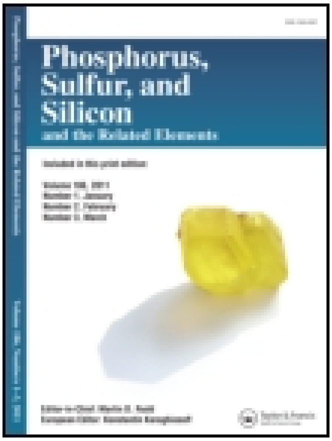

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SOLID-PHASE OXIDATION OF ORGANIC COMPOUNDS WITH BENZYLTRIPHENYLPHOSPHONIUM DICHROMATE

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Benzyltriphenylphosphonium dichromate could be used for oxidation of organic compounds such as alcohols, thiols and sulfides to the corresponding carbonyl, disulfide and sulfoxide derivatives under solid-phase conditions. This reagent is very easily prepared from an aqueous solution of benzyltriphenylphosphonium chloride with CrO_3 in 3 N HCl at room temperature. The reagent, is a stable orange powder, which may be stored for month without loss of its activity.

Keywords: Aldehydes and ketones; Oxidation; Sulfoxides; Disulfides; Alcohols; Thiols

INTRODUCTION

Heterogeneous reactions that are facilitated by supported reagents on various solid inorganic surfaces have received attention in recent years.[1-3]. The advantage of these methods over conventional homogenous reactions is that they provide greater selectivity, enhanced reaction rates, cleaner products and manipulative simplicity. In continuation of our ongoing program to develop environmentally benign methods using solid supports,[4] we now wish to report an extremely convenient method for oxidation of organic compounds with benzyltriphenylphosphonium dichromate ($(PhCH_2PPh_3)_2\ Cr_2O_7$) under solid phase conditions.

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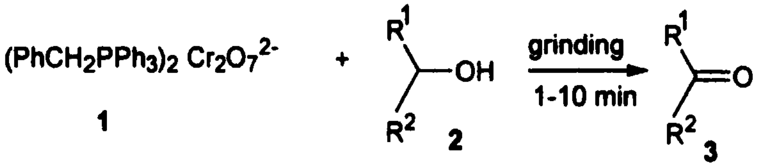
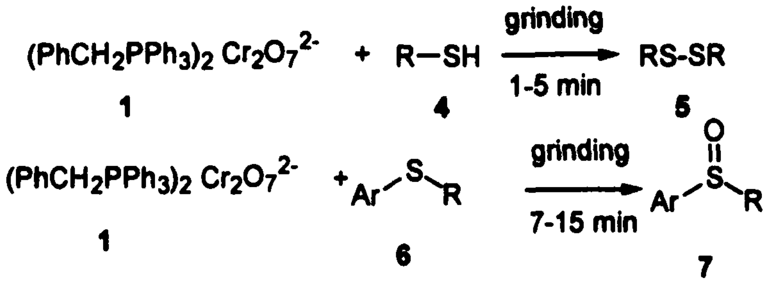
RESULTS AND DISCUSSION

The oxidation of alcohols with **1** proceeds well in solid-phase conditions (Scheme 1). Benzylic alcohols **2** are oxidized to the corresponding carbonyl compounds in high yields (Table I); allylic alcohols have also been selectively oxidized to α, β-unsaturated carbonyl compounds without cleavage of the C=C double bonds; α-hydroxy ketone was converted to α-diketone in excellent yield (Table I). Because of the low reactivity of aliphatic alcohols only benzylic and allylic alcohols could be converted into the corresponding carbonyl compounds. The process in its entirety involves a simple mixing of benzyltriphenylphosphonium dichromate ($(PhCH_2PPh_3)_2\ Cr_2O_7$) and alcohols **2** in a mortar (Scheme 1) and grinding the mixture for the time specified in Table I at room temperature. The yields of the reactions are excellent (90–100 %) and the reaction times are exceedingly short (1–10 min). The compounds **3** were characterized by ^1H NMR and IR analysis.



