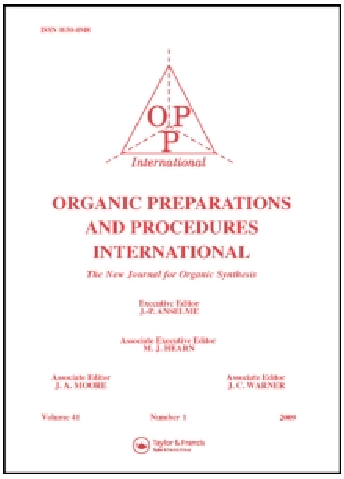

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8.0Hz), 6.28 (1H, d J = 5.9Hz), 5.90 (1H, d, J = 5.9Hz), 4.70 (1H, s), 4.40-4.50 (1H, m), 4.10 (2H, dd, J = 12Hz), 3.90 (1H, m), 3.70 (3H, s), 2.55 (1H, m), 2.10 (1H, m), 1.60 (4H, m), 1.40 (3H,s), 1.10 (2H, m). IR (film): 2980, 1786, 1412, 1261, 798 cm $^{-1}$. MS(m/z): 512 (M^+, 40), 497(10), 403(25), 327(35), 342(10), 101(100). $[\alpha]_D^{20}$ = -25.3° (c 0.13, acetone).

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BENZYLTRIPHENYLPHOSPHONIUM DICHROMATE AS A MILD REAGENT FOR THE OXIDATION OF ORGANIC COMPOUNDS

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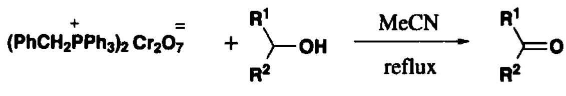
This paper describes the oxidation of organic compounds under non-aqueous and aprotic conditions using benzyltriphenylphosphonium dichromate (**1**, $(PhCH_2PPh_3)_2\,Cr_2O_7$) which is very easily prepared by mixing an aqueous solution of benzyltriphenylphosphonium chloride with CrO_3 in 3 N HCl at room temperature. This reagent, a stable orange powder which may be stored for month without loss of activity, is soluble in acetonitrile, chloroform and dichloromethane and slightly soluble in carbon tetrachloride, ether and hexane. The oxidation of organic compounds with **1** proceeds well in acetonitrile reflux. Benzylic and allylic alcohols **2** are oxidized to the corresponding carbonyl compounds in high yields; benzoin was converted to benzil in excellent yield (Table 1). In contrast, the oxidation of allylic alcohols with manganese dioxide require a large excess of this reagent and long reaction times.[1] Because of the low reactivity of aliphatic alcohols, only benzylic and allylic alcohols could be converted into the corresponding carbonyl compounds.



1 **2** **3** (1)

We also found that the oxidation of **1** with oximes (**4**) and substituted hydrazones (**5**) previously accomplished by a number of reagents,[2,3,5] in refluxing acetonitrile gave the corresponding carbonyl compounds (*Scheme 1*). No further oxidation to the carboxylic acids was observed (Tables 2 and 3). The mechanism of the product reaction is not readily apparent at this time.

A noteworthy advantage of this reagent lies in its ability to selectively oxidize oximes in the presence of other oxidizable functions such as alcohols and double bonds. When we retreated an equimolar amount of oxime (**4h** or **4l**) was treated with **1** in the presence of benzyl alcohol, the oxime was

4 5

a) $R = R^1 = (CH_2)_4$
b) $R = R^1 = (CH_2)_5$
c) $R = R^1 = C_6H_4\text{-}C_6H_4$
d) $R = H, R^1 = PhCH{=}CH$
e) $R = H, R^1 = Ph$
f) $R = H, R^1 = Ph$
g) $R = H, R^1 = 3,4(\text{-}MeO)_2C_6H_3$
h) $R = Me, R^1 = Ph$
i) $R = Ph, R^1 = Ph$
j) $R = PhCH_2, R^1 = Ph$
k) $R = H, R^1 = 3\text{-}NO_2C_6H_4$
l) $R = H, R^1 = 4\text{-}ClC_6H_4$
m) $R = H, R^1 = Ph$

