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/lsyc20

Tetrabutylammonium Peroxydisulfate in Organic Synthesis; IV.[1] An Efficient, Highly Selective and Oxidative Deoximation by Tetrabutylammonium Peroxydisulfate

Fener Chen [a], Anchang Liu [a], Qiongjiao Yan [a], Mingxing Liu [a], Daoming Zhang [a] & Lanying Shao [a]
[a] Department of Chemistry, Fudand University, Shanghai, 200433, People's Republic of China
Published online: 17 Sep 2007.

To cite this article: Fener Chen, Anchang Liu, Qiongjiao Yan, Mingxing Liu, Daoming Zhang & Lanying Shao (1999) Tetrabutylammonium Peroxydisulfate in Organic Synthesis; IV.[1] An Efficient, Highly Selective and Oxidative Deoximation by Tetrabutylammonium Peroxydisulfate, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 29:6, 1049-1056, DOI: 10.1080/00397919908086071

To link to this article: http://dx.doi.org/10.1080/00397919908086071

SYNTHETIC COMMUNICATIONS, 29(6), 1049-1056 (1999)

Tetrabutylammonium Peroxydisulfate in Organic Synthesis; IV.[1] An Efficient, Highly Selective and Oxidative Deoximation by Tetrabutylammonium Peroxydisulfate.

Fener Chen*, Anchang Liu, Qiongjiao Yan,
Mingxing Liu, Daoming Zhang and Lanying Shao.

Department of Chemistry, Fudand University, Shanghai, 200433,
People's Republic of China.

Dedicated to Professor Peiling Xu on the occasion of her 70th birthday.

Abstract: Tetrabutylammonium peroxydisulfate has been proved out to be an efficient and highly chemoselective reagent for the conversion of oximes to the corresponding carbonyl compounds under mild conditions.

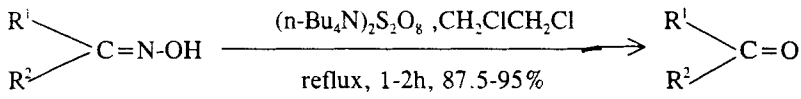
The cleavage of oximes to regenerate aldehydes and ketones is of great relevance to organic synthesis. The oximes are used to not only isolate and purify carbonyl compounds but also to protect and activate the C=O group .[2] In particular, oximes can also be prepared from non-carbonyl compounds, [3] the efficient deoximation would lead to an alternative route for the preparation of aldehydes and ketones.

* To whom correspondence should be addressed.

Classically, the recovery of the aldehydes or ketones from oximes has involved hydrolytic cleavage under suitable condition which removes the hydroxylamine from the equilibrium.[4] This method excludes acid-sensitive aldehydes or ketones. In order to overcome this drawback, a variety of oxidation[5] or reduction[6] procedures continue to be developed over the years. However, many of these existing methods either employ highly toxic reagents or give further oxidation of liberated aldehydes into carboxylic acids, therefore, careful controlling of reaction temperature and the quantity of oxidants are necessary.

Recently, we reported that tetrabutylammonium peroxydisulfate(n-$Bu_4N)_2$ S_2O_8 is an efficient reagent to oxidize tosylhydrazones of ketones to the parent ketones. Following the above finding, we investigated the possibility of extending this oxidation to oximes of carbonyl compounds. Such a reaction would afford a useful method for regeneration of the carbonyl compounds from oximes.

Analogous to tosylhydrazones, the aldoximes or ketoximes with $(n\text{-}Bu_4N)_2S_2O_8$ readily occurred in a single step to afford the corresponding parent aldehydes or ketones. Simple stirring of the aldoximes and ketoximes with $(n\text{-}Bu_4N)_2S_2O_8$ in 1, 2-dichloroethane at reflux temperature gave, after work-up and isolation, the corresponding aldehydes or ketones in excellent yields (scheme).The results are summarized in the Table.



Scheme

As revealed in the Table, the oxidative deoximation with $(n\text{-}Bu_4N)_2S_2O_8$ under neutral conditions worked well for both aldoximes and ketoximes without any over-oxidation products. The salient features of the method were high yield of recover parent carbonyl compounds and generality, which was indicated by the fact that other common functional groups in molecular such as olefinic double bond, ether, ester, halogen were unaffected by these reaction conditions.

