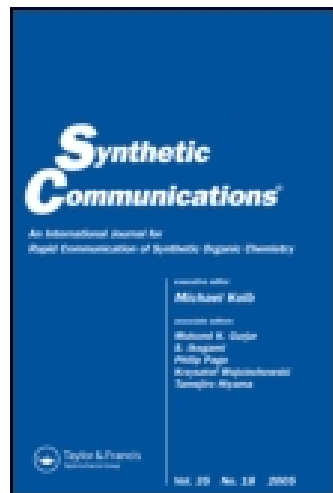


This article was downloaded by: [Eastern Michigan University]

On: 10 October 2014, At: 18:12

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
<http://www.tandfonline.com/loi/lscy20>

3,6-BIS(TRIPHENYLPHOSPHONIUM) CYCLOHEXENE PEROXODISULFATE AS AN EFFICIENT AND MILD OXIDIZING AGENT FOR CONVERSION OF ALKYL BENZENES TO CORRESPONDING CARBONYL COMPOUNDS

Rashid Badri^a & Mousa Soleymani^a

^a Chemistry Department, Chamran University, Ahvaz, Iran

Published online: 16 Aug 2006.

To cite this article: Rashid Badri & Mousa Soleymani (2006) 3,6-BIS(TRIPHENYLPHOSPHONIUM) CYCLOHEXENE PEROXODISULFATE AS AN EFFICIENT AND MILD OXIDIZING AGENT FOR CONVERSION OF ALKYL BENZENES TO CORRESPONDING CARBONYL COMPOUNDS, *Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry*, 32:15, 2385-2389, DOI: [10.1081/SCC-120006010](https://doi.org/10.1081/SCC-120006010)

To link to this article: <http://dx.doi.org/10.1081/SCC-120006010>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>



SYNTHETIC COMMUNICATIONS

Vol. 32, No. 15, pp. 2385–2389, 2002

**3,6-BIS(TRIPHENYLPHOSPHONIUM)
CYCLOHEXENE PEROXODISULFATE
AS AN EFFICIENT AND MILD OXIDIZING
AGENT FOR CONVERSION OF
ALKYLBENZENES TO CORRESPONDING
CARBONYL COMPOUNDS**

Rashid Badri* and Mousa Soleymani

Chemistry Department, Chamran University,
Ahvaz, Iran

ABSTRACT

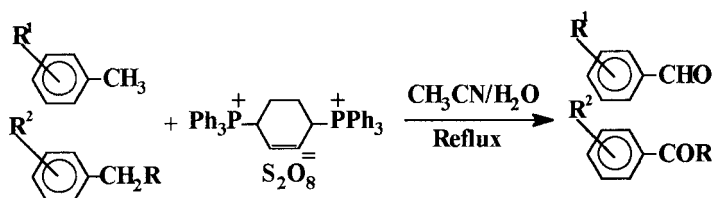
Oxidation of a series of alkylbenzenes by BTPCP under neutral conditions to corresponding carbonyl compounds is described.

Peroxodisulfate radical anion $\text{SO}_4^{\cdot-}$, is one of the most important and strong one-electron oxidant in organic synthesis. Its ability to oxidize a variety of organic compounds has been under intensive investigations in recent years.^[1–7] The conversion of alkylbenzenes to corresponding carbonyl compounds is important in organic synthesis and many reagents such as: Ceric amonium nitrate in aqueous acetic acid or in HClO_4 ^[8] and along with potassium bromate,^[9] Chromium trioxide in acetic anhydride followed by

