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n-Butyltriphenylphosphonium Peroxodisulfate $(\mathrm{Bu}^n\mathrm{PPh}_3)_2\mathrm{S}_2\mathrm{O}_8$: an Efficient and Inexpensive Reagent for the Cleavage of Carbon–Nitrogen Double Bonds under Non-aqueous and Aprotic Conditions†

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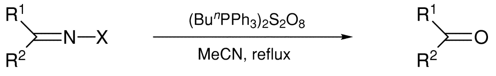
An efficient and convenient conversion of oximes, phenylhydrazones, *p*-nitrophenylhydrazones and semicarbazones to the corresponding carbonyl compounds with *n*-butyltriphenylphosphonium peroxodisulfate is reported.

Oximes, phenylhydrazones, *p*-nitrophenylhydrazones and semicarbazones are useful intermediates in organic synthesis because they are utilized as protecting groups in carbonyl chemistry. These derivatives are also highly crystalline and very useful for the isolation, characterization and purification of carbonyl compound. Regeneration of carbonyl compounds from their derivatives under mild and aprotic conditions is a useful transformation and is an important process in synthetic organic chemistry.

The classical method for the recovery of aldehydes and ketones from oximes is hydrolysis under acidic conditions which removes the hydroxylamine from the equilibrium.[1] This method however, is not suitable for acid sensitive compounds. Several oxidative methods have been introduced for deoximation which have found some advantages over acidic hydrolysis.[2–16] Little attention has been paid to the oxidative cleavage of phenylhydrazones, *p*-nitrophenylhydrazones and semicarbazones and only a few reports are available dealing with the conversion of these derivatives to their corresponding carbonyl compounds.[17–21] Thus, there is still a need to develop a new and facile procedure for the regeneration of the parent carbonyl compounds from their above-mentioned derivatives.

We now report an efficient and general method for the effective cleavage of the C=N bond of oximes, phenylhydrazones, *p*-nitrophenylhydrazones and semicarbazones with *n*-butyltriphenylphosphonium peroxodisulfate under non-aqueous and aprotic conditions.



X = OH, NHPh, $\mathrm{NHC_6H_4(NO_2\text{-}}p)$, $\mathrm{NHCONH_2}$

Table 1 Oxidative cleavage of carbon–nitrogen double bonds with $(\mathrm{Bu}^n\mathrm{PPh}_3)_2\mathrm{S}_2\mathrm{O}_8$

Entry	Substrate	*t*/min	Product[a]	Yield(%)[b,c]
1	Benzaldoxime	25	Benzaldehyde	89
2	4-Chlorobenzaldoxime	30	4-Chlorobenzaldehyde	87
3	3-Nitrobenzaldoxime	30	3-Nitrobenzaldehyde	86
4	4-Nitrobenzaldoxime	35	4-Nitrobenzaldehyde	80
5	3-Methoxybenzaldoxime	30	3-Methoxybenzaldehyde	89
6	Cinnamaldoxime	20	Cinnamaldehyde	89
7	Salicylaldehyde oxime	60	Salicylaldehyde	76
8	4-Chloroacetophenone oxime	40	4-Chloroacetophenone	94
9	Acetophenone oxime	35	Acetophenone	96
10	4-Phenylacetophenone oxime	30	4-Phenylacetophenone	96
11	Benzophenone oxime	30	Benzophenone	97
12	Cyclohexanone oxime	45	Cyclohexanone	92
13	3-Nitrobenzaldehyde phenylhydrazone	35	3-Nitrobenzaldehyde	70
14	4-Chlorobenzaldehyde phenylhydrazone	30	4-Chlorobenzaldehyde	77
15	3-Methoxybenzaldehyde phenylhydrazone	30	3-Methoxybenzaldehyde	82
16	Acetophenone phenylhydrazone	45	Acetophenone	96
17	4-Phenylacetophenone phenylhydrazone	30	4-Phenylacetophenone	97
18	Benzophenone phenylhydrazone	30	Benzophenone	98
19	4-Chlorobenzaldehyde-4-NPH[d]	35	4-Chlorobenzaldehyde	72
20	3-Methoxybenzaldehyde-4-NPH[d]	30	3-Methoxybenzaldehyde	74
21	Acetophenone-4-NPH[d]	40	Acetophenone	93
22	4-Chloroacetophenone-4-NPH[d]	45	4-Chloroacetophenone	96
23	Benzophenone-4-NPH[d]	45	Benzophenone	90
24	4-Methoxybenzaldehyde semicarbazone	40	4-Methoxybenzaldehyde	70
25	4-Chlorobenzaldehyde semicarbazone	45	4-Chlorobenzaldehyde	73
26	Acetophenone semicarbazone	40	Acetophenone	83
27	Benzophenone semicarbazone	35	Benzophenone	89

[a]All products were identified by comparison of their physical and spectral data with those of authentic samples. [b]Isolated yields. [c]In the reactions of aldehyde derivatives 10–20% of the corresponding carboxylic acids were isolated. [d]4-NPH represents 4-nitrophenylhydrazone.

This reagent can be readily and cheaply prepared by adding an aqueous solution of potassium peroxodisulfate to a solution of *n*-butyltriphenylphosphonium bromide in water–acetone (10:1). This white, non-hygroscopic solid is

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very stable and can be stored for months without losing its activity. It is soluble in acetonitrile, dichloromethane and chloroform, and slightly soluble in CCl_4 and diethyl ether.

The treatment of oximes, phenylhydrazones, *p*-nitrophenylhydrazones and semicarbazones with 1.5 equivalents of *n*-butyltriphenylphosphonium peroxodisulfate in acetonitrile at reflux gave the corresponding carbonyl compounds in 70–98% yield as shown in Table 1. It is noteworthy that the reaction medium was almost neutral, so that some sensitive functionalities such as the carbon–carbon double bond remained intact (entry 6).

In conclusion, we have developed a new and efficient method for the regeneration of aldehydes and ketones from their derivatives under non-aqueous and aprotic conditions.

Experimental

Preparation of n-Butyltriphenylphosphonium Peroxodisulfate.—To a solution of *n*-butyltriphenylphosphonium bromide (4.43 g, 11 mmol) in water–acetone (10:1, 120 ml) was added a solution of potassium peroxodisulfate (1.5 g, 5.5 mmol) in water (30 ml) and the mixture was stirred at room temperature for 15 min. The resulting white solid was filtered, washed with cold distilled water (15 ml) and dried in a desiccator over calcium chloride. Yield 4.4 g (95%) (Found: C, 63.58; H, 5.75; S, 7.86. $C_{44}H_{48}O_8P_2S_2$ requires C, 63.61; H, 5.78; S, 7.71%).

Regeneration of Carbonyl Compounds from Oximes, Phenylhydrazones, p-*Nitrophenylhydrazones and Semicarbazones. General Procedure.*—In a round-bottomed flask (50 ml) equipped with a condenser and a magnetic stirrer, a solution of the substrate (1 mmol) in MeCN (20 ml) was prepared. *n*-Butyltriphenylphosphonium peroxodisulfate (1.245 g, 1.5 mmol) was added to this solution and refluxed for 20–60 min. The progress of the reaction was monitored by TLC (eluent: CCl_4–Et_2O, 3:1). The reaction mixture was cooled to room temperature and filtered. The solid material was washed with MeCN (20 ml). The filtrates were combined and evaporated. The resulting crude material was purified on a silica gel plate or silica gel column with appropriate eluent. Evaporation of the solvent afforded the pure carbonyl compound; yield 70–98% (Table 1).

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