In conclusion, we have developed a new and efficient method for the r-

Table. Oxidative cleavage of oximes 1a-s to carbonyl compounds 2a-s with $(n\text{-}Bu_4N)_2S_2O_8$ in 1,2-dichloroethane[a]

NO:	Oximes of	Reaction time (h)	Yield[b] (%)
1a	2,4-$(CH_3O)_2C_6H_4CHO$	1.0	91.8
1b	6-Methoxy-2-naphthyl aldehyde	1.5	87.5
1c	Citronellal	1.0	89.8
1d	3-Octanone	1.0	92
1e	Benzil	1.5	93
1f	Ethyl cyclopentanone-2-carboxylate	1.5	94.3
1g	1-(5-Chloro-6-methoxy-2-naphthyl)propan-1-one	2	94.5
1h	$C_6H_5COCH_3$	1.5	90
1i	5-Cholesten-3-one	2	91
1j	2-Ethoxycarbonyl-2-methyl-cyclopentanone	1.5	93
1k	(-)-Menthone	2	92.5
1l	3-$C_6H_5CH_2C_6H_4COC_2H_5$	2	95
1m	3-Nonen-2-one	1.5	93
1n	4-Methyl-3-penten-2-one	1.5	94.8
1o	2-Propanonyl-2-methoxy-naphthalene	2	93.5
1p	$C_6H_5COCH{=}CHC_6H_5$	1.5	92.8
1q	4-iso-pr$C_6H_4COCH_3$	2	95
1r	$C_6H_5COCH_2COOC_2H_5$	1.5	92
1s	$CH_3CO(CH_2)_2CH_2Cl$	1.0	95

[a]All carbonyl compounds gave satisfactory microanalyses: C±0.26, H±0.22.

[b]Isolated yields calculated on the amount of oximes introduced.

egeneration of carbonyl compounds from their oximes. The process proceeds in high yields and has considerable advantages over other known procedures.

EXPERIMENTAL SECTION

All melting and boiling points were uncorrected. IR spectra were recorded on a Nicolet-Impact 420 spectrometer. ^{1}H NMR spectra were obtained on a Jeol Fx-90Q instrument. All oximes were prepared by standard methods[7]. $(n\text{-}Bu_4N)_2S_2O_8$ was readily prepared according to the known procedure.[8]

General Procedure for the Oxidative Cleavage of Oximes, 1a-s.

To a solution of $(n\text{-}Bu_4N)_2S_2O_8$(30mmol) in 1, 2-dichloroethane(125ml) was added a solution of **1a-s**(15mmol) in 1, 2-dichloroethane(50ml). The mixture was stirred at reflux for 1-2h under nitrogen. The reacton mixture was poured into water and extracted with 1, 2-dichloroethane(40ml×3), dried (Na_2SO_4). Evaporation of the solvent under reduced pressure gave crude product which was purified by distillation or recrystallization to afford pure parent carbonyl compounds **2a-s** in 87.5-95% yield (Table).

2a:m.p.70-72^{0}C(Lit.[9] m.p.70-71^{0}C); IR(KBr): 1670(C=O)cm^{-1}; ^{1}H NMR($CDCl_3$/-TMS): δ =10.29(s, 1H, CHO), 7.80(d, J=10Hz, 1H, C_6-H), 6.50(m, 1H, C_5-H), 6.47(brs, 1H, C_3-H), 3.88, 3.84(s, 3H, CH_3O).

2b:m.p.77-79^{0}C(Lit.[10] m.p.76-78^{0}C); IR(KBr): 1680(C=O)cm^{-1}; ^{1}H NMR(C-DCl_3/TMS): δ =10.1(s, 1H, CHO), 8.25-7.17(m, 6H, Ar-H).

2c:b.p.85-87^{0}C/10Torr, n_D^{20}=1.4512(Lit.[11] b.p. 79^{0}C/9Torr, n_D^{20}=1.4511); IR(f-ilm): 1722(C=O)cm^{-1}; ^{1}H NMR($CDCL_3$/TMS): δ =9.70(t, J=1.5Hz, 1H, CHO), 5.05(m, 1H, C=CH), 2.39-1.70(m, 4H, 2×CH_2), 1.67(brs, 3H, C=C-CH_3), 1.58(brs, 3H, C=C-CH_3), 1.60-1.12(m, 3H, CH_2, CH), 0.98(d, J=6Hz, 3H, CH_3).