SCHEME 1

The mildness of the reagent has been shown by the oxidation of thiols **4** to their disulfides **5** in excellent yields (Scheme 2 and Table II). This reagent is able to oxidize sulfides **6** to the corresponding sulfoxides **7** in high yield. No further oxidation to their sulfones was observed (Scheme 2 and Table III). These observations are in contrast to what, that is reported by our group recently for 1-benzyl-4-aza-1-azoniabicyclo[2.2.2]octane dichromate (BAABOD) which decomposes to DABCO, benzyl alcohol and Cr_2O_3 upon standing under solid-phase conditions.[5] Therefore BAABOD is not able to oxidize thiols and sulfides under these conditions, even by using 2 molar ratio of this reagent and grinding the reaction mixture for 60 min. The stability of benzyltriphenylphosphonium dichromate in compare to BAABOD is the reflection of the presence of phosphonium cation in the reagent, which is more stable than ammonium cation.



SCHEME 2

TABLE I Oxidation of alcohols **2** to Carbonyl Compounds **3**[a]

Cmpd	*R*^{1}	*R*^{2}	*Time (min)*	*Yield*[b] *(%)*
2a	C_6H_4	H	3	100
2b	4-$NO_2C_6H_4$	H	5	92
2c	3,4-$(MeO)_2C_6H_3$	H	10	95
2d	4-PhC_6H_4	Me	5	99
2e	2-pyridyl	C_6H_5	5	98
2f	C_6H_5	Me	5	100
2g	4-$MeOC_6H_4$	H	1	100
2h	2-$MeOC_6H_4$	H	5	100
2i	C_6H_5	C_6H_5	10	90
2j	3-$MeOC_6H_4$	H	5	93
2k	4-ClC_6H_4	H	3	94
2l	2-ClC_6H_4	H	4	96
2m	C_6H_5	$C_6H_5CH_2$	5	96
2n	4-BrC_6H_4	Me	10	91
2o	4-ClC_6H_4	Me	5	94
2p	C_6H_5	C_6H_5CO	5	95
2q	2,3-$(MeO)_2C_6H_3$	H	7	98
2r	$C_6H_4CH{=}CH$	C_6H_5	5	95
2s	$C_6H_4CH{=}CH$	Me	8	92
2t	4-$NO_2C_6H_4CH{=}CH$	H	10	96
2u	$C_6H_4CH{=}CH$	H	10	90

[a] Confirmed by comparison with authentic sample (IR, TLC and NMR)[5–7].

[b] Yield of isolated pure product.

TABLE II Oxidation of Thiols **4** to Disulfides **5**[a]

Entry	*R*	*Reaction Time (min)*	*Yield (%)*[b]	*mp °C or bp °C/torr (lit.*[7a,10]*)*
1	phenyl	1	98	58–60 (58–60)
2	4-nitrophenyl	3	87	184–6 (184–6)
3	2-pyridyl	3	92	56–58 (56–58)
4	2-benzimidazoyl	5	86	144–5 (142–5)
5	2-furyl	2	95	118–19/0.8 (112–15/0.5)

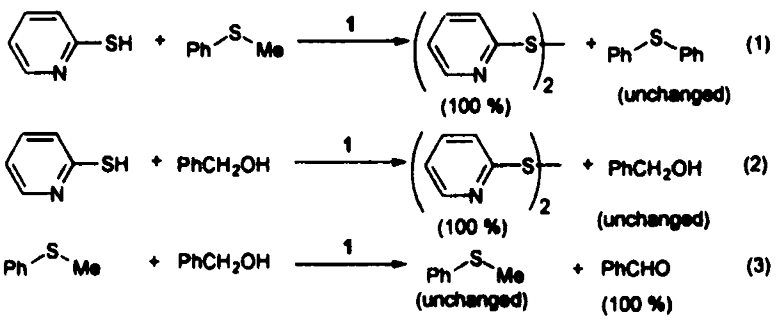
[a] Confirmed by comparison with authentic sample (IR, TLC and NMR).
[b] Yield of isolated pure product.

