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Triphenylmethylphosphonium Dichromate: An Effective and Chemoselective Reagent for Oxidation of Benzylic Alcohols to the Corresponding Aldehydes and Ketones

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Abstract: An efficient and straightforward method for oxidation of the benzylic alcohols to the corresponding aldehydes and ketones has been accomplished using triphenylmethylphosphonium dichromate (MTPPD) under solvent-free conditions with high chemoselectivity. The reaction is fast with good yields and straightforward workup.

Keywords: Alcohols, aldehydes, ketones, oxidation, triphenylmethylphosphonium dichromate

INTRODUCTION

Oxidation in modern organic chemistry is one of the most important reactions.[1] Classic reagents such as manganese dioxide (MnO_2), potassium permanganate ($KMnO_4$), chromium trioxide (CrO_3), potassium chromate (K_2CrO_4), and potassium dichromate have been introduced.[1] Some new methods have also been reported.[2–10] Although some of these methods have convenient protocols with good to high yields, most of

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them suffer at least from one of the following disadvantages: (1) high cost of preparation, (2) long reaction time, (3) hygroscopicity, (4) high acidity, (5) instability, (6) no selectivity, (7) photosensivity, (8) dangerous procedures for their preparation, and (9) tedious workup procedures. Reactions under solvent-free conditions have recently attracted attention.[11,12] The advantage of these methods over conventional classical methods is that they are cleaner reactions and have decreased reaction time and straightforward workup.

RESULTS AND DISCUSSION

In continuation of our ongoing program to develop environmentally benign methods under solvent-free conditions,[13–16] we report an extremely convenient method for oxidation of alcohols to their corresponding aldehydes or ketones using triphenylmethylphosphonium dichromate (MTPPD, **1**). This reagent was easily prepared by adding an aqueous solution of CrO_3 in HCl (3N) to a stirring aqueous solution of $MePh_3P^+Br^-$. After 15 min, MTPPD (**1**) was obtained as an orange precipitate in good yield (Scheme 1).

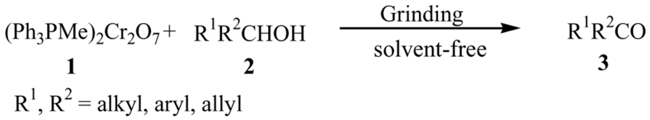
This reagent is soluble in acetonitrile, dimethylformamide (DMF), dimethylsulfoxide (DMSO), and N-methylpyrrolidone (NMP) and slightly soluble in ethyl acetate. By using this oxidant, various alcohols were converted to their corresponding carbonyl compounds in good to high yields within short reaction times (Scheme 2, Table 1).

In comparison to benzylic alcohols, oxidation of aliphatic ones with this reagent do not occur at all, even when using an excess amount of reagent and grinding for a longer time. The electron-donor functional groups on the phenyl ring of benzylic alcohols accelerate the reaction rate and the electron-acceptor ones decrease it. The rates for oxidation of primary alcohols in comparison to the secondary alcohols are faster and also the reaction times are shorter (Scheme 2, Table 1).

To evaluate the selectivity of the reagent, the competitive reactions shown in Eqs. (1–3) were carried out. When equimolar amounts of 2−phenylethyl alcohol and benzyl alcohol were treated with MTPPD (one molar ratio), only benzyl alcohol was selectively oxidized [Eq. (1)]. Treatment of benzyl alcohol with MTPPD (one molar ratio) in the

$$2\ Ph_3PMeBr \ + \ CrO_3/HCl\ (3\ N) \xrightarrow[r.t]{H_2O} \underset{\mathbf{1}}{(Ph_3PMe)_2Cr_2O_7}$$

Scheme 1. Preparation of triphenylphosphonium dichromate (MTPPD).



$$(Ph_3PMe)_2Cr_2O_7 + R^1R^2CHOH \xrightarrow[\text{solvent-free}]{\text{Grinding}} R^1R^2CO$$

1 2 3

R^1, R^2 = alkyl, aryl, allyl

Scheme 2. Oxidation of alcohols with MTPPD.

Table 1. Oxidation of alcohols by $(MePh_3P)_2Cr_2O_7$ (**1**) under solvent-free conditions[a,b]