2d:b.p.74-75^{0}C/30Torr(Lit.[12] b.p.75-76^{0}C/30Torr); IR(film):1712(C=O)cm^{-1}; ^{1}H NMR($CDCl_3$/TMS): δ =2.44(q, J=8.0Hz, 2H, $COCH_2CH_3$), 2.38[t, J=7.0Hz, 2H, $COCH_2(CH_2)_5CH_3$], 1.90-1.00(m, 6H, 3×CH_2), 1.70, 0.92(t, J=8.0Hz, 3H, CH_3).

2e:m.p.93-95^{0}C(Lit.[13] m.p.94^{0}C); IR(KBr): 1670, 1660(C=O), 1591(C=C)cm^{-1}; ^{1}H NMR($CDCl_3$/TMS): δ =8.12-7.81(m, 4H, Ar-H), 7.18-7.00(m, 6H, Ar-H).

2f:b.p.122-124^{0}C/10Torr(Lit.[13] b.p.86-89^{0}C/2.0Torr); IR(film):1740(ring-C=O),

1715(ester-C=0)cm^{-1}; ^{1}H NMR($CDCl_3$/TMS): δ =4.20(q, J=7.5Hz, 2H, CH_2O), 3.16(m, 1H, CH), 2.60-159(m, 6H, 3×CH_2), 1.30(t, J=7.5Hz, 3H, CH_3).

2g:m.p.129-130°C; IR(KBr): 1617(C=0)cm^{-1}; ^{1}H NMR ($CDCl_3$/TMS): δ =8.36-7.22(m, 5H, Ar-H), 4.00(s, 3H, CH_3O), 3.01(q, J=7.0Hz, 2H, CH_2), 1.24(t, J=7.0Hz, 3H, CH_3).

2h:b.p.79-80°C/1.0Torr (Lit.[5c] b.P.60°C/0.5Torr) ; IR(film): 1690(C=0) cm^{-1}; ^{1}H NMR($CDCl_3$/TMS): δ =6.96-7.58(m, 5H, Ar-H), 2.18(s, 3H, CH_3).

2i:m.p.118-120°C(Lit.[15] m.p.119°C); IR(KBr): 1730(C=0)cm^{-1}; ^{1}H NMR(CDCl$_3$/TMS): δ =5.30(m, 1H, C=CH), 3.28-2.70(m, 2H, CH_2C=C), 2.71-0.62(m, 41H, 4×CH, 14×CH_2 and 3×CH_3).

2j:b.p.103-105°C/12Torr(Lit.[13] b.p.103-104°C/12Torr); IR(film): 1760(ringC=0), 1730(ester-C=0)cm^{-1}; ^{1}H NMR($CDCl_3$/TMS): δ = 4.15(q, J=7.5Hz, 2H, CH_2O), 2.75-171(m, 6H, 3×CH_2), 1.28(s, 3H, CH_3), 1.26(t, J=7.5Hz, 3H, CH_3CH_2).

2k:b.p.80-82°C/11Torr, $[\alpha]_D^{20}$=-30° (c=1.0, CH_3OH); [Lit.[12] b.p.81°C/11Torr, $[\alpha]_D^{20}$=-29.9°(c=1.0, CH_3OH)]; IR(film): 1710(C=0)cm^{-1}; ^{1}H NMR($CDCl_3$/TMS): δ =2.56-1.15(m, 9H, 3×CH, 2×CH_2), 1.16-0.75(m, 9H, 3×CH_3).

2l:b.p.159-160°C/1.25Torr; IR(film): 1685(C=0)cm^{-1}; ^{1}H NMR($CDCl_3$/TMS): δ =7.72-7.13(m, 7H, Ar-H), 4.00(s, 2H, $C_6H_5CH_2$), 2.96(q, J=7.2Hz, 2H, CH_2), 1.19(t, J=7.2Hz, 3H, CH_3).

2m:b.p.87-89°C/10Torr(Lit.[13] b.p.88°C); IR(film): 1685(C=0), 1630(C=0)cm^{-1}; ^{1}H NMR($CDCl_3$/TMS): δ =6.83(dt, J_1=16Hz, J_2=7.0Hz, 1H, HC=C-C=0), 6.05(dt, J_1=16Hz, J_2=1.5Hz, 1H, C=CH-C=0), 2.19(s, 3H, $COCH_3$), 2.50-2.00(m, 2H, CH_2-C=C), 1.69-1.12(m, 6H, 3×CH_2), 0.90(t, J=5Hz, 3H,CH_3).