a) $R = R^1 = Ph, G = PhNH$
b) $R = Me, R^1 = Ph, G = PhNH$
c) $R = Me, R^1 = 3,4\text{-}(MeO)_2C_6H_3, G = PhNH$
d) $R = Me, R^1 = 4\text{-}PhC_6H_4, G = PhNH$
e) $R = Ph, R^1 = 2\text{-pyridyl}, G = PhNH$
f) $R = Me, R^1 = 4\text{-pyridyl}, G = PhNH$
g) $R = Me, R^1 = 4\text{-}MeOC_6H_4, G = PhNH$
h) $R = Me, R^1 = 2\text{-}MeOC_6H_4, G = PhNH$
i) $R = R^1 = Ph, G = p\text{-}NO_2C_6H_4NH$
j) $R = H, R^1 = 4\text{-}MeOC_6H_4, G = p\text{-}NO_2C_6H_4NH$
k) $R = Me, R^1 = 4\text{-}ClC_6H_4, G = p\text{-}NO_2C_6H_4NH$
l) $R = H, R^1 = 4\text{-}PhC_6H_4, G = p\text{-}NO_2C_6H_4NH$
m) $R = R^1 = Ph, G = NMe_2$
n) $R = Me, R^1 = Ph, G = NMe_2$
o) $R = Me, R^1 = 3,4\text{-}(MeO)_2C_6H_3, G = NMe_2$
p) $R = Me, R^1 = 4\text{-}MeOC_6H_4, G = NMe_2$
q) $R = Me, R^1 = Ph, G = NH_2CONH$
r) $R = Me, R^1 = Ph, G = NH_2CONH$
s) $R = Me, R^1 = 4\text{-}MeOC_6H_4, G = NH_2CONH$
t) $R = Me, R^1 = 3,4\text{-}(MeO)_2C_6H_3, G = NH_2CONH$

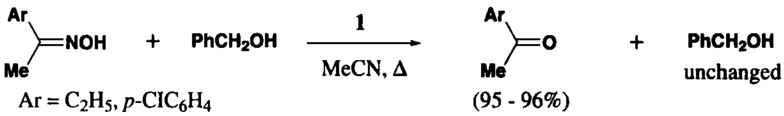
Scheme 1

Table 1. Oxidation of alcohols **2** to Carbonyl Compounds **3**[a]

Cmpd	R^1	R^2	Time (min)	Yield[b] (%)	mp. °C or bp. °C/torr (lit. [2-4])
2a	C_6H_4	H	8	100	179/760 (178)
2b	$4\text{-}NO_2C_6H_4$	H	15	92	104 (104-105
2c	$3,4\text{-}(MeO)_2C_6H_3$	H	20	95	82 (81-83)
2d	$4\text{-}PhC_6H_4$	Me	10	99	117-119 (117-119)
2e	2-pyridyl	C_6H_5	10	98	84/760 (83-85)
2f	C_6H_5	Me	10	100	119/760 (118-121)
2g	$4\text{-}MeOC_6H_4$	H	5	99	35-37 (35-37)
2h	$2\text{-}MeOC_6H_4$	H	10	95	47 (47-47-49)
2i	C_6H_5	C_6H_5	20	90	102/760 (100-103)
2j	$3\text{-}MeOC_6H_4$	H	10	99	45 (45-47)
2k	$4\text{-}ClC_6H_4$	H	10	94	196/760 (195-198)
2l	$2\text{-}ClC_6H_4$	H	5	96	212/760 (212-214)
2m	C_6H_5	$C_6H_5CH_2$	15	98	54 (54-55)
2n	$4\text{-}BrC_6H_4$	Me	20	95	49-50 (49-51)
2o	$4\text{-}ClC_6H_4$	Me	10	96	232/760 (232-234)
2p	C_6H_5	C_6H_5CO	10	90	95 (94-96)
2q	$2,3\text{-}(MeO)_2C_6H_3$	H	20	98	49-52 (49-53)
2r	$C_6H_4CH{=}CH$	C_6H_5	10	98	54-57 (54-57)
2s	$C_6H_4CH{=}CH$	Me	20	95	39 (39-40)
2t	$4\text{-}NO_2C_6H_4CH{=}CH$	H	20	95	138-142 (139-142)
2u	$C_6H_4CH{=}CH$	H	20	95	127/760 (125-128)

