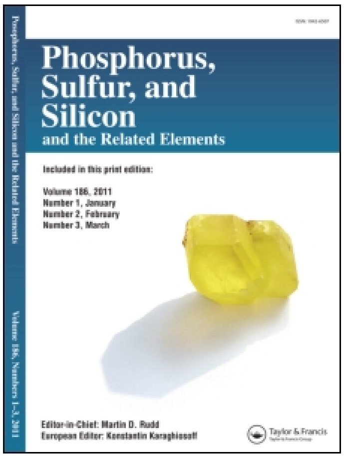


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Benzyltriphenylphosphonium Peroxodisulfate $(PhCH_2PPh_3)_2S_2O_8$: An Efficient and Convenient Reagent for the Oxidative Cleavage of Phenylhydrazones, Paranitrophenylhydrazones, and Semicarbazones to Their Parent Carbonyl Compounds

Mahmood Tajbakhsh; Iraj Mohammadpoor-Baltork; Farhad Ramzanian-Lehmali

To cite this Article Tajbakhsh, Mahmood , Mohammadpoor-Baltork, Iraj and Ramzanian-Lehmali, Farhad(2003) 'Benzyltriphenylphosphonium Peroxodisulfate $(PhCH_2PPh_3)_2S_2O_8$: An Efficient and Convenient Reagent for the Oxidative Cleavage of Phenylhydrazones, Paranitrophenylhydrazones, and Semicarbazones to Their Parent Carbonyl Compounds', Phosphorus, Sulfur, and Silicon and the Related Elements, 178: 12, 2621 — 2625

To link to this Article: DOI: 10.1080/714040975

URL: http://dx.doi.org/10.1080/714040975

Phosphorus, Sulfur, and Silicon, 178:2621–2625, 2003
Copyright © Taylor & Francis Inc.
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500390248259

BENZYLTRIPHENYLPHOSPHONIUM PEROXODISULFATE $(PhCH_2PPh_3)_2S_2O_8$: AN EFFICIENT AND CONVENIENT REAGENT FOR THE OXIDATIVE CLEAVAGE OF PHENYLHYDRAZONES, PARANITROPHENYLHYDRAZONES, AND SEMICARBAZONES TO THEIR PARENT CARBONYL COMPOUNDS

Mahmood Tajbakhsh,[a] *Iraj Mohammadpoor-Baltork,*[b]
and Farhad Ramzanian-Lehmali[a]
University of Mazandaran, Babolsar, Iran[a] *and*
University of Isfahan, Isfahan, Iran[b]

(Received May 24, 2003; accepted July 3, 2003)

Deprotection of phenylhydrazones, paranitrophenylhydrazones, and semicarbazones to their parent aldehydes and ketones in high yields has been carried out using benzyltriphenylphosphonium peroxodisulfate as a selective oxidant under mild conditions.

Keywords: Benzyltriphenylphosphonium peroxodisulfate; deprotection; paranitrophenylhydrazones; phenylhydrazones; semicarbazones

Derivatives of carbonyl compounds such as phenylhyrazones, paranitrophenylhydrazones, and semicarbazones not only are used for the characterization and purification of carbonyl compounds, but they also play an important role in the protection of carbonyl compounds, as they are highly crystalline and stable compounds. Thus, the regeneration of carbonyl compounds from their derivatives under mild condition is an important process in organic synthetic chemistry.

The classical method for the cleavage of phenylhyrazones, paranitrophenylhydrazones, and semicarbazones to aldehydes and ketones includes acid hydrolysis which is not suitable for acid sensitive compounds.[1]

We are thankful to the Mazandaran and Isfahan Universities Research Council for the partial support of this work.

Address correspondence to Mahmood Tajbakhsh, Department of Chemistry, School of Sciences, University of Mazandaran, PO Box 453, Babolsar, Iran. E-mail: tajbakhsh@umz.ac.ir

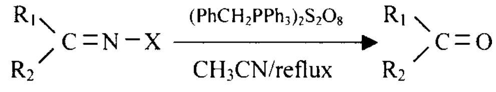
Several oxidative deprotection methods have been developed which have some advantages over the classical hydrolysis methods.[2–13] Little attention has been paid to the oxidative cleavage of phenylhyrazones, paranitrophenylhydrazones, and semicarbazones and only a few reports are available that deal with the conversion of these derivatives to their corresponding carbonyl compounds.[14,15]

RESULTS AND DISCUSSION

Benzyltriphenylphosphonium peroxodisulfate is an inexpensive and stable oxidizing agent. This reagent has been used for the oxidation of organic compounds under nonaqueous and aprotic conditions.[16] Recently, we introduced a new method for the oxidative deprotection of trimethylsilyl and tetrahydropyranyl ethers, ethylene acetals, and ketals to their corresponding carbonyl compounds in excellent yields.[17]

In continuation of our research in this area, we now report that benzyltriphenylphosphonium peroxodisulfate is an efficient reagent for the conversion of phenylhyrazones, paranitrophenylhydrazones, and semicarbazones to their corresponding carbonyl compounds. For this purpose, first, we have studied the oxidative deprotection of benzaldehyde phenylhydrazone to benzaldehyde with this reagent in common organic solvents such as dichloromethane, chloroform, tetrahydrofuran, cyclohexan, and acetonitrile. The experimental results show that acetonitrile is a suitable solvent for these oxidations (Table I).