*Corresponding author. E-mail: rashibadri@yahoo.com



hydrolysis,^[10] Potassium permanganate absorbed on alumina,^[11] Selenium dioxide,^[12] Chromyl chloride^[13] and Silver(II) oxide in phosphoric acid,^[14] have been used to accomplish such goals. However the above reagents either were used in aqueous acidic solution or in the presence of a metal ion as catalyst. Some of the recently developed reagents which involve the use of peroxodisulfate anion radical such as $K_2S_2O_8/Cu^{2+}$,^[15] $(NH_4)_2S_2O_8/Cu(OAc)_2$ ^[16] and $[Ag(Py)_4]S_2O_8$,^[17] show non or poor selectivity towards the presence of some selective functionalities. Recently we have reported the synthesis and application of 3,6-bis(triphenylphosphonium) cyclohexene peroxodisulfate (BTPCP) as an efficient and selective oxidant in nonaqueous medium.^[18] We now wish to report a simple, convenient, mild and selective method for the oxidation of alkylbenzenes to their corresponding carbonyl compounds with BTPCP under neutral conditions and in the absence of metal catalysts. This method shows to be of considerable utility for the oxidation of alkylbenzenes at benzylic position. The procedure developed consists of simply addition of BTPCP in small portions to a refluxing solution of alkylbenzene in aqueous acetonitrile. The results obtained are summarized in Table 1.





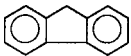
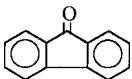

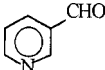
Results in Table 1 indicate that toluene and its substituted derivatives carrying both electron-withdrawing and electron-donating groups converted to corresponding aldehydes in good to excellent yields (Entries 1–10). Further oxidation of aldehydes to their carboxylic acids was not observed. The data also demonstrate that the yields obtained from toluenes with electron-donating groups (Entries 2–4) are to some extent higher than the yields from substrates with electron-withdrawing groups (Entries 5–10). With more complex alkyl side chains on the ring and with indane and fluorene (Entries 11–19) the products obtained are corresponding ketones in moderate to high yields. Methyl pyridine failed to give the corresponding



OXIDATION OF ALKYL BENZENES BY BTPCP

2387

Table 1. Oxidation of Alkylbenzenes to Carbonyl Compounds by BTPCP

Entry	Substrate	Product	Time (min)	Yield (%) ^a
1	PhCH ₃	PhCHO	22	91
2	<i>p</i> -MeC ₆ H ₄ CH ₃	<i>p</i> -MeC ₆ H ₄ CHO	25	93
3	<i>p</i> -OMeC ₆ H ₄ CH ₃	<i>p</i> -OMeC ₆ H ₄ CHO	25	95
4	<i>o</i> -OMeC ₆ H ₄ CH ₃	<i>o</i> -OMeC ₆ H ₄ CHO	25	92
5	<i>p</i> -ClC ₆ H ₄ CH ₃	<i>p</i> -ClC ₆ H ₄ CHO	25	88
6	<i>o</i> -ClC ₆ H ₄ CH ₃	<i>o</i> -ClC ₆ H ₄ CHO	25	86
7	<i>p</i> -BrC ₆ H ₄ CH ₃	<i>p</i> -BrC ₆ H ₄ CHO	30	83
8	<i>p</i> -NO ₂ C ₆ H ₄ CH ₃	<i>p</i> -NO ₂ C ₆ H ₄ CHO	45	55
9	<i>m</i> -NO ₂ C ₆ H ₄ CH ₃	<i>m</i> -NO ₂ C ₆ H ₄ CHO	45	57
10	<i>o</i> -NO ₂ C ₆ H ₄ CH ₃	<i>o</i> -NO ₂ C ₆ H ₄ CHO	45	59
11	PhCH ₂ CH ₃	PhCOCH ₃	25	91
12	PhCH ₂ CH ₂ Br	PhCOCH ₂ Br	25	84
13	PhCH ₂ CH ₂ CH ₂ OH	PhCOCH ₂ CH ₂ OH	30	56
14	Ph(CH ₂) ₃ CO ₂ Et	PhCO(CH ₂) ₂ CO ₂ Et	30	79
15	PhCH ₂ CH=CHCO ₂ Et	PhCOCH=CHCO ₂ Et	30	70
16	<i>o</i> -OHC ₆ H ₄ CH ₂ CH=CH ₂	<i>o</i> -OHC ₆ H ₄ COCH=CH ₂	25	74
17	PhCH ₂ Ph	PhCOPh	25	81
18			25	65
19			25	70
20			45	—

