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Phosphorus, Sulfur, and Silicon and the Related Elements

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To cite this Article Badri, Rashid and Shushizadeh, Mohammad Reza(2007) 'An Efficient Tandem Oxidative-Protection Reaction of Benzylic Alcohols to Corresponding Arylhydrazones and Oximes', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 182: 3, 601 – 605

To link to this Article: DOI: 10.1080/10426500601015724

URL: <http://dx.doi.org/10.1080/10426500601015724>

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An Efficient Tandem Oxidative-Protection Reaction of Benzylic Alcohols to Corresponding Arylhydrazones and Oximes

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A mild and efficient one-pot synthesis of hydrazones and oximes from the reaction of the oxidation product of benzyl alcohols and phenols by 3,6-bis(triphenylphosphonium)cyclohexene dichromate with phenylhydrazine, 2,4-dinitrophenylhydrazine, and hydroxylamine is described.

Keywords 3,6-bis(triphenylphosphonium)cyclohexene dichromate; hydrazones; oximes; oxidation; synthesis

INTRODUCTION

The oxidative conversion of alcohols and phenols to corresponding carbonyl compounds and quinones by the dichromate anion ($\text{Cr}_2\text{O}_7^{2-}$),^{1–6} and the simultaneous reaction of these derivatives with hydrazines and hydroxylamine offers a convenient one-pot synthetic route to hydrazones and oximes. The traditional dichromate anion oxidation of alcohols and phenols and the transformation of the products to hydrazones and oximes is a two-step synthesis, which is conducted under aqueous acidic conditions. Such conditions are usually associated with further oxidation of aldehydes to corresponding carboxylic acids and acetals, and therefore, they reduce yields.

A number of different chromium(VI)-based oxidants for the oxidation of organic substrates under non-aqueous and aprotic conditions, e.g., *n*-butyltriphenylphosphonium dichromate,⁷ and benzyltriphenylphosphonium dichromate,⁸ are reported in the literature. Here we report an extension of our previous studies^{9–11} of the one-pot conversion of benzylic alcohols and phenols to hydrazones and oximes.

Received August 12, 2005; accepted August 16, 2006.

We thank Shahid Chamran University, Ahvaz, Iran, for financial support of this work.

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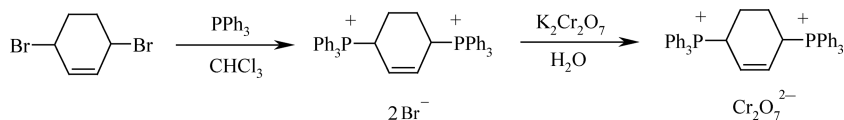
TABLE I Solvent-Free Synthesis of 2,4-Dinitrophenylhydrazones^a

Substrate	Time (min)	Yield (%)	Product	M.P. (lit. ¹²) (°C)
	20	85	Benzaldehyde-2,4-DNPH	235 (237)
	35	80	Acetophenone-2,4-DNPH	248 (250)
	20	86	4-methylbenzaldehyde-2,4-DNPH	237 (239)
	25	76	4-nitrobenzaldehyde-2,4-DNPH	319 (320)
	25	85	4-methoxybenzaldehyde-2,4-DNPH	252 (254)
	25	72	Benzoin-2,4-DNPH	187 (189)
	15	95	<i>p</i> -benzoquinone-2,4-DNPH	230 (231)
	31	80	<i>p</i> -benzoquinone-2,4-DNPH	229 (231)
	30	82	<i>p</i> -naphthoquinone-2,4-DNPH	277 (278)
	120	—	—	—

^aAll products were confirmed by comparison with authentic samples (IR, ¹H NMR, and TLC). The yield of isolated pure hydrazones. DNPH = 2,4-dinitrophenylhydrazine.

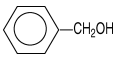
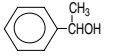
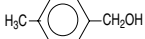
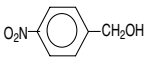
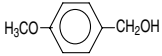
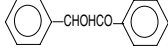
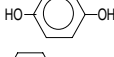

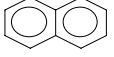

RESULTS AND DISCUSSION

The preparation of the oxidant 3,6-bis(triphenylphosphonium)cyclohexene dichromate (BTPCD) was accomplished according to the reported procedure.¹¹ Thus the reaction of 3,6-dibromocyclohexene with triphenylphosphine in refluxing chloroform afforded 3,6-bis(triphenylphosphonium)cyclohexene dibromide in an 80% yield. Treatment of this compound with K₂Cr₂O₇ in H₂O furnished the oxidant BTPCD in a 78% yield (Scheme 1).