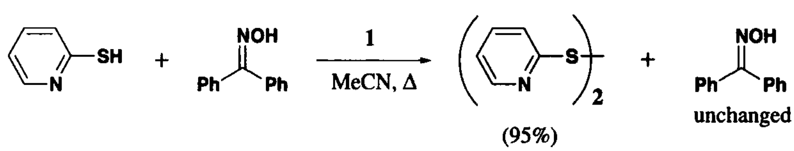
a) Confirmed by comparison with authentic sample (IR, TLC and NMR). b) Yield of isolated pure product after chromatography or distillation.

selectively oxidized (Eq. 2); the hydroxyl group of α,β-unsaturated alcohols and the C=NOH group

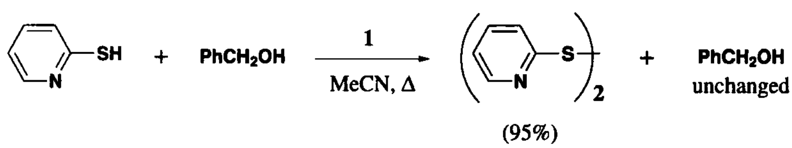


(2)

α,β-unsaturated oximes were oxidized to the corresponding carbonyl compounds; the double bonds remained intact (Table 2, oxime **3d** and Table 1, alcohols **2r**-**2u**). In order to evaluate the selectivity of reagent **1**, the competitive reactions shown in Eqs. 2-5 were carried out. In the presence of an



(3)



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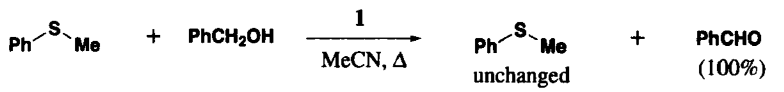

(5)

Table 2. Conversion of **4** to Carbonyl Compounds **3**

Starting Material	Product[a]	Reaction Time (min)	Yield[b] (%)	mp. °C or bp. °C/torr (lit.[2,3,5])
4a	**3a**	15	95	127-130/760 (127-130)
4b	**3b**	15	95	154-156/760 (154-156
4c	**3c**	15	98	177/760 (179)
4d	**3d**	20	97	240/760 (240)
4e	**3e**	15	99	42-44 (41-44)
4f	**3f**	15	100	204/760 (203)
4g	**3g**	15	100	49-52 (50-52)
4h	**3h**	15	97	55-57 (55-57)
4i	**3i**	30	95	58-60 (58-60)
4j	**3j**	15	98	80-83 (80-83)
4k	**3k**	20	95	232/760 (234)
4l	**3l**	15	98	117-119 (117-118)
4m	**3m**	25	94	126/760 (125-128)

a) Confirmed by comparison with authentic sample (IR, TLC and NMR). b) Yield of isolated pure product after chromatography or distillation.

equimolar amount of acetophenone oxime or of benzyl alcohol only 2-mercaptopyridine was selectively oxidized (Eqs. 3 and 4). Treatment of benzyl alcohol with **1** in the presence of thioanisole, led to exclusive oxidation of benzyl alcohol (Eq. 5).

In conclusion, we report here an efficient, rapid and inexpensive method for the conversion of oximes, hydrazones, semicarbazones, alcohols and thiols to the corresponding carbonyl compounds and disulfides which is superior to previously reported methods [1-38] in terms of selectivity, high yields, purity of products and facile work-up.