When a variety of phenylhyrazones, paranitrophenylhydrazones, and semicarbazones were treated with benzyltriphenylphosphonium peroxodisulfat, the corresponding carbonyl compounds were obtained in excellent yields (Scheme 1) (Table II).



$X = NHC_6H_5$, $NH(p\text{-}NO_2C_6H_4)$, $NHCONH_2$

SCHEME 1

Interestingly, the α,β-unsaturated phenylhydrazones, paranitrophenylhydrazones, and semicarbazones underwent deprotection very efficiently without rearrangement of the C=C bond, and the reaction is essentially chemoselective. Furthermore, functional groups such as chloro, methoxy, and alkyl also were inert to this reagent and no byproduct formation was observed (Table II).

TABLE I Percent Conversion of Benzaldehyde Phenylhydrazone to Benzaldehyde with $(PhCH_2PPh_3)_2S_2O_8$ in Different Solvents Under Reflux Condition

Entry	Solvent	Reaction period (h)	Yield (%)[a,b]
1	CH_2Cl_2	2	35
2	$CHCl_3$	2	30
3	THF	2	30
4	c-C_6H_{12}	2	15
5	CH_3CN	0.1	97

[a] Yields refer to isolated products.
[b] Substrate/oxidant (1:1).

In conclusion, we have developed a mild method for the regeneration of carbonyl compounds from phenylhydrazones, paranitrophenylhydrazones, and semicarbazones that possesses significant advantages over the existing methods such as simple procedure, high yield, and mild conditions.

EXPERIMENTAL

Products were isolated and their physical data were compared with those of known samples. Solvent was freshly distilled. Phenylhyrazones, paranitrophenylhydrazones, and semicarbazones were prepared according to the described procedure.[18] Benzyltriphenylphosphonium peroxodisulfate was prepared according to the literature.[17]

General Procedure for the Regeneration of Carbonyl Compounds from Phenylhydrazones, Paranitrophenylhydrazones, and Semicarbazones

To a solution of substrate (1 mmol) in acetonitrile (10 ml) in a round-bottom flask (50 ml) equipped with a condenser and magnetic stirrer, the oxidant (0.898 g, 1 mmol) was added. The reaction mixture was stirred magnetically under reflux conditions for 6–20 min. The progress of the reaction was monitored by TLC (eluent: hexane/ethyl acetate, 5:1). The reaction mixture was cooled to room temperature and filtered. The solid material was washed with acetonitrile (20 ml). The combined filtrates were evaporated on a rotary evaporator. The resulting crude material was purified on a silica-gel plate (eluent: hexane/ethyl acetate, 5:1) to afford the pure carbonyl compound, yield 78–98% (Table II).

TABLE II Oxidative Deprotection of Phenylhydrazones, Paranitrophenylhydrazones, and Semicarbazones with $(PhCH_2PPh_3)_2S_2O_8$ in Refluxing CH_3CN