**SCHEME 1**

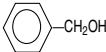
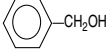
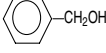
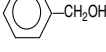
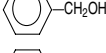
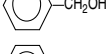
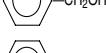
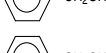
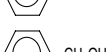
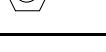
BTPCD was ground to a fine powder and then thoroughly mixed in a 1:1 molar ratio with alcohol or phenol. After 5 min, one equivalent of 2,4-dinitrophenylhydrazine, phenylhydrazine, or hydroxylamine was added to the reaction mixture. Grinding of the mixture was continued until TLC analysis indicated the completion of the reaction (9–35 min). The results obtained are summarized in Tables I–III. The results in all three tables indicate that benzyl alcohols and substituted derivatives thereof carrying both electron-withdrawing and electron-donating groups were converted to the corresponding 2,4-dinitrophenylhydrazones (Table I), phenylhydrazones (Table II), and oximes (Table III), in good to excellent yields. Application of this oxidation procedure to some phenols was also examined (Tables I–III). Among the phenols, *p*-hydroquinone underwent these conversions faster (9–15 min) than phenol itself and other derivatives. In contrast, β -naphthol

TABLE II Solvent-Free Synthesis of Phenylhydrazones^a

Substrate	Time (min)	Yield (%)	Product	M.P. (lit. ¹²) (°C)
	10	93	Benzaldehyde-PH	156 (158)
	18	84	Acetophenone-PH	104 (105)
	17	89	4-methylbenzaldehyde-PH	114 (114)
	21	72	4-nitrobenzaldehyde-PH	158 (159)
	20	90	4-methoxybenzaldehyde-PH	119 (120)
	18	75	Benzoin-PH	105 (106)
	9	98	<i>p</i> -benzoquinone-PH	150 (152)
	22	83	<i>p</i> -benzoquinone-PH	150 (152)
	24	85	<i>p</i> -napthoquinone-PH	205 (206)
	120	—	—	—

^aAll products were confirmed by comparison with authentic samples (IR, ¹H NMR, and TLC). Yield of isolated pure hydrazones. PH = phenylhydrazone.

TABLE III Solvent-Free Synthesis of Oximes^a

Substrate	Time (min)	Yield (%)	Product	M.P. (lit. ¹²) (°C)
	15	90	Benzaldehyde-oxime	35 (35)
	25	86	Acetophenone-oxime	58 (59)
	23	90	4-methylbenzaldehyde-oxime	109 (110)
	18	70	4-nitrobenzaldehyde-oxime	128 (129)
	20	89	4-methoxybenzaldehyde-oxime	131 (133)
	22	75	Benzoin-oxime	150 (151)
	12	94	<i>p</i> -benzoquinone-oxime	239 (240)
	35	82	<i>p</i> -benzoquinone-oxime	239 (240)
	26	79	<i>p</i> -naphthoquinone-oxime	205 (207)
	120	—	—	—

^aAll products were confirmed by comparison with authentic samples (IR, ¹H NMR, and TLC). Yield of isolated pure oximes.

did not react even after 2 h of grinding and was recovered without any change.

CONCLUSION

In summary, the conditions presented here afforded an efficient one-pot synthesis of hydrazones and oximes in moderate to good yields. Neutral and mild reaction conditions as well as simple work-up are advantages of this method.

EXPERIMENTAL

All starting materials were purchased from Merck (Darmstadt, Germany) and Aldrich (London, England). Melting points were

measured on a Mettler FP5 apparatus and are uncorrected. IR spectra were recorded on a Shimadzu 470 infrared spectrometer. ^1H NMR spectra were recorded with a 250 MHz Bruker spectrometer. The purity of substrates and the course of the reactions was checked by TLC using silica-gel polygram SIGL/UV254 plates.

GENERAL PROCEDURE

A mixture of the substrate (0.5 mmol) and oxidant (0.5 mmol) were ground in a mortar for 5 min at an ambient temperature. To this mixture was either added 2,4-dinitrophenylhydrazine (0.5 mmol), phenylhydrazine (0.5 mmol), or hydroxylamine (0.5 mmol) in one portion, and grinding was continued until TLC monitoring showed completion of the reaction (9–35 min). Then the mixture was washed with dichloromethane or diethylether (20 mL). The combined solutions were filtered and dried over anhydrous magnesium sulfate. Evaporation of the solvent afforded the pure products (for yields, see Tables I–III).

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