2n:b.p.128-130°C(Lit.[13] 130°C); IR(film): 1690(C=0)cm^{-1},^{1}H NMR($CDCl_3$/TMS): δ =6.09(m, 1H, CH=C), 2.13(s, 1H, CH_3), 1.88(d, J=1.0Hz, 3H, CH_3).

2o:m.p.112-114°C(Lit.[14] 112-114°C); IR(KBr):1685(C=0)cm^{-1}; ^{1}H NMR($CDCl_3$/TMS): δ =8.41-7.15(m, 6H, Ar-H), 3.11(t, 2H, CH_2CO), 1.30(q, 3H, CH_3).

2p:m.p.55-57°C(Lit.[15] m.p.56-57°C); IR(KBr):3020(vinyl-CH), 1665(C=0)cm^{-1}; ^{1}H NMR($CDCl_3$/TMS): δ =8.15-7.84(m, 2H, Ar-H), 7.80-7.20(m, 10H, Ar-H, CH=CH).

2q:b.p.115-117°C/12Torr(Lit.[13] b.p.115-116°C/12Torr); IR(film):1690(C=0)cm^{-1}; ^{1}H NMR($CDCl_3$/TMS): δ =7.24, 7.29(d, 2H, J=8.4Hz, Ar-H), 2.90(sept, J=17.5Hz,

1H, CH), 2.52(s, 3H, CH_3CO), 1.21(d, J=7.5Hz, 6H, $2\times CH_3$).

2r:b.p.103-105^{0}C(Lit.[13] b.p.103-105^{0}C); IR(film): 1745(ester-C=0), 1690(ket-one-C=0)cm^{-1}; ^{1}H NMR(CCl_4/TMS): δ =8.12-7.35(m, 5H, Ar-H), 4.20(q, J=6.0Hz, 2H, $CH_2$0), 4.03(s, 2H, CH_2), 1.20(t, J=6.0Hz, 3H, CH_3).

2s:b.p.58-60^{0}C/12Torr(Lit.[13] b.p.58-59^{0}C/12Torr); IR(film): 1725(C=0)cm^{-1}; ^{1}H NMR($CDCl_3$/TMS): δ =3.52(t, J=7.0Hz, 2H, CH_2Cl), 2.58(t, J=7.0Hz, 2H, CH_2CO),2.10(s, 3H, CH_3CO), 1.99(m, 2H, CH_2).

REFERENCES

1. For part 3, Chen, F. E. , Wan, J. L. , Guan, C. S. ,Yang , J. S. and Zhang, H. , Synth. Commun. **1996**, 28,253.
2. Curran, O. P. , Brill, J. F. and Rakiewicz, D. M. J. Org. Chem. **1984**, 49, 1654.
3. (a)Barry, R. H. and Hartung, W. H. J. Org. Chem. **1947**, 12, 460.
   (b)Hartung, W. H. and Gressley, F. Org. Synth, Coll. Vol. II**1943**, 363.
   (c)Barton, D. H. R. , Beaton, J. M. , Geller, L. E. and Pechet, M. M. J. Am. Chem. Soc. **1961**, 83, 4076
   (d)Barton, D. H. R. and Beraton, J. M. J. Am. Chem. Soc. **1961**, 83, 4083.
   (e)Komeichi, Y. , Tomioka, S. , Iwaski, T. and Watanable, K. Tetrahedron Lett. **1970**, 53, 4677.
   (f)Stiver, S. and Yate, P. J. Chem. Soc, Chem. Commun. **1983** 2, 50
   (g)Safiullah and Ansari, S. A. J. Indian Chem. Soc. **1987**, 64, 443.
   (h)Kabalka, G. W. , Pace, R. D. and wadgaonka, P. P. Synth. Commun, **1990**, 20, 2453.
4. Hershberg, E. B. J. Org. Chem. **1984**, 13, 542.
5. (a)Depug, C. H. and Ponder, B. W. J. Am. Chem. Soc. **1959**, 81, 4629.
   (b)Chamberlin, E. M. and Chamerda, J. M. J. Am, Chem. Soc. **1955**, 77, 1221.
   (c)Maloney, J. R. , Lyle, R, E. , Saavedra, J. E. and Lyle, G. G. Synthesis **1978**, 212.
   (d)Drabowicz, J. Synthesis **1980**, 125.
   (e)Satish, S. and kalyanam, N. Chem. & Ind. (London) **1981**, 809.
   (f)Rao, C. G. , Radhakrishna, A. S. , Singh, R. B. and Bhatnagar, S. P. Synthesis **1983**, 808.