Entry	Substrate (1)	Time (min)	Yield (%)	Mp or bp (°C)/torr (lit.[15,16])
1	Benzyl alcohol	3.0	95	176–178/760 (178–179/760)
2	4-Nitrobenzyl alcohol	10.0	90	103–105 (103–106)
3	3,4-Dimethoxybenzyl alcohol	4.0	94	280–282/760 (281/760)
4	4-Methoxybenzyl alcohol	3.0	93	141–143/50 (141–143/50)
5	2-Methoxybenzyl alcohol	3.0	95	37–39 (37–39)
6	1,1-Diphenylmethanol	6.0	95	46–48 (47–49)
7	3-Methoxybenzyl alcohol	3.0	93	141–143/50 (143/50)
8	4-Chloroybenzyl alcohol	5.0	95	45–48 (45–47)
9	3-Chloroybenzyl alcohol	5.0	93	211–213/760 (213–214/760)
10	1-Phenylethanol	6.0	95	200–2002/760 (200–2002/760)
11	1-(p-bromophenylethanol)	5.0	93	49–52 (49–52)
12	1-(p-chlorophenyl)ethanol	3.0	90	231–232/760 (232/760)
13	Benzoin	10.0	0	—
14	1-(p-Bromophenyl)-2-bromoethanol	6.0	93	107–110 (108–110)
15	Cyclohexanol	30.0	0	—
16	1-Tetralol	7.0	90	126–127/23 (127/23)
17	*n*-Heptanol	20.0	0	—
18	*n*-Pentanol	20.0	0	—
19	L-Menthol	20.0	0	—
20	1-Indanol	5.0	82	242–244/760 (243–245/760)
21	9-Fluorenol	7.0	82	81–83 (80–83)
22	4-*t*-Decylcyclohexanol	20.0	0	—
23	2-naphthalene-methanol	4.0	92	80–82 (79–91)
24	2-Phenylethanol	30.0	0	—
25	3-Methylcyclohexanol	30.0	0	—
26	4-Methylphenylethyl alcohol	30.0	0	—

[a] Confirmed by comparison with authentic samples (IR, TLC, and NMR).[15,16]
[b] Yield of isolated products.

presence of diphenylmethanol (1mmol) led to exclusive oxidation of diphenylmethanol [Eq. (2)]. Interestingly, in the oxidation of alcohols, the overoxidation of products to the corresponding carboxylic acids was not observed. When we treated benzyl alcohol (1mmol) with MTPPD (one molar ratio) in the presence of thioanisol (1mmol), only the benzyl alcohol was selectively oxidized [Eq. (3)].

$$\mathrm{PhCH_2CH_2OH + PhCH_2OH} \underset{10\text{ min., grinding}}{\overset{\text{Solid-state}}{\longrightarrow}} \underset{\text{unchanged}}{\mathrm{PhCH_2CH_2OH}} + \underset{95\%}{\mathrm{PhCHO}} \tag{1}$$

$$\mathrm{PhCHOHPh + PhCH_2OH} \underset{5\text{ min., grinding}}{\overset{\text{Solid-state}}{\longrightarrow}} \underset{100\%}{\mathrm{PhCOPh}} + \underset{\text{unchanged}}{\mathrm{PhCH_2OH}} \tag{2}$$

$$\mathrm{PhSMe + PhCH_2OH} \underset{10\text{ min., grinding}}{\overset{\text{Solid-state}}{\longrightarrow}} \underset{\text{unchanged}}{\mathrm{PhSMe}} + \underset{95\%}{\mathrm{PhCHO}} \tag{3}$$

EXPERIMENTAL

General

Yields refer to isolated pure products. The products were characterized by comparison of their spectral (IR, ^{1}H NMR) and physical data with those of authentic samples.[15,16] All ^{1}H NMR spectra were recorded at 300 and 500 MHz in $CDCl_3$ relative to tetramethylsilane (TMS) (0.00 ppm), and IR spectra were recorded on Shimadzu 435 IR spectrometer. All reactions were carried out under solvent-free conditions at room temperature in a hood with strong ventilation. The reaction is safe, and we did not observe any dangers using this procedure under solvent-free conditions.

Preparation of Methyltriphenylphosphonium Dichromate (MTPPD)

A solution of CrO_3 (10 mmol, 1.0 g) in HCl 3 N (10 mL) was added to a solution of methylriphenylphosphonium bromide (10 mmol, 3.57 g) in water (25 mL) under stirring at room temperature. After 30 min of stirring, an orange precipitate was formed. The mixture was filtered, washed with water (2 × 15 mL), and dried at room temperature (3.85 g, 96% yield), which decomposed at 220–222°C to a dark-brown material. IR (KBr) 3100, 2980, 1600, 1495, 1480, 1260, 1190, 1050, 860, 750, 690 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ, ppm: 7.9–7.7 (m, 15 H), 3.19

(d, $J = 14.6$, P-$\underline{\mathrm{CH}}_3$). ^{13}CNMR: δ 134.5, 134.4, 132.5, 132.3, 129.7, 129.3, 116.4. Anal. calcd. for $C_{38}H_{36}Cr_2O_7P_2$: C, 63.16; H, 4.99%. Found: C, 63.25; H, 4.90%.

Oxidation of Benzyl Alcohol with MTPPD to Benzaldehyde

In a mortar, 0.36 g of MTPPD (0.5 mmol) and the alcohol (1 mmol) were ground with a pestle for the time specified in Table 1. The progress of the reaction was monitored by thin-layer chromatography (TLC; silica gel, EtOAc/*n*-hexane = 20/80) until the alcohol disappeared. When the reaction was completed, the product was extracted with Et_2O (2 × 10 mL) and dried ($MgSO_4$), and the solvent was evaporated to yield the pure product without any further need for purification.

CONCLUSION

In conclusion, we report an efficient and versatile method for converting alcohols to their corresponding carbonyl compounds with the following advantages: (a) our reagent is inexpensive and easily handed and can be stored on the bench for months without losing its activity; (b) the procedure is simple and occurs under solvent-free conditions at room temperature; (c) the reaction is environmentally green; (d) the reaction time is short; and (e) the isolation of the product is straightforward.

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