 0.224 g (90%) of 4-chlorobenzaldehyde (**IIc**).

The authors are gratefull to the research affairs, Gilan University (Rasht, Iran) and Bu-Ali Sina University (Hamadan, Iran) for the financial support of this work.

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