^aYields refer to isolated products. Products were characterized by comparison of their physical data, IR and ¹H NMR spectra with those of known samples.

aldehyde. Chemoselectivity of oxidant is shown by Entries 13, 15 and 16 in which some selective functionalities such as carbon-carbon double bond and hydroxy groups remained intact. It is noteworthy that the same procedures were carried out in other solvents such as: CH₂Cl₂, CHCl₃, THF, Et₂O, hexane and C₆H₆, but only with aqueous acetonitrile the reactions were clean and afforded high yields.

In conclusion, neutral and mild reaction conditions, absence of a metal ion catalyst, high chemoselectivity of the oxidant, easy work-up



2388

BADRI AND SOLEYMANI

and good to excellent yields of desired products are advantages of this method.

GENERAL PROCEDURE FOR THE OXIDATION OF ALKYL BENZENES

To a solution of substrate (1 mmol) in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (5/1, 10 mL) in a 50 mL round-bottomed flask equipped with a condenser and a magnetic stirrer and under reflux condition was added 3,6-bis(triphenylphosphonium) cyclohexene peroxodisulfate (2 mmol) in small portions over (22–45) min. The progress of the reaction was monitored by TLC (eluent; $\text{CCl}_4/\text{CH}_3\text{CO}_2\text{Et}$: 6/1). After completion of the reaction, the mixture was filtered and the solvent was evaporated. The resulted crude material was purified on a silica-gel plate with appropriate solvent. Pure carbonyl compounds were obtained in 55–95% yields (Table 1).

ACKNOWLEDGMENT

We thank Chamran University for financial support of this work.

REFERENCES

1. Mohammadpoor-Baltork, I.; Hajipour, A.R.; Haddadi, R. *J. Chem. Res.* **1999**, 102.
2. Hashemi, M.M.; Ahmadi Beni, Y. *J. Chem. Res.* **1999**, 434.
3. Mohammadpoor-Baltork, I.; Hajipour, A.R.; Mohammadi, H. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1649.
4. Varma, R.; Meshran, H.M. *Tetrahedron Lett.* **1997**, 5427.
5. Didier, B.; Philipe, C. *Tetrahedron Lett.* **1996**, *43*, 7725.
6. Chen, F.; Wan, J.; Guam, C.; Yang, J.; Zhang, H. *Synth. Commun.* **1996**, 253.
7. Dave, P.; Byum, H.S.; Engel, R. *Synth. Commun.* **1986**, *16*, 1343.
8. Trahanovsky, W.S.; Toung, L.B. *J. Org. Chem.* **1966**, *31*, 2033.
9. Ganin, E.; Amer, I. *Synth. Commun.* **1995**, 3149.
10. Nishimura, T. *Org. Synth.* **1956**, *36*, 58.
11. Zhao, D.; Lee, D.G. *Synthesis* **1994**, 915.
12. Kaplan, H. *J. Am. Chem. Soc.* **1941**, *63*, 2654.
13. Richter, V.V. *Chem. Ber.* **1886**, *19*, 1060.
14. Syper, L. *Tetrahedron Lett.* **1967**, 4193.



OXIDATION OF ALKYL BENZENES BY BTPCP

2389

15. Bhat, M.V.; Perumal, P.T. *Tetrahedron Lett.* **1981**, 22, 2605.
16. Walling, C.; Zhao, C.; El-Taliawi, G.M. *J. Org. Chem.* **1983**, 48, 4910.
17. Firouzabadi, H.; Salehi, P.; Mohammadpoor-Baltork, I. *Bull. Chem. Soc. Jpn.* **1992**, 65(10), 2878.
18. Badri, R.; Shalhaf, H.; Heidari, M.A. *Synth. Commun.* in press.

Received in Japan May 21, 2001



MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

©2002 Marcel Dekker, Inc. All rights reserved. This material may not be used or reproduced in any form without the express written permission of Marcel Dekker, Inc.