Entry	Substrate	Time (min)	Products	Yield (%)[a]
1	$C_6H_5CHNNHC_6H_5$	6	C_6H_5CHO	97
2	$(C_6H_5)_2CNNHC_6H_5$	7	$(C_6H_5)_2CO$	95
3	*o*-$ClC_6H_4CHNNHC_6H_5$	6	*o*-ClC_6H_4CHO	96
4	*p*-$ClC_6H_4CHNNHC_6H_5$	6	*p*-ClC_6H_4CHO	96
5	*m*-$MeOC_6H_4CHNNHC_6H_5$	6	*m*-$MeOC_6H_4CHO$	98
6	*p*-$MeOC_6H_4CHNNHC_6H_5$	7	*p*-$MeOC_6H_4CHO$	95
7	*o*-$MeOC_6H_4CHNNHC_6H_5$	6	*o*-$MeOC_6H_4CHO$	97
8	$C_6H_5C(p\text{-}ClC_6H_4)NNHC_6H_5$	8	$C_6H_5C(p\text{-}ClC_6H_4)O$	97
9	*p*-$MeC_6H_4CHNNHC_6H_5$	8	*p*-MeC_6H_4CHO	95
10	$C_6H_5CH_2CH_2CHNNHC_6H_5$	12	$C_6H_5CH_2CH_2CHO$	90
11	Cyclohexanone phenylhydrazone	15	Cyclohexanone	89
12	Camphor phenylhydrazone	16	Camphor	92
13	Cinnamaldehyde phenylhydrazone	15	Cinnamaldehyde	89
14	$C_6H_5CHNNHCONH_2$	8	C_6H_5CHO	95
15	*p*-$MeC_6H_4CHNNHCONH_2$	9	*p*-MeC_6H_4CHO	94
16	*o*-$MeOC_6H_4CHNNHCONH_2$	8	*o*-$MeOC_6H_4CHO$	98
17	*m*-$MeOC_6H_4CHNNHCONH_2$	10	*m*-$MeOC_6H_4CHO$	94
18	*p*-$MeOC_6H_4CHNNHCONH_2$	8	*p*-$MeOC_6H_4CHO$	95
19	*o*,*p*-$MeOC_6H_3CHNNHCONH_2$	10	*o*,*p*-$MeOC_6H_3CHO$	98
20	*p*-$BrC_6H_4CHNNHCONH_2$	10	*p*-BrC_6H_4CHO	93
21	*p*-$ClC_6H_4CHNNHCONH_2$	10	*p*-ClC_6H_4CHO	95
22	$C_6H_5C(p\text{-}ClC_6H_4)NNHCONH_2$	8	$C_6H_5C(p\text{-}ClC_6H_4)O$	95
23	$(C_6H_5)_2CNNHCONH_2$	9	$(C_6H_5)_2CO$	94
24	$C_6H_5C(CH_3)NNHCONH_2$	10	$C_6H_5COCH_3$	92
25	*p*-$ClC_6H_4C(CH_3)NNHCONH_2$	8	*p*-$ClC_6H_4COCH_3$	95
26	$C_6H_5CH_2CH_2CHNNHCONH_2$	15	$C_6H_5CH_2CH_2CHO$	87
27	Cyclohexanone semicarbazone	18	Cyclohexanone	78
28	Camphor semicarbazone	16	Camphor	89
29	Cinnamaldehyde semicarbazone	14	Cinnamaldehyde	86
30	$C_6H_5CHNNH(p\text{-}NO_2C_6H_4)$	6	C_6H_5CHO	97
31	*p*-$CH_3C_6H_4CHNNH(p\text{-}NO_2C_6H_4)$	6	*p*-$CH_3C_6H_4CHO$	95
32	*p*-$ClC_6H_4CHNNH(p\text{-}NO_2C_6H_4)$	7	*p*-ClC_6H_4CHO	94
33	$(C_6H_5)_2CNNH(p\text{-}NO_2C_6H_4)$	6	$(C_6H_5)_2CO$	96
34	$C_6H_5C(p\text{-}ClC_6H_4)NNH(p\text{-}NO_2C_6H_4)$	8	$C_6H_5C(p\text{-}ClC_6H_4)O$	95
35	$C_6H_5C(CH_3)NNH(p\text{-}NO_2C_6H_4)$	7	$C_6H_5COCH_2$	96
36	Cyclohexanone paranitrophenylhydrazone	16	Cyclohexanone	88
37	Camphor paranitrophenylhydrazone	18	Camphor	86
38	Cinnamaldehyde paranitrophenylhydrazone	20	Cinnamaldehyde	89

[a] Yields refer to isolated products.

REFERENCES

[1] E. B. Hersberg, *J. Org. Chem.*, **13,** 542 (1984).

[2] N. Kirkd and J. Sladec, *Tetrahedron Lett.*, **21,** 651 (1980).

[3] E. J. Eisenbraum, R. P. Wesely, R. S. Budhram, and Dewprasad, *Chem. Ind.*, 584 (1989).

[4] R. N. Ram and N. Varshak, *Tetrahedron Lett.*, **32,** 5829 (1991).

[5] M. Curini, O. Rosayi, E. Pisani, and U. Costantino, *Synthesis*, 333 (1996).

[6] D. Subhas and A. Venkant Narasaiah, *Synth. Commun.*, **30,** 1153 (2000).

[7] I. Mohammadpoor-Baltork and Sh. Pouranshirvani, *Synth. Commun.*, **26,** 261 (1996).

[8] H. Firouzabadi, M. Seddighi, A. Ahmadi, and A. R. Sardarian, *Synth. Commun.*, **19,** 3385 (1989).

[9] G. S. Zhang, D. H. Yang, H. F. Chen, and K. Cai, *Synth. Commun.*, **28,** 2221 (1995).

[10] G. S. Zhang, D. H. Yang, and M. F. Chen, *Synth. Commun.*, **28,** 3721 (1998).

[11] H. Firouzabadi, N. Iranpoor, F. Kiaeezadeh, and J. Toofan, *Tetrahedron*, **42,** 719 (1986).

[12] H. Firouzabadi and I. Mohammadpoor-Baltork, *Synth. Commun.*, **24,** 489 (1994).

[13] H. Firouzabadi, E. Mottaghinejed, and M. Seddighi, *Synth. Commun.*, **19,** 469 (1989).

[14] Z. Gui-Sheng and Y. De-Hong, *Synth. Commun.*, **28,** 607 (1998).

[15] Z. Gui-Sheng, Y. De-Hong, and C. Mi-Feng, *Synth. Commun.*, **29,** 1167 (1999).

[16] I. Mohammadpoor-Beltork, A. R. Hajipour, and H. Mohammadi, *Bull. Chem. Soc. Jpn.*, **71,** 1649 (1998).

[17] M. Tajbakhsh, I. Mohammadpoor-Beltork, and F. Ramzanian-Lehmali, *Chem. Research (S)*, 185 (2001).

[18] A. I. A. Vogel, *Textbook of Practical Organic Chemistry* (Longmans, London, 1978), 4th ed.