Table 3. Conversion of **5** to Carbonyl Compounds **3**[a]

Starting Material	Product[a]	Reaction Time (min)	Yield[b] (%)	mp. °C or bp. °C/torr (lit.[2,3,5])
5a	**3a**	30	95	48 (47-49)
5b	**3b**	15	98	82-85/760 (83-85)
5c	**3c**	30	95	48 (47-50)
5d	**3d**	25	98	118 (117-119)
5e	**3e**	30	96	42 (41-43)
5f	**3f**	25	96	78/760 (76-79)
5g	**3g**	25	96	38 (37-39)
5h	**3h**	25	91	244-249/760 (245-248)
5i	**3i**	30	85	49 (47-49)
5j	**3j**	30	85	120/760 (118-121)
5k	**3k**	40	90	232/760 (232)
5l	**3l**	40	85	118-120 (117-119)
5m	**3m**	20	91	48 (47-49)
5n	**3n**	20	95	84/760 (83-85)
5o	**3o**	25	100	48-49 (47-50)
5p	**3p**	35	98	37-39 (37-39)
5q	**3q**	40	90	178-190/760 (177-179)
5r	**3r**	40	80	84-85 (83-85)
5s	**3s**	40	85	38 (37-39)
5t	**3t**	40	70	47-49 (47-50)

a) Confirmed by comparison with authentic sample (IR, TLC and NMR). b) Yield of isolated pure product after chromatography or distillation.

EXPERIMENTAL SECTION

All yields refer to isolated products after purification. Products were characterized by comparison with authentic samples (IR and NMR spectrum, thin layer chromatography, melting and boiling point).[2-5] All reactions were carried out in acetonitrile; all ^1H NMR spectra were recorded at 90 and 250 MHz in $CDCl_3$ and CCl_4 relative to TMS (0.00 ppm). Elemental analysis was performed by the Research Institute of Petroleum Industry, Tehran, I. R. Iran.

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 product was collected, washed with water (20 mL) and dried in a desiccator under vacuum over calcium chloride, to yield 9.54 g (94%) of orange solid product, mp. 210-212°. ^{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, 11.95

Oxidation of 2, 4 and 5 to 3. General Procedure.- The alcohol **2** (oxime 4, hydrazone or semicarbazone **5**) (1 mmol) was added to a stirred solution of the oxidant **1** (1 mmol, 0.92 g) in acetonitrile (10 mL). The mixture was heated at reflux until TLC showed complete disappearance of starting material, which required 5-40 min depending on substrate (Tables 1-3). The mixture was cooled and 2 g of silica gel was added to the reaction mixture. It was stirred for 5 min. The solid was then separated by suction filtration through Celite and washed with acetonitrile (2x10 mL). Evaporation of the solvent gave the carbonyl compounds **3**. The products were purified by short-path distillation or column chromatography on silica gel using a mixture of ethyl acetate and hexane as eluent (90:10).

Competitive Oxidation. Typical Procedure.- A mixture of benzyl alcohol (1 mmol, 0.11 g) and acetophenone oxime (1 mmol, 0.14 g) was added to a stirred solution of the oxidant **1** (1 mmol, 0.92 g) in acetonitrile (20 mL). The mixture was heated at reflux until TLC showed complete disappearance of acetophenone oxime (15 min). The other competitive reactions for Eqs. 2-5 are the same as above.

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PREPARATION AND CHARACTERIZATION OF NEW SUBSTITUTED 5- METHOXY-2-STYRYL-4-PYRONES

Submitted by (12/24/98)

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During the last several decades, many 4-pyrones or compounds containing 4-pyrone moieties has been found to be biologically active; bactericidal, insecticidal, herbicidal, fungicidal, antiallergenic, cytotoxic and potential anticancer activity has been reported.[1] Some 4-pyrones with the styryl group possess anticancer activity[2] and 5-hydroxy-2-styryl-4-pyrone has been used in the formulation of skin-lightening cosmetics,[3] and the use of such pyrones in the synthesis of polycondensed heterocyclics has been described.[4] Previous papers of this series described some reactions of 5-hydroxy-4-pyrones.[5] The transformation to corresponding *N*-substituted-5-hydroxy-4-pyridones (useful as chelating agents),[5a-d] photochemical isomerizations[5e] and ring-contraction reactions[5f] have been studied. Our continuing interest in the photochemistry of 4-pyrones, especially in regard to the difference between reactions of 5-hydroxy and its methylated analogues, prompted us to study styryl-substituted 4-pyrones.

Herewith we report the synthesis of several aryl-substituted 5-methoxy-2-ethenyl-4-pyrones (**4a-4f**) presumably capable of exhibiting various photochemical reactions. Several 5-hydroxy-2-