TABLE III Oxidation of Sulfides **6** to Sulfoxides **7**[a]

Entry	*Ar*	*R*	*Reaction Time (min)*	*Yield (%)b*	*mp °C or bp °C/torr (lit.11)*
1	benzyl	benzyl	9	93	134–136 (133–135)
2	phenyl	benzyl	7	97	120–122 (122–124)
3	4-nitrophenyl	phenyl	15	90	107–108 (107–108)
4	benzyl	nbutyl	10	96	63–64 (62–63)
5	phenyl	methyl	10	93	124–126/0.8 (139–141/14)
6	phenyl	nbutyl	10	92	103–105 (102–104)

[a] Confirmed by comparison with authentic sample (IR, TLC and NMR).
[b] Yield of isolated pure product.

Another noteworthy advantage of this reagent lies in its selectivity the OH group of α,β-unsaturated alcohols were selectively oxidized to the corresponding carbonyl compounds and the double bonds remained intact (Table I, alcohols **2r-2u**). In order to evaluate the selectivity of reagent **1**, the competitive reactions shown in Eqs. 1–3 was carried out. When we treated one molar ratio of oxidizing reagent **1** and an equimolar amount of thioanidole in the presence of 2-mercaptopyridine; only 2-mercaptopyridine was selectively oxidized (Eq. 1). Treatment of a mixture of benzyl alcohol and 2-mercaptopyridine with this reagent **1**, resulted exclusively in the oxidation of 2-mercaptopyridine (Eq. 2). In eventually treatment with reagent **1** on benzyl alcohol in the presence of thioanidole, showed only benzyl alcohol was oxidized (Eq. 3).



In conclusion, we report here an efficient, rapid and inexpensive method for the oxidation of alcohols, thiols and sulfides to the corresponding carbonyl, disulfide and sulfoxide compounds under solid-phase conditions. This methodology is superior to previously reported methods[5–42] in terms of selectivity, high yields, and purity of products and facile work-up.

EXPERIMENTAL

General

All yields refer to isolated products after purification. The products were characterized by comparison with authentic samples (IR and NMR spectrum, tin layer chromatography, melting and boiling point).[5–11] All reactions were carried out under solid-phase conditions. The ^1H NMR spectra were recorded at 90 and 250 MHz in $CDCl_3$ and CCl_4 relative to TMS (0.00 ppm). IR spectra were recorded on Shimadzu 435 IR spectrophotometer. Spectra of solids were carried out using KBr pellets. The Research Institute of Petroleum Industry, Tehran, I.R. Iran performed elemental analysis.

Preparation of benzyltriphenylphosphonium dichromate 1

To an aqueous solution of benzyltriphenylphosphonium chloride (8.55 g, 22 mmol, 75 ml H_2O), was added a solution of chromium (VI) oxide

(11 g, 11 mmol) in HCl 3 N (220 ml). The reaction mixture was stirred at room temperature for 15 min. The resulting orange solid products was collected, washed with water (20 ml) and dried in a desiccator under vacuum over calcium chloride, yield 9.43 g (10.34 mmol, 94 %) of (1), mp 210–212°C. ^{1}H NMR: δ 7.93–6.87 (m, 20 H), 4.7 (d, J=25.6 Hz, $C\underline{H}_2$-P). ^{13}C NMR: δ 133.50, 133.20, 130.20, 129.60, 129.40, 128.10, 127.70, 127.2, 117.30 (d, J=85.5 Hz, P-$\underline{C}H_2$). IR (KBr): 1298, 1269, 1098, 1060, 700, 658, 590, 546 cm^{-1}. Anal Calcd for $C_{50}H_{44}Cr_2O_7$: C, 69.70; H, 5.15; Cr, 12.08%. Found: C, 69.60; H, 50.20; Cr, 11.90%.

General procedure

A mortar was charged with alcohol **2**, sulfide **4** or sulfoxide **6** (1 mmol) and oxidant **1** (1 mmol, 0.91 g). The mixture was grinding with a pestle until TLC showed complete disappearance of starting material. The mixture was then extracted with CCl4 (2x10 ml) Evaporation of the solvent gave the pure products.

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