(g)Mckillop, A. , Hunt, J. O. , Naylor, R. O. and Taylor, E. C. J. Am. Chem. Soc. **1971**, 93, 4918.

(h)Corey, E. J. , Hopkins, P. B. , Kim, S. , Yoo, S. , Nambiar, K. P. and Falck, J. R. J. Am. Chem. Soc. **1979**, 101, 7131.

(i)Maeda, K. , Moritani, I. , Hosokawa, T. and Murahash, S. I. Tetrahedron Lett.**1974**, 797.

(j)Olah, G. A. , Vankar, Y. D. and prakash, G. K. S. Synthesis. **1974**, 113.

(k)Ho, T. L. Synth. Commun. **1980**, 10, 465.

(l)Barton, D. H. R. , Lester, O. J. and Ley, S. V. J. Chem. Soc. Chem. Commun. **1977**, 445.

(m)Olah, G. A. and Ho, T. L. Synthesis **1976**, 610.

(n)Narayaran, C. G. , Ramaswamy, O. S. and Wadia, M. S. Chem. &Ind (London) **1977**, 454.

(o)Bird, J. W. and Diaper, D. G. M. Can . J. Chem. **1969**, 47, 145

(p)Erickson, R. E. , Andrulis, P. J. Jr. , Collins, J. C. , Lungle, M. L. and Mercer, G. D. J. Org. Chem. **1969**, 34, 2961

(q)Bandgar, B. P. , Kunde, M. L. B. and Thote, J. L. Synth. Commun. **1997**, 27, 1149.

(r)Butler, R. N. , Morris, G. J. and O'Donohue, A. M. J. Chem. Res, Synop. **1981**, 61.

(s)Araujo, H. C. , Ferrreira, G. A. L. and Mahajan, J. R. J. Chem. Soc. Perkin Trans. I **1974**, 2257.

(t)Shim, S. B. , Kim, K. and Kim, Y. H. Tetrahedron Lett. **1987**, 28, 645.

(u)Salmon, M. , Miranda, R. and Angeles, E. Synth. Commun. **1986**, 16, 1827

(v)Moriarty, R. M. , Prakash, O. and Vavilikolanu, R. Synth. Commun. **1986**, 16. 1247.

(w)Vankar, P. , Rathore, R. and Chandrasekaran, S. J. Org. Chem. **1986**, 51, 3063.

(x)Chidambaram, N. , Satyanarayana, K. and Chandrasekaran, S. Synth. Commun. **1989**, 19, 1724.

(y)Baltork, I. M. and Pouranshirvani, S. Synth. Commun. **1996**, 26, 1.

(z)Bandgar, B. P. , Shaikh, S. I. and Lyer, S. Synth. Commun. **1996**. 26.1163.

6. (a)Corey, E. J. , Richman, J. E. J. Am. Chem. Soc. **1970**, 92, 5276
(b)Monti, D. , Gramatica, P. , Speranza, G. , Tagliapietra, P. and, Manitto, P. Synth. Commun. **1986**. 16, 803.
(c)Curran, D. P. , Brill, J. F. and Radkiewicz, D. M. J. Org. Chem. **1984**, 49, 1684.
7. Vogel, A. I. "Textbooks of Practical of Organic Chemistry" Longman Group Limited. **1978**.
8. Jung, J. C. , Chio, H. C. and Kim, Y. H. , Tetrahedron Lett. , **1993**, 34, 3581.
9. Sommers, A. H. , Michaele, R. J. and Weton, A. W. J. Am. Chem. Soc. **1952**, 74, 5546.
10.Terashia, S. , Tseng, C. C. and Koga, k. Chem. Pharm. Bull. **1979**, 27, 747.
11.Omura, D. K. and Swern, D. Tetrahedron **1978**, 34, 1651.
12.Staab, H. A. and Jost, E. Liebigs Ann. Chem. **1962**, 655, 90.
13.Tietze, L. F. and Eicher, T. "Reaktionen und Synthesen im Organisch-Chemischem Prakti Kum." Georg Thieme Verlag Stuttgart, New York, **1981**.
14.Chen, F. E. , Dong, F. L. and Shao, L. Y. Chinese J. Pharm. **1992**, 23, 388(Chem. Abstr. , **1993**, 118, 254491w).

Accepted 8-8-98